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Color Centers in Alkali Halides

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С II по I3 октября I965 г. в Иллинойском университете (Соединенные Штаты Америки, Урбана) состоялся международный симпозиум "Центры окраски в щелочногалоидных кристаллах". Материалы этого симпозиума в виде полных текстов докладов и статей публиковаться не будут. Ниже приводятся тезисы 208 оригинальных работ, представленных на этот симпозиум.

1 Magnetic Properties of Lattice Imperfections in Alkali Halide Single Crystals

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College Station, Texas

A sensitive torque magnetometer has been used to study the magnetization caused by lattice imperfections in single crystals of lithium fluoride, potassium chloride, and sodium chloride. The uniaxial anisotropy of the susceptibility which could produce the observed torque vs. angle of magnetic field curve has led us to conclude that the magnetic centers are along dislocation lines or at special clusters of vacancies.

2 Effect of Plastic Strain on the F, M, and R Center Formation in Gamma-ray Irradiated Sodium Chloride*

F. AGULLÓ-LOPEZ† and P. W. LEVY, Brookhaven National Laboratory, Upton, New York

Previously it has been shown that when (Harshaw) NaCl single crystals are colored into stage III, subjected to plastic compression or strain, and then subjected to additional irradiation, the subsequent growth of F centers is increased. A "jump" appears in the growth curve and the formation rate is increased. In crystals strained as much as seven percent, both the jump and increase in rate is proportional to the strain. Plastic deformation also causes a "jump" and an increase in rate of formation of M centers. The F and M center concentrations are related by the expression $[M] = C[F]^2 + D$. The parameter C is the same in both strained and unstrained samples, but D increases in proportion to the strain. R center formation is also increased by plastic strain. The room temperature stability of both F and M centers is affected by compression. At low F and M center concentrations, i.e., after irradiations less than 4×10^6R, an appreciable fraction of the centers decays after irradiation. At high concentrations, i.e., after exposure to a dose greater than 4×10^6R, a considerably smaller fraction decays. For doses of 6×10^6R or larger the F centers decrease slightly while the M centers continue to increase over a ten day period. Plastic deformation, applied after coloring into stage III, also enhances the formation of M centers by F-light bleaching. Below three percent strain this enhancement is negligible but at larger strains the quantum efficiency is increased approximately fifty percent. It is known that a large part of the deformation occurs in narrow bands, i.e., in the operating glide systems. Photoelastic studies, using M light, show that the M centers produced by F-light bleaching are concentrated in or near the glide systems. These results provide new evidence indicating that vacancies are formed during plastic flow.

* Research performed under the auspices of the U.S. Atomic Energy Commission.
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3 Alignment of Electron Deficiency Centers by Mechanical Stresses

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The alignment of hole centers by elastic deformation of the host lattice is being studied by means of measurements of the stress induced dichroism in the near ultraviolet at low temperatures.

The H centers in KCl align readily at temperatures above 10°K. At 11°K the reorientation time upon removing the stress is of the order of a few seconds. Below 10°K the centers freeze in.

Application of uniaxial stress along [001] results in a preferred orientation perpendicular to the stress axis. The coupling of the H centers to the lattice was determined by optically measuring the relative numbers of centers oriented perpendicular to the stress axis (orientations [110] and $[1\bar{1}0]$) and at 45° to the stress axis (orientations [101], $[10\bar{1}]$, [011] and $[01\bar{1}]$). Evaluation of the Boltzmann factor yields an energy difference between the two orientations that is given by $\Delta E = \beta X$, where X designates the stress. For the factor β one finds about $40 \times 10^{-24} cm^3$. This is five times the corresponding factor for the O_2^- center, which has the same symmetry. The stress induced dichroism permits an accurate determination of the position and width of the H band. At 20°K the center of the band is at 3350 Å and the half width is 0.65 eV.

In the course of these investigations another center was found that gives rise to a stress-induced dichroism in the same spectral region. Preliminary measurements indicate that it is the V_1 center. The results are compatible with a ⟨110⟩ symmetry axis and incompatible with a ⟨111⟩ symmetry.

Attempts to produce aligned V_K centers by means of mechanical stresses have failed. This has to be expected on the basis of the accepted model for this center.

4 An Elastic Collision Mechanism for the Radiation Induced Defect Generation in Ionic Crystals

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The reason and the mechanism for the typical coloration at low temperatures by soft energetic irradiation, e.g. with 50 keV x-ray quanta, is as yet not well understood, although many attempts have been made to explain them by electronic processes. Hitherto, elastic collisions have been excluded from consideration since the first rough estimate for the displacement threshold energy, E_d, was given by Seitz to be 25 eV.

As was shown by the author,[1] elastic collisions in the form of focussing collision chains are possible in ionic crystals. In alkali halides (NaCl-type) direct focussing can take place in the ⟨110⟩ halogen rows. By means of a Born-Mayer potential and with ionic parameters given by Pauling, the focussing threshold energy E_d is estimated.[2] The potential barrier at the position (¼, ¼, 0) for all alkali halides is smaller than 1-2 eV. The threshold energy E_d for the generation of stable, not spontaneously recombining Frenkel defects should not be much higher than this potential barrier, and so it would be of the order of a few eV. The collision chains in the irradiated crystals are initiated by energy transfer from photoelectrons to lattice ions. The primary photoelectrons obtain nearly all of the energy of the ionizing x-ray quanta. Every such photoelectron is able to initiate a number of focusons ($\sim 10^1$ to 10^2). The movement of a part of the focusons is connected with replacement collisions; the duration of one replacement is of the order of 10^{-13} sec. During the displacement process, the neighboring cations relax insignificantly and they pick up only a little kinetic energy, in contradistinction to the corresponding situation in the Varley type mechanisms. Thus the focuson is stopped relatively slowly and covers a path of several atomic distances, thereby creating anion-Frenkel-defects preferentially in the perfect bulk and in addition at dislocations and other lattice imperfections.[2, 3] This fact agrees with the experimental results and explains why the colorability can be increased by preceding deformation, quenching and so on. For ionic crystals other than with the NaCl lattice, the direction of focussing can also be stated; as a rule the anion rows are preferred. Finally, the following general relation can be mentioned: E_d decreases as one progresses from the metallic over to the covalent and then the heteropolar bonded materials.

[1] M. Balarin, ZfK-WF 22 (1962).
[2] M. Balarin, Kernenergie 7, 434 (1964).
[3] M. Balarin, ZfK-WF 15 (1962).

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5 Isotope Effects in the U Center*

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The experimental investigation of the ultraviolet U band in KCl, KBr and RbCl crystals containing H^- and D^- ions has revealed the following isotope effects: a) at liquid helium temperature the halfwidths of the U_H band are from 3 to 15% larger than those of the U_D band for the three crystals studied. b) In the temperature range 4 to 400°K the U_H bands occur at energies $\sim$ 0.02 eV smaller than those of the U_D bands. In order to describe these results the momentum method in the Condon approximation is applied to the U center. From the symmetry of the defect it is shown that only the vibrational modes which transform according to the Γ_{15}^- representation of the full cubic point group can be responsible for the isotope effects; these modes are just the infrared active ones. Then, in order to detect isotope effects, it is sufficient to study the difference between the ground and upper states concerning the Γ_{15}^- modes. It is found that during optical transitions, allowed in the dipole approximation, the Γ_{15}^- modes suffer, via the electron-vibrations interaction, only a frequency shift, and that only the local mode has to be taken into account in order to predict the isotope effect, since the contribution coming from the Γ_{15}^- continuum is negligible. Therefore the effect observed experimentally is accounted for in terms of the local mode frequencies due to the U_H and U_D centers in the ground and the excited states. The experimental and theoretical results are in excellent agreement if we assume that the local mode frequencies of the two centers in their excited states are approximately equal. It is also interesting to note that the isotope effects are slightly dependent upon the temperature, since both peak positions and halfwidths are functions of temperature through the continuum modes only.

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6 Shift of the Infrared U Band by Lattice Parameter Variation

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1. In alkali halide mixed crystals, the U center vibrational absorption undergoes a shift to lower frequencies with increasing lattice parameter. In the case of KCl:Rb the dependence on Rb concentration of the x-ray lattice parameter is well known, and we find relative changes of frequency ν and nearest neighbor distance "a" which are related as

$$-d\nu/\nu = 3.3\ da/a$$

2. By application of uniaxial stress, the infrared U band is split up and the splitting is linear with stress. The shift of the component which is polarized parallel to stress in ⟨100⟩ direction is 0.7 cm^{-1} at 200 kp/cm^2 in KCl:H (90°K); the shift of the component perpendicular to the stress axis is then about $-0.05\ cm^{-1}$. Using the elastic constants of the pure crystal we obtain the same dependence of frequency shift and nearest neighbor distance (measured in the direction of stress) as under 1.

We consider a simple potential for the H^- ion which is determined by the repulsive energy between the H^- ion and its nearest neighbors (K^+). We then find that the experimental results for the frequency shift can be explained by a repulsive potential for the H^- ion which is the same as that for a Cl^- ion in the vacancy. In this calculation we assume, as does Fiesche et al.,[1] that the H^- ion is polarized in the vibration. We estimate the magnitude of the spring constant between the H^- shell and nucleus describing the polarizability from the experimental oscillator strength 0.5 (effective charge: 0.7) of the infrared band.

Additional information may be obtained from the dependence of the H^- frequency on the lattice constant in the series KCl–KBr–KI. This dependence is roughly linear but weaker than one might extrapolate from the behavior under stress. The difference can be explained by an inward displacement of the nearest neighbors of the defect which is greater at an H^- in a larger anion vacancy. The displacement needed to explain the measurements in KBr is about −1.6% of "a" (inward relaxation). From x-ray measurements[2] of the lattice constant in KBr:H a similar relaxation of −1.9% can be estimated using Eshelby's theory.[3]

[1] R. Fieschi, G. F. Nardelli, and N. Terzi, Phys. Letters 12, 290 (1964).
[2] R. Hilsch and R. W. Pohl, Trans. Faraday Soc. 34, 883 (1938).
[3] J. D. Eshelby, *"Solid State Physics"* (Academic Press, New York, 1956), Vol. 3, p. 79.

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7 ESR and ENDOR Study of the Self-Trapped Hole Associated with Lithium in Sodium Fluoride*

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Self-trapped holes (V_K centers) produced in NaF:Li by x-irradiation at 77°K have been associated with the Li^+ impurity ions upon warming the crystal to −115°C. The generic name V_{KA} center has been chosen to designate a V_K center associated with an alkali impurity in an alkali halide. The lithium V_{KA} center in NaF, aside from being a new color center, is of interest because of the close resemblance of its ESR spectrum to that of the "bent-bond" V_K center in LiF identified by Känzig[1] as the antimorph of the F center (V_F center). ESR and ENDOR studies have shown that the Li^+ occupies the cation lattice site nearest the F_2^- molecule-ion, and that the molecular bond is "bent" by 0.6° ± 0.2°. The ESR and ENDOR spectra were quantitatively analyzed by computer diagonalization of the spin Hamiltonian matrix. The anisotropic g factor of the unpaired electron, the hyperfine constants of the molecular fluorine nuclei, and the hyperfine constants of nuclei in five shells surrounding the molecule-ion were determined. ENDOR lines were identified for nuclei in two other shells.

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† Alfred P. Sloan Foundation Fellow.

[1] W. Känzig, Phys. Rev. Letters 4, 117 (1960); J. Phys. Chem. Solids 17, 80 (1960).

8 Influence of the Host Lattice on Color Centers*

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A general survey of the electronic states of ionic crystals is presented. Existing detailed calculations and semiquantitative results based on simplified models are reviewed. It is shown how the electronic states depend on the states of the constituent atoms and on the symmetry of the lattice. The interactions with the phonon field and with the polarization field are also considered and their effect on the electronic structure and on the effective masses of holes and electrons is estimated. The problem of self-trapping is also reviewed for electrons and holes.

The additional electronic states produced by charged point defects (such as F centers) are examined, in relation to the band structure of the material, and are compared to the exciton states. Strong similarities between excitons and F centers are disclosed. In particular, the problem due to excitons with energies higher than the forbidden gap is described and compared with that of excited states of the F centers above the continuum. Theoretical attempts to explain these states are reviewed.

The effect of phonons on color centers is examined, with particular regard to the lifetime of excited states. Evidence for localized vibrations from optical transitions of color centers is examined.

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9 Band Structure of Alkali Halides

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An attempt has been made to obtain the main features of the energy bands of alkali halide crystals, using a simplified model.

The position of the highest valence band is established by lowering the electron affinity of the halogen atom by the Madelung energy. The $\underset{\sim}{k}$ dependence of the valence band can be inferred from previous tight-binding calculations;[1] the width of the valence band is considered to be less than 1 eV. The conduction bands are computed by perturbing the free electrons with a model pseudopotential,[2] which is the sum of pseudopotentials of positive[3] and negative ions. In the pseudopotential of the negative ion a parameter α is included, which cannot be determined from atomic data.

The results obtained for the NaCl structure indicate that the minimum of the conduction band is the s-like state Γ_1 at $\underset{\sim}{k} = 0$. This state is insensitive to small changes in the lattice constant, but decreases considerably when the difference between the ionic radii increases; this leads to energy gaps in fair agreement with experiment for all alkali halides. The general structure of the higher conduction states agrees with that postulated by J. C. Phillips[4] to explain the optical excitation spectra.[5] We also obtain a forbidden gap in the conduction states, whose width depends on the value of the parameter α. This may be useful for explaining the exciton states above the energy gap and the L bands of the F center.

The electronic states for the CsCl structure have also been investigated and similar results have been obtained.

* On leave of absence from Argonne National Laboratory, Argonne, Illinois.

[1] L. P. Howland, Phys. Rev. 109, 1927 (1958) and W. B. Fowler, Phys. Rev. 132, 1591 (1963).

[2] F. Bassani and V. Celli, J. Phys. Chem. Solids 20, 64 (1961) and M. L. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961).

[3] We are grateful to Dr. V. Heine for sending us pseudopotentials for the alkali ions.

[4] J. C. Phillips, Phys. Rev. 136A, 452 (1964).

[5] J. A. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. 116, 1099 (1959) and H. R. Philipp and H. Ehrenreich, Phys. Rev. 131, 2016 (1963).

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10 Photon Induced Reorientation of M Centers in Potassium Chloride

R. DE BATIST,* Y. HAVEN,** and T. J. TURNER***

The kinetics of the reorientation of M centers in KCl single crystals has been investigated as a function of temperature and of the intensity of the polarized F light causing the rotation of the M centers. The results obtained for different geometrical conditions (polarization of the exciting F light and polarization of the light used for the measurement of the optical density) have shown that the time dependence of the dichroism (resulting from a nonequilibrium distribution of the M centers over the six possible orientations) can be expressed by one or two relaxation times, in agreement with the theoretical results described elsewhere.[1]

The main results of this investigation can be summarized as follows:

1. The orientation of M centers as a result of the absorption of light in the M_F band can be described assuming nearest neighbor ionic jumps, occurring presumably during the non-radiative transitions between the excited π states and the excited Σ_u state.

2. The quantum efficiency is about 3 times as large after absorption of M_F light polarized along $\langle 001 \rangle$ as after absorption of M_F light polarized along $\langle 011 \rangle$.

3. The process can be described by an activation energy of 0.036 eV, and a preexponential factor of ≈ 1.5.

Furthermore, the data indicate that at constant temperature the quantum yield decreases with increasing light intensity.

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[1] R. De Batist, Y. Haven, and T. J. Turner, see Abstract No. 11.

11 Relaxation Modes for Reorientation of M Centers in Alkali Halides

R. DE BATIST,* Y. HAVEN,** and T. J. TURNER***

The double F-center model for the M center being adopted, six orientations of the M center along the ⟨011⟩ directions are possible.

The populations n_i of the six directions by M centers can be described with relaxation modes

$$n_i = \sum_l A_{il} e^{-t/\tau_l}$$

where the number of modes l is equal to, or smaller than, the number of directions under discussion.

Group theoretical arguments show how the rate equations must be grouped together for finding the relaxation times easily.

The contribution from M centers to mechanical relaxation can be described with two relaxations of symmetry species E_g and T_{2g} of group O_h excited by unidirectional compressional stresses and shearing stresses, respectively.

In the case of optically induced reorientation, the jump rates differ so much for different directions of the axis of the M center that the process can only be described by symmetry species of the lower symmetry groups. Irradiation with ⟨001⟩ polarized F light induces the representation $2A_1 + B_1 + B_2 + E$ of group D_4 (resp. g-terms of group D_{4h}) and irradiation with ⟨011⟩ polarized F light induces $3A_1 + B_1 + B_2 + B_3$ of group D_2 (resp. the g-terms of D_{2h}).

Each of the irreducible representations corresponds with a relaxation mode. The population of the modes contributing to dichroism are:

		⟨001⟩ F light (D_4)				⟨001⟩ F light (D_2)			
directions	XYZ	Ψ_1 (A_1)	Ψ_2 (A_1)	Ψ_3 (B_1)	Ψ_5 (E)	Ψ_7 (A_1)	Ψ_8 (A_1)	Ψ_9 (A_1)	Ψ_{12} (B_3)
1	110	0.1	1	0	0	0	1.13	−0.3	1
2	$\bar{1}10$	0.1	1	0	0	0	1.13	−0.3	1
3	$0\bar{1}1$	0.2	−0.5	1	1	0	1	1	0
4	$\bar{1}01$	0.2	−0.5	−1	0	0	1.13	−0.3	−1
5	011	0.2	−0.5	1	−1	1	−5.52	−0.2	0
6	101	0.2	−0.5	−1	0	0	1.13	−0.3	−1

Ψ_1 and Ψ_7 are equilibrium modes and the relaxation times are

$1/\tau_2 = 4K_{001} + K_{011}$

$1/\tau_3 = 3K_{011}$

$1/\tau_5 = 2K_{011}$

$1/\tau_{8,9} = 2.25K_{011} + 0.5K_{001} \pm [4.062\ K_{011}^2 + 0.25K_{001}\ (K_{001} + K_{011})]^{1/2}$

$1/\tau_{12} = 3K_{001} + 1.5K_{011}$

$K_i = I_o \eta_i k_i$, I_o = intensity, η_i = quantum yield,

k_i = absorption coefficient per M center.

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12 Phonon Combination Bands of U Centers

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The infrared absorption of U centers measured at low temperatures consists of a sharp resonance peak at the local mode frequency and symmetrically displaced side bands. The side bands have been interpreted as combination bands: in the high frequency side bands, a phonon is created together with a localized quantum; in the low frequency side bands, a phonon is destroyed together with excitation of the local mode. We have measured these combination spectra in the following alkali halides: NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, and RbBr. The more interesting cases are those with the largest anion to cation mass ratio (NaBr, KBr, NaI, and KI). In these crystals side band peaks are seen with displacements in the range of acoustic and of optical phonon frequencies, and a comparison can be made with available phonon spectra and dispersion curves. For the cases of KBr and NaI, the dispersion curves are known from neutron spectrometry data. The contributions to the side band peaks come from the following branches:

TA	(1, 0, 0)	(KBr: 43 cm^{-1}; NaI: 39 cm^{-1})
TA	(½, ½, ½)	(NaI: 53 cm^{-1})
LA		(KBr: 83 cm^{-1}; NaI: 75 cm^{-1})
TO		(KBr:113 cm^{-1}; NaI: ~120 cm^{-1})

The symmetry point (100) itself should not contribute to the absorption according to selection rules given by R. Loudon.[1] However, frequencies in the vicinity of this point in the TA branch produce an absorption peak in all spectra.

The assignment given above for these side bands in KBr and NaI allows conclusions about the phonon spectra in the other crystals. This is of special interest in NaBr and KI, as calculations by Karo and Hardy[2] predict a gap between acoustical and optical frequencies to occur as in the case of NaI. This gap also appears in the side band absorption and lies between 105 and 125 cm^{-1} in NaBr and 68 and 91 cm^{-1} in KI. (The lower limit of the optical frequencies may be modified since a critical point at TO (½, ½, ½) is forbidden in absorption.)

[1] R. Loudon, Proc. Roy. Soc. (London) 84, 379 (1964).
[2] A. M. Karo and J. R. Hardy, Phys. Rev. 129, 2024 (1963).

13 Far Infrared Absorption Induced by Local Changes of Mass and Force Constant in Alkali Halides*

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The far infrared absorption induced by a substituted impurity ion in the alkali halides was studied including in the perturbation on the dynamical matrix both changes of mass and force constant. Starting from the expression of the complex dielectric constant of an imperfect cubic polar crystal, the electric dipole contribution to the impurity induced absorption coefficient was found to be:

$$\alpha(\omega) = (2\pi e_T^{*2} n / M_\pm c)\, \omega / (\omega^2 - \omega_T^2)^2$$

$$\mathrm{Im}\langle q = 0, \mathrm{TO} | K^{(\Lambda)}(\omega^2 + io^+) | \mathrm{TO}, q = 0 \rangle$$

where

$$K^{(\Lambda)}(Z) \equiv \Lambda(\omega^2)\, [I - (Z - L_o)^{-1} \Lambda(\omega^2)]^{-1}.$$

n is the impurity concentration, c the light velocity, e_T^* the transverse effective ionic charge, $M_\pm$ the mass of the foreign ion, ω_T the transverse optic frequency at wavevector $q = 0$; L_o the dynamical matrix of the perfect lattice and $\Lambda(\omega^2)$ the frequency dependent perturbation.[1]

The absorption spectra of Ag^+-doped KCl, KBr, KI, and NaCl were considered and was evaluated for the acoustic range frequencies. It was found that the change of force constant has a large effect on the peak frequency of the absorption band; so the analysis of the experimental data gives useful information on the interaction between the foreign ion and its surrounding. Both overlap (Huggins-Mayer form: $c_{+-} b_+ b_- \exp(-r/\rho)$) and Van der Waals potentials up to dipole quadrupole term were considered in the ion-ion interaction. The value of ρ in the Ag^+-halogen overlap potential was chosen as a free parameter in order to fit the experimental peak frequency. Effects of elastic relaxation were taken into account.

The ρ-values so deduced are: $\rho(\mathrm{AgI}) = 0.259$; $\rho(\mathrm{AgBr}) = 0.271$ and $\rho(\mathrm{AgCl}) = 0.251$ (consistently in both NaCl and KCl host crystals), in agreement with Mayer's values.

* This research has been sponsored by EOAR under Grant N965-05 with the European Office of Aerospace Research — U.S. Air Force.

[1] R. Fieschi, G. F. Nardelli, and N. Terzi, Phys. Rev. 138, 203 (1965).

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14 Infrared Absorption and Paramagnetic Resonance of Hydrogen in Calcium Fluoride

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A theoretical and experimental investigation of the absorption spectrum due to localized vibrations of H^- ions in CaF_2 has been carried out. Measurements in the region 1-14μ show, in addition to the fundamental frequency, a second harmonic and two third harmonics of the fundamental vibration. The spectrum is assigned to the vibrations of H^- ions in the anharmonic tetrahedral potential well at fluorine sites. Broad side bands are observed on both sides of the localized vibrational lines due to combined excitation of localized and lattice band modes. The temperature dependent intensity, width and shift of the localized vibrational lines have been measured. The temperature dependent effects and the presence of side bands arise from anharmonic interactions with lattice band modes. The spectrum of D^- ions has also been investigated.

After X-irradiation of CaF_2:H crystals in an X-band microwave cavity at 77° K we observe the EPR spectrum of hydrogen atoms on fluorine sites. On warming the crystals to 124° K the substitutional atoms move into interstitial sites and are stable in these sites at room temperature. The EPR spectra of substitutional and interstitial hydrogen atoms are readily distinguishable since in the former case one observes a resolved hyperfine interaction with six nearest neighbour fluorine nuclei and in the latter case with eight nearest neighbor fluorine nuclei.[1] The interaction of the substitutional hydrogen atoms with more distant fluorine shells has been investigated by the ENDOR method.

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** Now at Physics Department, University of California, Los Angeles.
*** Now at R.R.E. Malvern, England.
[1] J. L. Hall and R. T. Schumacher, Phys. Rev. 127, 1892 (1962).

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15 Theory of the Infrared Absorption Due to U Centers in Alkali Halides

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Recent measurements of the infrared absorption due to U centers by Fritz et al.[1, 2, 3] have led to results on the line width, the temperature dependent shift of the resonance peak, and the structure of the combination bands. These results are discussed using the anharmonic potential of the defect and its nearest neighbors.

The *cubic* anharmonic coupling between the defect ion and the neighbouring alkali ions determines the two-phonon decay of the local mode (D^-) at low temperatures and the side band structure (D^- and H^-); it contains a term lowering the H^- and D^- band-frequencies while another one increases the D^- frequency only.

The *quartic* anharmonicity of the local mode itself causes the observed T^2-behaviour of the line width[3, 4] and strongly contributes to a shift to higher frequencies.[3] The three-phonon decay due to quartic anharmonicity gives a nearly temperature independent H^- band width which is to be observed in the helium temperature range.

We have calculated the side band absorption for $KCl:H^-$ using different cubic anharmonic coupling parameters and lattice vibration eigenvectors calculated by Kucher.[5] The best fit to the experimental curve is obtained by taking into account nearest neighbours only. A similar calculation with second order dipole moment parameters turns out to be inconsistent with experiment. An interpretation of the side band shape in other alkali halides can be derived from the calculation on KCl.

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[1] B. Fritz and U. Gross, see Abstract No. 56.

[2] P. Bäuerle and B. Fritz, see Abstract No. 12.

[3] B. Fritz, U. Gross, and D. Bäuerle, to be published.

[4] W. Hayes, G. D. Jones, H. F. Macdonald, C. T. Sennett, and R. J. Elliott, to be published.

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16 Temperature Dependence of the Rotational Structure of the Local Mode in Potassium Iodide Containing No_2^-

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In the gap of the phonon-frequency spectrum of KI (70-90 cm^{-1}) with NO_2^- impurities, several absorption lines have been discovered by Sievers and Lytle[1] as well as by Renk.[2] These lines are found to be due to a local mode at 71 cm^{-1} and its coupling to rotational transitions (lines at 73, 78, 79.5, 88 and 89 cm^{-1}).[3]

The integral absorption of the local mode is nearly independent of temperature. The rotational transitions, however, generally show a strong temperature dependence proportional to $T^{-3/2}$ except for the lines at 79.5 and 88 cm^{-1}. Each one corresponds to a series of transitions with nearly equal frequencies determined by the selection rules $\Delta J = 0$, $\Delta K = 2$.

The splitting of these lines due to the deviation of the NO_2^- ion from a symmetric top and to the influence of the crystal field should be small. The summation over all transitions belonging to one line leads to a weak temperature variation proportional to $T^{-1/2}$ above 20° K. This explains the corresponding observations by Sievers, Lytle and Renk. The expected ratio of intensities (1:2) of the integral absorption at 79.5 cm^{-1} (transitions $K = 0 \rightarrow K = 2$) to that at 88 cm^{-1} (transitions $K = 1 \rightarrow K = 3$) is in good accordance with experiments.[3]

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17 Density Changes and F-Center Formation in Potassium Chloride Crystals by X Irradiation at Room Temperature

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KCl single crystals were uniformly colored with x rays at room temperature. The irradiation was interrupted for the density measurements, which were made using a hydrostatic flotation technique. Then the sample was annealed at 300°K and was subjected to a second series of irradiations under identical conditions for the measurement of the F-center growth (the total concentration of F-aggregate centers was less than 10% of the F-center concentration in all cases). Crystals purchased from Dr. K. Korth, Kiel, Germany, showed a strong Stage I coloration (saturation concentration 1.8×10^{17} cm^{-3}) and only a weak, linear coloration in Stage II. The F-center formation in Stage I was accompanied by a pronounced density change. Assuming that no loss of mass occurred during the irradiation, a volume change of 1.3 a^3 was obtained for each F center formed in Stage I, a being the interionic distance. This volume change is comparable to the volume change of each F center formed during Stage II, indicating that in Stage I the F centers were also formed from vacancies which were created by the irradiation. It is speculated that the Stage I F-center formation proceeds via ejection of impurity ions from their lattice sites into nearby interstitial positions. Harshaw crystals, which showed very little Stage I-coloration (2×10^{16} F centers cm^{-3}), were irradiated up to 1.2×10^{18} F centers cm^{-3}. The density change was found to be strictly proportional to the F-center concentration. The volume change per Stage II F center was (1.36 ± 0.03) a^3. Taking into account the volume change due to the lattice relaxation around the F center (see next paper), it is felt that this value is in much better agreement with a Frenkel-defect production mechanism than with a mechanism leading to formation of cation and anion vacancies. In KCl crystals containing 2×10^{17} U-centers,[1] the volume change due to the reaction $U \rightarrow F$ was found to be (1.12 ± 0.03) a^3.

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[1] The KCl:KH crystals were kindly supplied by the II. Physikalische Institut der Technischen Hochschule, Stuttgart, Germany.

18 Irradiation-Induced Color Centers in Magnesium Fluoride*

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Color centers have been observed in MgF_2 (rutile structure) produced by 50 kV x rays. Both electron and x-ray irradiation up to 250 kV seem to produce similar results. The work described here was done at room temperature, since the bands show marked thermal stability at room temperature and are difficult to produce at low temperature. The lower symmetry of the crystal structure should aid in the eventual identification of the centers. A strong band is initially produced with $E \perp c$ and $E \parallel c$ components near 255 and 265 mμ, respectively, which is largely and irreversibly bleached by light in this band yielding a strong band at 370 mμ and several weak bands including one at 320 mμ. Neither of these have observable $E \parallel c$ components.[1, 2] The 320 mμ band can be enhanced with a 370 mμ band bleach and vice versa. Optical bleaching, in general, appears to give no over-all loss in total band strength. Ultraviolet-excited luminescence bands have been observed including one at 420 mμ ($E \perp c$) and a second at 560 mμ (isotropic).

Detailed polarized bleaching experiments indicate that the 320 mμ band arises from centers lying along the ⟨110⟩ axes. A possible model is one in which the 320 mμ band arises from single holes trapped at two adjacent anions as in the V_K centers of alkali halides. The initial 260 mμ band could arise from holes trapped at cation vacancies. The 370 mμ band appears cylindrically symmetric about the c-axis and would thus remain unexplained, but is not wholly inconsistent with a V_K type center.

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* Research supported by the Advanced Research Projects Agency.

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19 EPR Spectrum of Cu^{+2} in Sodium Chloride Crystals

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In NaCl containing Cu, we have succeeded in reversibly converting $Cu^{+1} \rightleftarrows Cu^{+2}$ by annealing at high temperatures in a chlorine or nitrogen atmosphere. However, the EPR spectrum in thermally quenched NaCl — Cu^{+2} crystals (Cu concentration $10^{-5} \sim 10^{-3}$) showed only broad resonance lines indicating clustering of Cu^{+2} ions.

To produce the resolved hyperfine spectrum, NaCl with Cu^{+1} or NaCl with Cu^{+1} and Ag^{+1} was irradiated with gamma ray at liquid nitrogen temperature. Subsequent measurements without warming showed signals from Cu^{+2} and V_K centers in the former case and Cu^{+2}, Ag^{+2}, Ag^0 and V_K centers in the latter.

The Cu^{+2} spectrum shows up clearly after suitable warm-up and recooling for measurements. With the magnetic field parallel to the [100] direction — the z-axis — the four most intense lines are from the parallel spectrum with $g_z = 2.37$, $A/g_z\beta = 97$ gauss and a line width of 30 gauss. While warming towards room temperature, these lines combine to a single line with $g = 2.20$, indicative of a Jahn-Teller distortion. The perpendicular spectrum, reduced in intensity compared to that of the z-direction, has $g_\perp = 2.04$, $B/g_\perp\beta = 34$ gauss and a line width of 10 gauss. These spin Hamiltonian constants are in accord with those obtained by Tucker[1] on AgCl-Cu^{+2}. With reduced magnetic field modulation, the four Cu^{+2} resonances of the parallel spectrum show a resolved superhyperfine spectrum of approximately 6 gauss separation with the number of resonances estimated to be 19 — the number expected from six chlorine ligands.

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20 Rare Earth Ions in the Alkali Halides

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The main feature of part of the optical spectrum of rare earth ions in ionic crystals is that it consists of very narrow spectral lines. Half widths are typically of the order of 1Å at helium temperatures. One immediate consequence is that detailed crystal field studies may be readily carried out through the measurements of crystal field splittings of transitions between pure electronic states of the rare earth ion of the type $4f^n \rightarrow 4f^n$. Assignments of transition moments and crystal field terms can readily be made through measurements of the behavior of crystal field levels under applied magnetic, electric or strain fields or under polarized excitation. Such a study, which has been done for divalent samarium in the alkali halides, has led to a detailed description of the divalent impurity ion-vacancy complex and its immediate surroundings.

In addition to the spectra from transitions between pure electronic states, vibronic spectra due to the coupling of electronic states to the vibrational motion of lattice ions may also readily be observed. In the alkali halides two types of vibronic spectra are found. One, which consists of series of evenly spaced, sharp lines, has been shown to result from coupling to pseudo-localized vibrational modes, which arise in the vicinity of the rare earth ion. A second type of vibronic spectra, which contains broader, unevenly spaced lines, arises from a more extended coupling to the vibrations of lattice ions sufficiently removed from the localized vibrations. The latter vibronic structure may be used to study certain parts of the density of states of the lattice vibrations.

Finally, the electron-lattice coupling determines the life time of excited electronic states against non-radiative decay, and therefore the line widths of the narrow spectral lines. Some insight into the non-radiative decay processes, some of which involve many-quanta steps, may be obtained in this way.

21 A Dynamical Pseudo-Jahn-Teller Effect at Eu^{2+} Impurities in Alkali Chlorides

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Vibronic spectra have recently been observed in alkali halides containing divalent rare-earth impurities (Eu^{2+}, Sm^{2+} or Yb^{2+}). The theory of these spectra and an analysis of the experimental results has been given by the authors. The defect is of C_{2v}-symmetry and exhibits two main pseudo-localized modes, one of A_1 and the other of B_1 type. (Two further but less important local modes of the same symmetry types do not concern us here.) Non-degenerate electronic terms can only couple to the A_1-mode. Nearly degenerate terms, however, may couple also to the B_1-mode. But exact degeneracy being forbidden by symmetry, the electronic levels cannot cross each other by a theorem due to Neumann and Wigner. Thus the potential curves of the B_1-mode separate into one of a high effective frequency, and one of a lower frequency which is less significant. A further increase of the vibronic frequency follows from the approximate selection rule $\Delta m = 0, \pm 2$, which is a consequence of the special type of coupling to the B_1-mode.

In this way a striking dynamical effect can be expected which is observed in the spectra of Eu^{2+} in the alkali chlorides, where the vibrational frequency observed on an absorption band is strongly increased by a factor of 3 to 4 over that observed on emission bands.

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22 Faraday Rotation of Silver Atoms in Potassium Chloride

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A well defined absorption band appears at 425 mμ when KCl crystals containing silver impurity ions are X-irradiated at 77°K. It has been suggested,[1] as a result of spin resonance and optical absorption studies, that the main part of this band is due to a transition from the $4d^{10}\ 5s,\ {}^2S$ ground state to the $4d^{10}\ 5p,\ {}^2P$ first excited state of silver atoms formed by the trapping of electrons at silver ions on potassium lattice sites. This assignment has been verified by observation of the Faraday rotation pattern for the 425 mμ band as a function of temperature down to 4.2°K and for a variety of high magnetic fields. The results were obtained in fields up to 80 kilo-oersteds using a two inch I.D., water cooled, two megawatt solenoid and an optical rotation apparatus capable of scanning the ultraviolet-visible region of the spectrum. The recorded patterns were analyzed by the method of moments[2] and they show a large positive paramagnetic Faraday rotation. This indicates that the spin-orbit coupling constant is positive as expected for a $4d^{10}\ 5p$, ^2P state and is in contrast with the negative paramagnetic rotation obtained for the F center.[3] A comparison of the observed spin-orbit coupling constant of the ^2P state in the solid with that of the free atom is of interest.[4]

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23 Dielectric Relaxation Changes Due to Optical Conversion of F to Z_1 Centers in Potassium Chloride

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Many models for the Z_1 center have been proposed, but there is no definite experimental evidence for any of them.[1] Correlated measurements of optical absorption and dielectric relaxation, which is proportional to the impurity-vacancy dipole concentration,[2] provide new information on the nature of the Z_1 center.

We have studied the dielectric losses of additively colored KCl containing 10^{-3} $SrCl_2$. Z_1 centers have been obtained by an intense F-light illumination of 30 seconds at $T = 40°C$. This temperature is chosen in order to avoid the formation of Z_2 centers, which give rise to an intense Debye peak, masking the relaxation of the dipole "divalent impurity — positive ion vacancy" (I.V.).

The additively colored crystals, containing only F centers ($\approx 1.3.10^{17}$ cm^{-3}) shows only the known Debye losses of the I.V. dipoles. Subsequent F-light irradiation provides the conversion $F \rightarrow Z_1$. Optical absorption measurements indicated that the Z_1 band reached saturation ($\simeq 7.8 \times 10^{16}$ Z_1 centers cm^{-3}) immediately after the illumination: no increase of the Z_1 band has been detected afterwards. Dielectric losses measurements, performed immediately after the illumination of the sample, show that the dipoles concentration is unchanged. Thereafter the dipoles concentration decreases slowly reaching 92% of the initial value within 25 minutes. The former result shows that impurity vacancy dipoles are not involved in the formation of Z_1 centers. It is likely that the Z_1 center is an electron trapped at an isolated impurity (Seitz model). The Z_1 formation breaks the thermodynamical equilibrium between single impurities, cation vacancies and I.V. dipoles; the new equilibrium configuration is attained gradually, with the dissociation of a fraction of dipoles.

These conclusions are confirmed also by measurements of ionic thermocurrents, before and after the optical F → Z_1 conversion.

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24 Ionic Thermoconductivity in Alkali Halides*

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Dielectric polarization can be studied by means of ionic thermoconductivity (ITC):[1] one measures the depolarization current of a sample while the temperature increases linearly; the relaxation processes in the dielectrics yield bands of current i(T) whose analysis provides information on the parameters characteristic of the relaxation mechanism, i.e. in the case of dipolar orientation, one can measure number of dipoles, activation energy E and temperature independent factor of the relaxation time τ_0; ($\tau = \tau_0 \exp [E/kT]$). The method has a high sensitivity and with a single measurement one can obtain complete qualitative information on the relaxation processes taking place in dielectrics. Several measurements have been carried out on alkali halides. The following phenomena have been detected: 1) relaxation of "divalent metal impurity-positive ion vacancy" dipoles (I.V. bands) ($200 \lesssim T \lesssim 280$°K); 2) strong ITC bands, probably due to surface effects ($350 \lesssim T \lesssim 420$°K); 3) space charge relaxation ($T \gtrsim 400$°K). The activation energy E of the I.V. relaxation can be derived from the initial rise of the ITC band.[1] A more accurate analysis is obtained from the analysis of the whole i(t) band; in fact one can easily show that:

$$\ln\left[\int_t^{\infty} i(t')\,dt'\right] - \ln i(t) = \ln \tau_0 + E/kT.$$

A plot of the left hand side, whose first term can be determined by graphical integration of the discharge curve, as a function of 1/kT yields directly E and τ_0. Results have been obtained in the case of NaCl, KCl and KBr doped with $SrCl_2$, $CaCl_2$ and $BaCl_2$. Besides the main I.V. bands, however, other I.T.C. bands appear in the first range of temperatures, which are probably due to dipoles of different configuration and to dipolar complexes; their relative intensity depends on the thermal treatment of the sample.

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25 Electron-Nuclear Double Resonance of Z_1 Centers in Potassium Chloride*

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The structure of the Z_1 center in potassium chloride, containing strontium or calcium as an impurity, has been investigated by the electron-nuclear double resonance (ENDOR) technique. There are considerable qualitative similarities, but quantitative differences, between the ENDOR spectra in strontium and calcium doped crystals. The largest isotropic hyperfine constants (32-34 Mc/sec.) differ by only about 1% between calcium and strontium doped crystals, suggesting, in agreement with previous optical work, that the effect of the divalent impurity is almost entirely due to its effective positive charge with respect to the lattice. Two similar structures, both present in calcium and strontium doped crystals, but in different relative concentrations, are proposed to explain the ENDOR results. Both structures contain a divalent impurity and a cation-anion vacancy pair, as originally proposed by Kleefstra. One arrangement of these defects is that proposed by Gebhardt and Lüty, i.e., a nearest neighbor ⟨100⟩ vacancy pair, with the impurity in a ⟨110⟩ position with respect to the positive-ion vacancy, away from the negative-ion vacancy. The other (linear) arrangement also contains a nearest-neighbor ⟨100⟩ vacancy pair, but the impurity is in a ⟨200⟩ position with respect to the positive ion vacancy, away from the negative ion vacancy. Resolved hyperfine structure of Z_1 centers containing strontium enriched in the magnetic isotope Sr^{87}, expected on the basis of the Seitz model, was not observed showing that the model is incorrect. A search was made for ENDOR absorption due to Z_2 centers in strontium doped KCl, but only lines due to the F centers also present were found. This preliminary result tends to confirm the diamagnetism of the Z_2 center reported by Ohkura and Murase.

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26 Production of Ultrapure Alkali Halides — A Survey*

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It has become increasingly apparent in recent years that many of the variations in the radiation induced electronic and optical properties of alkali halides are caused by the presence of trace amounts of certain impurities. Consequently, considerable effort is being expended to develop means of producing much purer alkali halides than previously have been available. The overall problem of ultrapure alkali halide production may be divided conveniently into three areas: purification of starting material, growth of crystals and analysis techniques. This paper describes representative methods being used at various laboratories to secure purified starting material, discusses some of the problems involved in crystal growth and in the characterization of "crystal purity," and reviews some of the more significant analytical techniques now in use.

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27 Color Centers in Deformed Potassium Bromide and Rubidium Bromide

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The environment of F centers formed by Co-60 irradiation (low dosages) of deformed potassium bromide and rubidium bromide was studied by means of optical absorption. Splitting of the beta band (exciton band localized at the F center) and shift of the F-center peak toward the blue were observed on both deformed potassium bromide and rubidium bromide at low temperatures. The beta band splitting is about 70 cm^{-1} for potassium bromide and 140 cm^{-1} for rubidium bromide at liquid nitrogen temperature. The experimental observations support the hypothesis[1] that the source of vacancies in deformed alkali halides is the dislocation dipoles generated within the material from plastic deformation and that the F centers formed upon Co-60 irradiation are perturbed by the dipole stress fields.

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28 Modulated F-Center Absorption in Potassium Chloride

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Additively colored alkali halide crystals irradiated with F light chopped at frequency ν_0 develop a population of electrons in the first excited state of the F center which changes at the same frequency. As a consequence, the population of the fundamental state varies with frequency ν_0 and opposite phase. Under such conditions the absorption coefficient due to transitions starting from the fundamental level of the F center (as well as from the first excited state) shows a modulation at frequency ν_0 which can be detected with great sensitivity by use of synchronous amplifiers. Variations of the absorption coefficient of the order of 10^{-5} cm^{-1} are easily detected over most of the optical spectrum.

The results obtained for KCl crystals at liquid nitrogen temperatures show clearly the presence of "modulated" absorption of appropriate phase at the position of F, K, L_1, L_2, and L_3 bands and confirm beyond reasonable doubts that the K, L_1, L_2, and L_3 bands are caused by transitions starting from the fundamental state of the F center. At both sides of the F band, a signal with opposite phase originates from modulated F′ absorption. The dependence of the modulated absorption upon ν_0 shows that two processes limit the life time of the electrons in the excited F* level: namely: i) luminescent de-excitation and ii) a process

$$F^* + F \rightarrow F' + \text{Vacancy},$$

followed by the reaction:

$$F' + \text{Vacancy} \rightarrow 2\,F.$$

Process ii) has a characteristic time in the range of 10^{-1}, 10^{-2} sec and is predominant at low chopping frequencies. Its dependence upon the concentration of F centers is also discussed.

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29 V Bands in Potassium Chloride and Potassium Bromide

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The V_2, V_3, and V_4 bands in KBr appear to be due to intrinsic centers, as opposed to impurities, since their height shows no tendency to saturate as a function of irradiation dose. In KCl the V_2 and V_3 bands show similar properties to the KBr bands of the same name, but the band which appears to be analogous to the KBr V_4 band is not the one labeled V_4 by Dorendorf. Instead it is a band, called V(240) by Kingsley, which is slightly to the low energy side of the V_2 but unresolved from it. These three bands are produced (along with the F band) by x-ray irradiation in different temperature ranges. In KCl at least, they can transform one into another. These transformations occur by raising the temperature, not as a result of optical excitation, and they are irreversible. These facts suggest that the three centers are related to each other, but that they differ not merely electronically (i.e., in their state of ionization). Bleaching experiments with polarized light indicate that the V_2 and V_4 centers have a ⟨100⟩ symmetry axis. No anisotropic behavior is observed in the V_3 center, at least between 100° and 400°K.

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30 The Polarization of M-Center Luminescence in Sodium Chloride, Potassium Chloride, and Lithium Fluoride

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A study has been made of the variations in the polarization of the M-center luminescence excited by F-band light in NaCl and KCl. The variations are shown to be a consequence of the reorientation of the M centers under light stimulation. Thus the degree of polarization depends not only upon the electronic configuration at the defect, but upon the details of the reorientation process. The most likely process appears to be the movement of a neighboring negative ion into one of the sites of an F-aggregate center. The kinetics of such processes have been investigated and it is found that the Van Doorn and Haven model of the M center can be made consistent with the experimental result at the commencement of the polarized excitation, but cannot be reconciled with the time dependence of the results.

There is a temperature dependence of the rate of reorientation of M centers in NaCl and KCl; measured values of the degree of polarization at the commencement of polarized excitation are also found to be dependent upon the original electron irradiation dose in NaCl. Possible explanations of this result have been considered.

No appreciable M-center reorientation has been observed in LiF at 300°K for excitation with light in the 4500 Å band. Measurements of polarization as a function of the wavelength of the fluorescence excited by light in the 4500 Å band have been made. The emission consists of several overlapping bands, each of which appear to be due to anisotropic centers. By considering the ratio of the degrees of polarization excited by [100] and [110] polarized exciting light it is concluded that the center which emits on the long wavelength side of what is believed to be the M emission, has a ⟨100⟩ symmetry axis.

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31 Pulsed Radiation Studies of Color Centers in the Alkali Halides*

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Studies of the coloration of the alkali halides by short intense pulses of radiation have proved a useful tool in understanding some aspects of the formation, interaction, and interconversion of these centers. The experimental method consists of using short (10 nsec to 4 μ sec) pulses of high energy (30 Mev) electrons from a linear accelerator to color crystals. Such pulses deliver up to 10^{25} eV cm^{-3} sec^{-1}. The optical transmission at one or several suitable wavelengths is monitored during and after the radiation pulse by a fast-response optical system. Optical emission and electrical conductivity may also be measured. The kinetics of coloration and conductivity have been studied in this way for several materials, including KCl, KCl:Pb and KBr. In early-stage coloration, F-center formation continues for a few microseconds after the end of the radiation pulse. A value for the capture cross-section for electrons of the α center can be obtained from this, and from the decay of conductivity at the end of the radiation pulse. Many of the F centers formed by a pulse spontaneously bleach in a few seconds after the end of the pulse. This process is greatly enhanced by impurities such as lead, and their marked effect[1] on late-stage coloration is associated with a reduction in the number of *stable* F centers, rather than in the number formed by radiation. The kinetic behavior of hole centers during spontaneous bleaching of F centers has been studied, but no 1:1 relationship has yet been found. Measurements of radiation-destruction of M centers, with subsequent re-formation taking some 30 secs at 300°K, have been made. Studies of fluorescence during and after irradiation indicate that the self-absorbed radiation-produced fluorescence does not play an important role in color center interconversions. Intense F-center fluorescence is observed during the formation of F centers even at 300°K.

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32 Distribution of F Centers in X Irradiated Potassium Chloride

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The concentration quenching of the luminescence of F centers has been reported by several workers.[1, 2, 3] An idealized model to describe the quenching considers that two F centers separated by a distance greater than R_C can luminesce with unit quantum efficiency. If the two F centers are closer than R_C, it is assumed that neither can luminesce. If the distribution of F centers is completely random, it can be shown[4] that the efficiency for luminescence, η_F, will be

$$\eta_F = \exp\left(-4\pi/3 \ R_C^3 \ n_F\right). \tag{1}$$

Miehlich[3] has shown that this relationship is valid for additively colored KCl. The F centers were dispersed by a rapid quench in the dark. Measurements were made at 90°K. R_C was found to be 82.3 ± 4.5 Å. The quantum efficiency for the luminescence of F centers formed by x-irradiation deviated from the prediction of Eq. (1) at low concentrations.

In the present experiment, KCl was irradiated at 77°K with 50 kV filtered x rays. The irradiations were interrupted to allow measurement of the relative quantum efficiency for luminescence. F′ centers were removed by optical bleaching prior to the measurement. Concentrations were varied between 2×10^{14} and 1.1×10^{18} F centers cm^{-3} with several crystal thicknesses being used to cover the range of concentrations. No differences were found in measurements of the luminescence made at 77°K or 4°K. A plot of the logarithm of the reciprocal of the relative quantum efficiency for luminescence as a function of concentration was a straight line over the entire range of concentrations, in agreement with Eq. (1). R_C was found to be 77 ± 1 Å. A comparison of the luminescent efficiency of F centers in additively colored crystals with the luminescent efficiency of F centers formed by x irradiation indicated that the *absolute* efficiency is essentially the same for both systems.

If it is assumed that the quenching process utilized by Miehlich produced a random distribution of F centers, it appears that irradiation with x rays generates a distribution that is only slightly less random. This would suggest that a *large* fraction of the F centers can not be formed with small separations near the end of the track of a photoelectron. The small difference between the crystals which are additively colored and x-irradiated may be a result of this, however.

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33 Calculation of Zero and One Phonon Line Shapes by Green's Function Methods

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Calculation of the moments of the line shape as developed by Lax and Burstein[1] does not yield explicitly the line shape function. Furthermore, the adiabatic approximation must be introduced at the beginning of calculation. Recent advances in Green's function methods (e.g., the temperature-dependent double-time Green's functions of N. N. Bogoliubov[2]) can be readily adapted to calculate line shapes themselves (rather than their moments) by use of a modified Kubo formalism.[3] Recently, Barrie and Nishikawa[4] used the Green's function technique to obtain an approximate expression for the spectral function of a shallow impurity level. However, their formulation of the problem leads to an infinite hierarchy of equations connecting Green's functions of different orders. The approximations made to "decouple" this hierarchy assume a small coupling constant of the impurity and the phonons, and a large effective number of phonon modes interacting with the impurity. However, Markham's review[5] shows that for a trapped carrier center the number of phonon modes is more likely to be small rather than large. We have succeeded in avoiding this approximation by introducing a differently-formulated Hamiltonian for the interacting electron-phonon system.[6, 7] Instead of the conventional raising and lowering operators of the harmonic oscillator as phonon creation and annihilation operators, we introduce phonon-mode creation and annihilation operators by employing the rigorous second-quantization procedure of quantum field theory in writing down our fundamental Hamiltonian.[8] With this Hamiltonian the hierarchy of Green's function equations terminates exactly at a finite order (for finite lattices). Furthermore, the set of equations for the Green's functions of highest order is self-contained (i.e., contains Green's functions of only one order), so that these Green's functions may be calculated to any given order in the coupling constant. Then the Green's functions of any lower order may be obtained by forming appropriate sums over the highest-order Green's functions. No assumptions about the number of phonon modes need be made at any point in this procedure. We have used this method to calculate the qualitative form of the zero- and one-phonon spectrum of a carrier trapped in a lattice defect,[9] and we obtain good agreement with the experimental results.[10]

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34 Creation of Defects in Alkali Halides by Ionizing Radiation*

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Since the first evidence that, besides the conversion of pre-existing imperfections into color centers, new defects are created by the irradiation of alkali halide crystals, attempts have been made to establish the mechanism for this radiolysis. Despite 15 years of research the issue is yet in doubt and, although the several mechanisms that have been put forward have points in their favor, each seems to have some difficulty that prevents its complete acceptance. These proposed mechanisms include: vacancy-pair creation by recombination energy at dislocation jogs, suggested by Seitz; multiple ionization of an anion, originally postulated by Varley; and concurrent ionization by adjacent halide ions, as described by Klick and elaborated by Williams. Evidence supporting each will be summarized, but to anticipate the outcome it can be stated that the experimentally determined energy required to create an anion vacancy by irradiation below 10°K is inconveniently smaller than that expected from either of the last two mechanisms, and that the rate of defect production at low temperature is virtually insensitive to dislocation density.

In another quarter, namely room temperature irradiation, the situation which was formerly regarded as hopelessly complicated is not quite so bleak. Recent experiments relating to pulsed-radiation, influence of impurity and ionization intensity upon F-center yields, radiation hardening, and the difference in the optical stability of F centers introduced at various temperatures all seem to suggest that those remaining after irradiation near 300°K are the residuum after extensive relaxation, and that the extent of this back reaction is sensitive to the steady-state carrier concentrations and their mode of recombination. In this view, vacancies and interstitials are created in the same yield (and by the same mechanism) as at low temperature and subsequent recombination occurs to the extent that mobile interstitials have not been trapped or otherwise stabilized in some combined form.

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35 ENDOR Study of the H Center in Lithium Fluoride*

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A detailed ENDOR study was carried out on the H center in LiF. Hyperfine constants for five sets of nonequivalent neighboring nuclei have been determined. The results give good support to the model of Känzig and Woodruff.[1]

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36 ENDOR Hyperfine Constants of the V_K Center*

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The hyperfine interaction between the unpaired spin of the V_K center and a neighboring nucleus can be expressed as $\underset{\sim}{I}\cdot\underset{\sim}{A}\cdot\underset{\sim}{S}$. By fitting the ENDOR spectrum of the neighboring nucleus to the complete spin Hamiltonian of the V_K center plus its neighbor, we determine the principal values and principal axes of the hyperfine tensor $\underset{\sim}{A}$. These values are the ENDOR hyperfine constants, $A_i = B_i + a$ ($i = x, y, z$), where the B's and the a denote the dipole-dipole and the Fermi contact interactions and i is a principal axis. The ENDOR hyperfine constants of the V_K center in LiF have been measured by Gazzinelli and Mieher[1] for the three lithium shells and the three fluorine shells nearest to the center. For the V_K center in

NaF we measure the ENDOR hyperfine constants of the three nearest fluorine shells and the nearest sodium shell. Also these ENDOR hyperfine constants and their principal axis directions are calculated using the self-consistent field molecular orbital for the F_2^- molecule-ion obtained by Wahl. The dependence of these constants on lattice relaxations and core polarization of the closed shell V_K orbitals is shown and compared with the experimental results.

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[*] This work was supported in part by the National Science Foundation under Grant NSF-GP 3385 and in part by the Joint Services Electronics Program under Contract DA-28-043 AMC-00099(E).

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37 Magneto-Optic Effects in the K Band of Rubidium Chloride, Rubidium Bromide, and Potassium Chloride

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The circular dichroism of the K band in RbCl, RbBr and KCl was studied at liquid helium temperature. At a given wavelength the magnetic field induces a change in the absorption of right circularly polarized light which is proportional to the absorption at this wavelength, and to the spin polarization $\langle S_z \rangle$ in the ground state with $\langle S_z \rangle = 1/2 \tanh g\beta H/2KT$ where K is the Boltzmann constant. One finds $(1/\langle S_z \rangle)(\Delta k/k) = 0.10$ for RbCl, 0.17 for RbBr, and 0.043 for KCl. These results may be explained if one assumes a strong mixing of the K levels with the first p state. Applying the method of moments[1] to the extreme case of forbidden transitions made allowed by distortions of the lattice, one calculates the variation of the area of the absorption curve induced by a magnetic field: $\Delta A/A = 4\langle S_z \rangle \Delta/[3(E_K - E_F)]$ where Δ is the spin orbit splitting of the first excited state, E_K and E_F are the average energies of the K and F levels. Using the known values of Δ[2, 3] and E_K one finds $(1/\langle S_z \rangle)(\Delta A/A) = 0.097$ for RbCl, 0.15 for RbBr, 0.033 for KCl. Considering the lack of precision in the determination of the absorption curve and in the knowledge of Δ, the experimental values of $\Delta k/k$ and the values of $\Delta A/A$ calculated for the above model agree relatively well. One may conclude that the mixing of the K levels with the first p state is strong and is responsible for a large part of the intensity of the K band.

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38 Trapped Hole Centers in the Alkali Halides*

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The pioneering work of Känzig and his co-workers in which electron spin resonance absorption was used to study the (halogen)$_2^-$, or V_K, centers gave us the first really detailed knowledge of any trapped hole centers in the alkali halides. Since this work, the progress in the knowledge concerning trapped hole centers has continued; an attempt will be made to review this progress over the three years since the Color Center Symposium in Stuttgart. Among the subjects to be reviewed will be (a) holes trapped in the neighborhood of impurity ions such as alkali metal ions, other metal ions, oxygen ions, and halide ions; (b) hydrogen atoms in the alkali halides; (c) electron-hole recombination processes; and (d) recent results concerning V_1, V_2, V_3, V_4, and H centers.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

39 Luminescence Processes in X Irradiated Potassium Chloride Crystals with Silver*

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ESR measurements have shown that after x irradiation at 77°K, KCl-Ag crystals contain Cl_2^- (V_K centers) and Ag^0 (silver atoms). If these crystals are maintained at 77°K after x irradiation, a long persistent luminescence (afterglow), which does not follow a simple exponential decay, is observed. The intensity of the afterglow is almost independent of temperature over the range 5 — 140°K. The energy distribution of the luminescence peaks at about 2.3 eV and is essentially identical in nature to the luminescence observed in the first thermal-glow peak of the system at about −70°C. The first glow peak results from the recombination of trapped electrons and holes. If the Cl_2^- ions are preferentially oriented along one of the ⟨110⟩ directions in the crystal, by bleaching with polarized light, the afterglow is polarized in the same direction as the oriented Cl_2^- ions. When the crystal is warmed slowly through the temperature region in which Cl_2^- ions disorient, the degree of polarization of this emission changes slowly from a positive value through zero to a negative value and finally comes back to zero. These results can be explained if it is assumed that the afterglow arises from the recombination of nearby pairs of Cl_2^- and Ag^0 through an anisotropic tunneling process. Very similar results have been obtained on the system KCl-Tl except that in this case the energy distribution of the luminescence peaks at about 3.0 eV.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

40 Optical Properties of Tl_2^+ Ions in Irradiated Potassium Chloride Containing Thallium*

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At 77°K ionizing radiation produces thallium atoms (Tl^0) and Cl_2^- molecule ions in crystals of KCl containing moderate amounts of thallous chloride. If the concentration of thallous ion is increased, it is observed that in addition to the two above mentioned species, a new species identified as Tl_2^+ is formed. Tl^0 is formed when isolated Tl^+ captures an electron, while Tl_2^+ is formed when a pair of nearest neighbor Tl^+ ions capture an electron. The amount of Tl_2^+ formed is roughly proportional to the square of the Tl^+ concentration. Correlated studies on nonirradiated KCl-Tl crystals show ultraviolet absorption bands whose intensity varies with the square of the Tl^+ concentration and are probably associated with nearest neighbor Tl^+ pairs, similar to the work on KI-Tl.[1] Tl_2^+ shows optical absorption bands at 1760, 860 and 480 mμ. The symmetry of this center has been studied through the use of polarized light bleaching experiments. Whereas, Tl^0 shows no optical anisotropy down to temperatures as low as 5°K, Tl_2^+ shows optical anisotropy almost up to 300°K. The axes of the dipole moments of the 1760, 860, and 480 mμ transitions coincide and are oriented along the ⟨110⟩ directions in the crystal.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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41 EPR and ENDOR of F Centers in Alkali Hydrides

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Alkali halides and hydrides have the same crystal lattice type, ionic charge, electronic configuration, and defect structure. In most physical and chemical properties the hydrides fall between the corresponding fluorides and chlorides. Under x irradiation both halides and hydrides develop a strong F band. In LiH the F centers coagulate rapidly at room temperature to form lithium metal, but in all the other hydrides F centers are stable. Because of the comparatively small hyperfine interaction with the singly charged anion nuclei in the alkali hydrides and deuterides, all but KH show a well resolved nearest neighbor hyperfine splitting in their EPR spectra, consistent with the deBoer structure of this F center. In NaD, KD, and RbH the peak separations are 25.6, 7.9, and 36.6 gauss, respectively. In CsH the splitting is large and second order terms are present in the resolved pattern. ENDOR measurements confirm the EPR nearest neighbor interactions, and in NaH, KH, and RbH give second nearest neighbor isotropic hyperfine constants of 8.0, 4.6, and 4.2 mc, respectively. Anisotropic terms and interactions with more distant neighbors are also present. Spin lattice relaxation rates differ considerably from one hydride to another with ostensibly similar sample preparation.

The lattice constant is a scaling parameter for the position of the optical F band ($\lambda_m d^2 \sim$ constant; Mollwo-Ivey rule) and the nearest neighbor isotropic hyperfine interaction constant ($|\psi|^2 d^3 \sim$ constant; Seidel's rule). The F band positions in NaH and KH are in approximate agreement with the Mollwo-Ivey rule. Only LiH exhibits a gross departure from this regularity in the alkali halides and hydrides. In contrast, all of the hydrides exhibit a pronounced, but similar, departure from Seidel's rule. These discrepancies suggest that high frequency polarizability and lattice distortion of the host crystal exert an appreciable influence on the F center in the hydrides. Similar, but smaller, effects must be present in the alkali halides.

42 Dielectric Relaxation in Potassium Chloride Containing Hydroxyl Ions

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The dispersion of the complex dielectric constant of hydroxyl doped KCl crystals has been studied in the temperature range between 1.5°K and 20°K for samples with OH^- concentrations of 15, 310 and 2200 ppm. At frequencies below 12 Mc/sec the measurements were carried out with a conventional Q — meter using the "Resonance Rise Method." For frequencies above 25 Mc/sec a short piece of coaxial line was resonated with the sample. The relaxation behavior of the hydroxyl dipoles was taken from the dispersion of the real part of the dielectric constant and from the loss angle. The results can be summarized as follows:

1. The relaxation behavior indicates a spread of relaxation times. Above 8°K this spread is almost negligible and it increases with decreasing temperature.
2. The average relaxation time increases with increasing concentration.
3. Between 1.5°K and about 10°K the temperature dependence of the average relaxation time can be approximated by $T^{-\alpha}$ where $\alpha \approx 1$ for the very dilute samples (15 ppm) and $\alpha \approx 2$ for the concentrated samples (2200 ppm).

43 Absorption, Emission and Recombination Processes of X_2^-, Tl^+, and F Centers in the Alkali Halides

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Previous research on the Tl^+ center in KI, KBr, and KCl has been concerned with the absorption and emission spectra, the decay constants of the luminescence at temperatures between liquid helium temperature and room temperature, and the polarization of the emission when excited with polarized light at liquid helium temperature.

The emission spectrum of KI:Tl at low temperatures reveals three emission bands that are direct transitions from the known A, B, and C absorption bands, whereas two additional emission bands appear to be from other excited states that are not populated directly by absorption. The polarization of the three emission bands and the short time-constants agree with this assignment. The long-wavelength emission band that results from excitation in the D absorption band appears to be an anomalous behavior.

The emission spectra of the pure alkali halides upon excitation in the fundamental absorption region have been identified independently by Kabler and Murray as emission resulting from the recombination of a self-trapped hole and an electron.

Current research interests are: (1) details of recombination emission of self-trapped holes, thallous ion centers, and F centers, (2) possible transitions of the thallous-ion centers from the lowest excited state to higher excited states, (3) competition between Tl^+ emission and X_2^- recombination emission with various electron traps present, (4) measurements of surface concentrations of F and X_2^- centers after ultraviolet irradiation using reflected polarized light at Brewster's angle, (5) comparison of glow curves of x irradiate and ultraviolet irradiated samples.

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44 ESR-Measurements on the Aggregation of F Centers in Rubidium Chloride by Light

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Bleaching by light at room temperature of F centers in RbCl decreases the resolution of the partially resolved hyperfine structure in the ESR-spectrum of the remaining F centers.[1] In order to explain this decrease in resolution one has to assume a shortening of the spin-spin-relaxation time T_2 which is equivalent to an increase of the width of individual spin packets. By measuring T_1T_2 and T_1 from saturation experiments one gets for T_2 the approximate values $T_2 = 2 \cdot 10^{-8}$ sec (unbleached F centers) and $T_2 = 2.5 \cdot 10^{-9}$ sec (F centers after optical bleaching at room temperature). In order to explain the decrease in resolution of the hyperfine structure one needs for T_2 a value of $3 \cdot 10^{-9}$ sec which is in good agreement with the measured value. This is the result of a computer calculation of the ESR-spectrum taking into account both Rb-isotopes and the interaction with the shells I, II and III.

The decrease in T_2 is explained as the result of a light-induced loose aggregation of the F centers. If one takes into account dipole-dipole-interaction only, the measured T_2 corresponds to an average distance of 5 interionic distances between F centers in the clusters. There is no experimental evidence for or against an additional influence of exchange interaction.

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45 An Investigation of F Centers, U Centers, and M Centers in Potassium Bromide, Potassium Chloride, and Sodium Chloride Containing Hydrogen

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A study has been made of F centers, M centers and U centers in crystals of KBr, KCl, and NaCl which have been additively colored and heated with hydrogen at high pressures (15 atmospheres).

It is found that the behavior of the F and M centers differs from their behavior in crystals which have only been additively colored. M centers do not form in KBr:H and, although formed in KCl:H, relax spontaneously and bleach rapidly with U band illumination. F centers convert back to U centers in KBr:H when irradiated with F band light.

It is found that the amount of hydrogen dissolved (beyond that incorporated in the U centers) is greatest in KBr, less in KCl, and least in NaCl. The magnitude of the effects described correlates with the amount of excess hydrogen in the lattice, and mechanisms which explain these effects in terms of interactions between the various centers and hydrogen are presented.

The oscillator strengths for the U center in KCl:H and KBr:H relative to the F center oscillator strength, have been measured and are reported. Also reported is a value for the relative oscillator strength of the M_1 transition of the M center, obtained by a method which does not involve measuring the F band.

46 Photochemical Reactions in Potassium Chloride Containing HS^- Ions†

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The occurrence of photochemical reactions induced by ultraviolet light in KCl crystals containing HS^- impurity ions was first observed by Papazian[1] and Grassano[2] but credit for the correct assignment of the impurity responsible for the observed effects belongs to Rolfe[3] and to Fischer and Gründig.[4, 5] HS^- ions are present to a considerable extent[2] in crystals grown from A.R. KCl; chlorination of the melt is an effective method of preventing contamination. Rolfe has introduced HS^- impurity by growing crystals from KCl and KBr with added hydrated alkali sulphides while Fischer and Gründig grew their crystals under H_2S. We have used the latter method and have also annealed pure crystals in H_2S and grown crystals from molten KCl containing added anhydrous KHS.

On photolysis bands form at 193, 212, 235, and 255 mμ. For short irradiation times absorption coefficients at 193 and 235 mμ are very similar, as are those at 212 and 255 mμ. After long irradiation times the 235 mμ absorption falls while that at 212 mμ continues to rise and that at 255 mμ saturates. The decrease in k(235) is caused by the well-known[6] mobility of interstitial H atoms. Some of this decrease is due to recombination of H atoms with S^- centers (shown by the simultaneous decrease in the 193 mμ absorption) but the second-order kinetics confirm that the main mechanism for the disappearance of H atoms is the recombination reaction: $H + H \rightarrow H_2$. The activation energy for this process is 0.23 eV.

The growth kinetics under irradiation strongly suggest that two photochemical reactions occur

$$SH^- \rightarrow S^-(193) + H_i(235)$$
$$SH^- \rightarrow H^-(212) + S_i(255)$$

Fischer and Gründig have an alternative explanation[5] for the 255 mμ band. We feel, however, that the 193 and 255 mμ bands cannot be associated with the same center because measurements of the change in the halfwidth of these bands between 4°K and 225°K have enabled approximate values for the ground state frequencies to be found. These values differ by around 50%, thus indicating that the same ground state is not involved in the two absorptions.

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47 Theoretical Models of Some V-Centers in Magnesium Oxide

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Wertz and co-workers have reported in the last three years several ESR spectra in MgO, which they tentatively associated with a hole trapped by a positive ion vacancy. The spectra are definitely anisotropic ($g_{||} = 2.0032$, $g_{\perp} = 2.0385$) and have axial symmetry.

Several models were considered in an attempt to explain these spectra.

1. The strongly localized hole:
   The defect was assumed to consist of an O^- ion next to the Mg^{++} vacancy in a crystal field due to point ions, all ions at equilibrium sites. Ionic states were represented by Slater determinants composed of Hartree-Fock one-electron states for the free ion. The crystal field, spin-orbit interaction and an external magnetic field were treated as successive perturbations, the spin-orbit constant being determined from isoelectronic data for Na^{++}, Ne^+, F°. The deviation of the g-tensor from the free electron case was found to be $\Delta g_{||} = 0$, $\Delta g_{\perp} = 0.0245$.

Subsequently, electron nuclear resonance experiments indicated the existence of the related defect having the same symmetry, but with a fluorine nucleus on the principal axis (presumably opposite the O^- ion). The hyperfine splitting constants were: a (contact term) $=.12$ gauss, b (dipole-dipole term) $= 3a$. The strongly localized hole model was used to calculate the contact interaction of the hole with an F^- ion two sites away. This gave a value of a which was too small by three orders of magnitude. This suggested that the hole might be shared by all first neighbors of the vacancy.

2. The weakly localized hole:
   We first considered the effect of placing the hole on the F^- ion itself. The resulting contact term (for F° next to the Mg^{++} vacancy) was completely negligible. However a hole on an $O^=$ second neighbor of the F^- ion gave the right order of magnitude for the contact term. This strongly suggests a model in which the hole is shared (anisotropically) by the six first neighbors of the vacancy. A detailed analysis of this model is in progress, and will be reported on.

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48 Isotope Effects in Lithium Fluoride Narrow-Line Spectra*

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The effect of isotopic composition on zero-phonon absorption lines and associated vibrational structure in LiF has been investigated. Measurements of the position and intensity of these features at 4°K were made for the lines at 3912Å, 5236Å, 8333Å, and 10408Å in x-ray irradiated crystals of Li^6F ($>95\%$ Li^6) and Ii^7F ($\sim 100\%$ Li^7). The first line is due to the R center and the rest are due presumably to other F-aggregate centers, although a definite identification has not been made.

The decrease in lithium mass from 7 to 6 in the host lattice produces two readily measurable effects on the 8333Å and 10408Å lines: a shift of the zero-phonon line of $-\ 0.0009 \pm .0001$ eV and $+\ 0.0012 \pm .0001$ eV, respectively; and a shift in the spacing of the peaks in the vibrational sidebands, corresponding to frequency ratios ω_6/ω_7 ranging from 1.009 to 1.072. These shifts are identical in enriched crystals obtained from two different sources. Also, the shift of the lines for a 50% Li^6 crystal is half as large. The isotope shifts in the 3912Å and 5236Å lines are much smaller than this.

We attribute the shift of the 8333Å and 10408Å lines to two separate effects. One, a red shift due to the fractional increase in lattice constant of 2×10^{-4}, we infer to be $-$ 0.0008 eV and $-$ 0.0001 eV from our measurements of the pressure shift of these lines. The second, due to the change in vibrational spectrum, is specifically the differential change in the zero-point energies of the coupled modes. Using the spectral density of coupled modes determined from the one-phonon sideband spectrum for the two isotopes, we have computed a shift of the right magnitude.

The small isotope effects expected in the temperature dependence of the breadth, position and intensity of these lines are now being sought.

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49 Photostimulated Thermoluminescence in Sodium Chloride*

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A) Thermoluminescence (TL) stimulated by monochromatic light is a much simpler phenomenon than standard TL, since traps filled by only one type of carrier can be obtained.[1, 2] In the present work we study, in the temperature range 80 $-$ 280°K, the TL of NaCl X-rayed at $T \geqslant 290$°K and subsequently photostimulated at 80°K. Our main purpose is to examine in detail the photostimulation spectra of electrons and of holes; stimulation at intervals of 5mμ with bandwidth of 1.2 mμ is performed. B) The photostimulated glow curve, as already known, depends strongly on the sample. In each sample however, the glow curve has the same peaks, independent of the stimulating wavelength: this, in agreement with reference 1, shows that carriers of only one kind are released by light and are trapped. As will be seen in points C and D below, these carriers are only electrons. C) The intensity of each glow peak — for the same dose of incident light — depends on the wavelength of the stimulating radiation. A prominent maximum of the emission intensity is obtained after stimulation at 450 mμ corresponding to the F-band absorption. Other maxima of TL are found when the sample is stimulated with light of shorter wavelength; 310 mμ, 280 mμ, and 265 mμ. These electronic bands, observed through the photostimulated TL, have the properties of the L bands. In fact, the ratio of the stimulation yield in the F absorption region and in the "L band" region does not depend appreciably upon the sample, hence upon the impurity content; moreover this ratio is approximately independent of the F-center concentration. D) In contrast with the results of other authors,[3] no maximum emission is found in samples stimulated at wavelengths corresponding to absorption in the V bands, even at very high illumination doses. E) The nature of the traps has also been studied.

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† Gruppo Nazionale di Struttura della Materia del C.N.R.

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50 Optical Properties of the HSe⁻, Se⁻, and Se⁻⁻ Ion in Potassium Chloride and Potassium Bromide Crystals

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Infrared and ultraviolet absorption bands caused by the hydroselenide ion (HSe^-) have been observed in KCl and KBr single crystals grown from melts containing KHSe. The infrared absorption due to the stretching vibration of the Se-H bond occurs near 4.36 microns. The ultraviolet absorption consists of two bands, in KCl at 6.40 eV and 6.13 eV, in KBr at 6.13 eV and 5.87 eV (20°K).

Irradiation into the hydroselenide bands at 20°K causes the same quantitative photochemical decomposition as in the case of hydrosulfide: $HSe^- \rightarrow Se^- + H_i^0$. The Se^- ions produce two new bands, in KCl at 6.15 eV and 5.96 eV, in KBr at 5.83 eV and 5.66 eV. After the thermal bleaching of the U_2 band above 110°K, the hydrogen has reacted in part with the Se^- ions to re-form HSe^-. Moreover, in KBr a band at 4.98 eV (halfwidth 0.46 eV) occurs, which probably belongs to a new hydrogen center. This becomes unstable above 210°K.

By reducing treatment of the HSe^- ions with F centers, one gets a quantitative conversion into Se^{--}, and U centers: $HSe^- + 2F \rightarrow Se^{--} + U + \square$. After quenching to room temperature such crystals are yellow and in the UV light they show a yellow orange fluorescence. The absorption at 20°K consists of a double band in the blue and near ultraviolet, in KCl at 3.41 eV and 3.14 eV, in KBr at 3.32 eV and 3.05 eV. It belongs to the Se^{--} center. In KCl two other bands are observed at 4.23 eV and 3.96 eV. These are exciton bands belonging to deposited K_2Se. After annealing below 400°C the long wavelength bands disappear. In KCl the exciton bands are increased, and in KBr they appear at the same wavelength as in KCl.

The energy distance in all double bands of HSe^-, Se^{--}, and the deposited K_2Se is 0.27 eV. This is interpreted as the spin orbit splitting.

51 Production and Optical Absorption of Potassium Chloride Crystals Containing O_2^- and O^{--} Centers

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A method is described that produces single crystals of potassium chloride with high concentrations of O_2^- (about 10^{19} cm^{-3}). The crystals are grown by the Kyropoulos-method from a KO_2 doped melt of KCl in a vacuum tight apparatus, strictly excluding spurious amounts of water which would react to KOH. The KO_2 is produced by direct reaction of the elements. The absorption in the ultraviolet shows the known band at 5.09 eV ($H = 1.2$ eV), and two other bands at 6.41 eV ($H = 0.56$ eV, 78°K) and 7.0 eV. Reducing treatment with F centers transforms the O_2^- quantitatively into O^{--} and anion vacancies. The O^{--} centers have four bands at 2.82 eV ($H = 0.38$ eV), 4.34 eV ($H = 0.39$ eV), 5.77 eV ($H = 0.50$ eV), and 6.4 eV. Another band at 7.1 eV ($H = 0.4$ eV) is due to the anion vacancies (α centers). All bands of the O^{--} center can be interpreted as electron transfers from O^{--} to the surrounding K^+ ions considering different excited states of the potassium atom. Irradiation of O^{--} doped crystals at 20°C yields F centers and O^- centers. The O^- centers are detected by their band at 6.7 eV. The concentration of the O^{--} centers (and of the original O_2^- centers) can be determined from the magnitude of the F band. O^{--} centers in high concentration can be stabilized in an atomic dispersion only by rapid quenching to room termperature. Annealing below 400°C finally causes deposition of colloidal particles of K_2O.

52 Zero-Phonon Transitions*

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A survey of current understanding of the necessary conditions for and properties of zero-phonon lines in the low-temperature optical absorption and emission spectra of color centers will be presented. Recent developments discussed will include work on line luminescence in NaF as well as

LiF, models for the analysis of phonon coupling and temperature dependence, static strain shifts and splittings, and isotope effects.

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* Work supported in part by the U.S. Atomic Energy Commission and the Advanced Research Projects Agency.

† Alfred P. Sloan Fellow.

53 Theory of Optical Transitions in the Electron-Excess Centers*

W. BEALL FOWLER, University of Illinois, Urbana, Illinois

Since the 1962 Stuttgart Conference, much has been learned about the nature of the states involved in optical transitions in electron-excess centers. At the time of that Conference there had recently been performed a number of important experiments whose results had not been predicted by theory and were not very well understood. Among these newly discovered phenomena were the long lifetime of the excited F center, the existence and properties of the K and L bands, the structure of the F bands in the cesium halides, the existence and properties of the many excited states of the M center, and the concentration quenching of F center luminescence.

Since that time new theories have appeared while older theories have been re-examined and extended. The results of further ingenious experiments, while often raising new questions, have made it possible in a number of cases to test the alternative theoretical possibilities. At the present time there exist theories which seem capable of explaining to a greater or lesser degree all of the phenomena mentioned here (and others as well), with the exception of concentration quenching.

In this talk we shall review some of the general theoretical considerations that should be involved in any treatment of the electronic states. We neglect most effects associated with lattice dynamics; these will be treated in other papers. We shall try to relate some of the common approximations (such as the point-ion and semicontinuum methods) and assess their regions of validity, and shall then indicate how successful theories have been formulated for the K band and (to some extent) the L bands, for the F center in emission, and for the M-center excited states. We shall also comment on the present theoretical understanding of other electron-excess centers and of certain other phenomena (such as spin-orbit splittings). A fairly general conclusion emerges: A given center may possess a number of bound states of quite different character; these may include localized states, large-radius states influenced by electronic polarization, and large-radius states influenced by lattice polarization.

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54 The Contribution of Electron and Hole Self-Energies to Optical Band Gaps and to Binding Energies of Excitations in Insulators*

W. BEALL FOWLER, University of Illinois, Urbana, Illinois

The optical absorption energy required to create large-radius excitations (excitons or excited impurity states) or to excite an electron into the conduction band in insulators includes large and important negative contributions from the self-energies of the electron and the hole (or impurity center) with respect to *electronic* polarization. These self-energies may be calculated by a static approximation developed by Mott and Littleton, which is valid for most insulators (but not for most semiconductors, where dynamic effects are important). Because of self-energy corrections the optical band gap in alkali halides may be as much as 5 eV smaller than the gap that a conventional one-electron band structure calculation would yield.

Clearly self-energies are important in determining the binding energies of those small-radius excitations whose absolute energies are independent of dielectric properties. We have used the transfer model to analyze experimental binding energies of low-lying excitons in alkali halides and rare gases. It is thereby possible to understand the "anomalous" case of LiCl, which has a *negative* exciton binding energy, a result which is also predicted for LiI. For these cases the self-energies are so large that less energy is required to excite an electron to the conduction band than to create a small-radius exciton which has little electronic self-energy.

These results suggest that excited F centers in LiCl and LiI should also have negative binding energies, which implies that the K band may lie on the *low*-energy side of the F band. This could lead to some interesting experimental results. Although large negative binding energies are predicted for silver halide excitons, a breakdown of the transfer model may invalidate this result.

* Research supported by a grant from the U.S. Air Force Office of Scientific Research.

55 Green's Function Calculations of Electronic States in Insulators*

W. BEALL FOWLER, University of Illinois, Urbana, Illinois

Several Green's function techniques are discussed and that of Anderson developed for computing the energies of impurity states (and their "widths," should they be in resonance with band states) in insulators. It is argued that a reasonable condition for negative-ion impurities in alkali and silver halides to have "localized exciton" states at lower energies than the pure-crystal exciton absorption is that the one-electron valence states of the impurity be higher in energy than those of the pure crystal. We then study the one-electron states by the Green's function theory and conclude the following:

(1) If the negative-ion impurity state lies within the valence band it will mix so thoroughly with the band states that no discrete "exciton" absorption associated with the impurity will emerge.

(2) Negative-ion impurities of larger atomic number in alkali halides (such as Br^- in KCl) will have localized valence states; an essential contribution to their discreteness is an increase in 2-center repulsive energy associated with the impurity.

(3) Such impurities in silver halides will have localized states only if their energies are higher than the valence p-state at $\mathbf{k} = 0$ by more than $\approx 1.5 - 2$ eV, the valence band width associated with indirect transitions. This condition obtains for I^- in AgCl, but not for Br^- in AgCl, for which the virtual-crystal approximation gives a better description of the direct exciton region.

(4) The energies associated with moving an electron to or from an ion in the classical transfer model involve the centers of the conduction or valence bands, not the edges, and so transition energies obtained in von Hippel's treatment should be reduced by approximately one-half the sum of valence- and conduction-band widths.

* Research supported by a grant from the U.S. Air Force Office of Scientific Research.

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56 Low Temperature Half Width of Infrared U Bands

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Saturation values of the temperature dependent half-width of local mode absorption bands in NaCl:D^- and KCl:D^- were measured in the liquid helium range. The band widths are then $H(O) = 0.4$ cm^{-1} for KCl and 1.1 cm^{-1} for NaCl. H^- bands in the same crystals seem to assume still lower half-widths, which are below the limit of spectral resolution.

Above 100°K, both H^- and D^- bands are broadened according to an approximate T^2-dependence. This T^2-dependence also holds for H^- centers below 100°K, while D^- absorption band widths tend to saturate in this region.

The observed difference in the damping of the local modes may follow from different possibilities for decay of local mode quanta into lattice phonons: for the D^- mode (360 cm^{-1} in KCl), decay into two phonons is allowed, while this is forbidden for the H^- mode, which has more than twice the maximum phonon energy (500 cm^{-1}). A decay into three phonons, however, is possible for the H^-, and a longer lifetime is to be expected, since this requires fourth order anharmonic terms instead of third order terms for the two-phonon decay.

The T^2-broadening, observed with both isotopes, cannot be explained by the 2 or 3 phonon decay processes. Instead of that one needs a phonon scattering mechanism according to that discussed by Hayes et al.[1] This scattering process can be studied especially well in NaBr:H^- and NaBr:D^-. The infrared absorption bands in these crystals appear to be broader by one order of magnitude than in NaCl and KCl, when measured at 100°K, but nevertheless attain low temperature widths of about 1 cm^{-1}. Above 20°K an increase of bandwidth with temperature is found, which is even stronger than T^2.

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[1] W. Hayes et al., J. Phys. Chem. Solids, Suppl. 1, Lattice Dynamics (1965).

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57 Reorientation and Emission of Optically Excited F_A Centers

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Seven different F_A-center systems (in KCl, KBr, RbCl and RbBr) were studied with the following results:

1. *In absorption* all F_A-center systems show a similar double band structure with a separation between 0.17 and 0.27 eV. The effective frequency associated with the broadening of the F_A-absorption is very close to that of the corresponding F bands.

2. Two distinctly different types of F_A-center *reorientation* occur under optical excitation: In four cases (KCl:Na, KBr:Li, RbCl:Na and RbBr:K) the reorientation rate freezes in at low temperatures and can be described by an Arrhenius type equation with activation energies near 0.1 eV. ("Type I F_A centers"). In KCl:Li, RbCl:Li and RbBr:Li on the other hand the reorientation rate is completely independent of temperature, measured down to 2.8°K. ("Type II F_A centers").

3. The *emission properties* of these two types of F_A centers are again drastically different: Type I F_A centers behave in emission "F-like" with respect to lifetime, spectral position, halfwidth and coupling to lattice vibration of rather high frequency. The emission of type II F_A centers is characterized by a small lifetime, unusually big Stokes shift, and a rather narrow ($H = 0.045$ eV) emission band at 0.46 eV, which is broadened by coupling to a low frequency mode.

4. The *polarization of the emission* is again typically different for the two F_A center types: Type I F_A centers, when studied at low temperatures (with frozen-in orientation), have an emission consisting of a large amount of isotropic radiation ($\sim$86%) the rest being of dipole characteristic (with axis parallel to the F_A-center axis) — independent of excitation in the F_{A1} or F_{A2} band. Towards higher temperature the degree of

polarization is reduced by increasing reorientation in quantitative agreement with the assumption that reorientation takes place in the excited state *before* emission. The emission of type II F_A centers is composed of 75% isotropic and 25% of dipole characteristic (dipole axis parallel to center axis) independent of temperature.

These correlated differences in reorientation, lifetime and emission suggest that the lattice relaxation after optical excitation takes place in completely different ways for the two types of F_A centers.

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58 Excited F-State Spectroscopy Using a Q-Switched Laser*

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The relaxed excited state of F centers of several alkali halides was strongly populated using a Q-switched ruby laser. The laser delivered about 5×10^{17} photons in a 30 nanosecond pulse. Changes in transmission induced by the laser pulse could be observed with a spectrometer. The detector had a time resolution of 10^{-7} seconds. This arrangement allowed measurement of the absorption of the crystal in the presence of excited states. In addition the time dependence of changes of absorption connected with ground state F centers or with excited state F centers could be monitored. These changes in absorption reflect directly the time dependence of the change of population of either state. Lifetime measurements can thus easily be performed in a convenient wavelength region.

The method was used to measure absorption in the presence of excited states in KI, CsI and RbBr at 7°K. In all cases an absorption was found in the ultraviolet region of the spectrum. This absorption shows considerable structure and is interpreted as being due to exciton states formed in the vicinity of excited F centers. The lifetimes of the relaxed excited state of F centers in KI, CsI, RbBr and CsF was determined between 7°K and the quenching temperature of luminescence. For KI the time dependence of the population change of ground and excited state was measured for a range of F concentrations from 2×10^{16} to 5×10^{17} F/cm.^{3} A strong interaction between centers develops for higher concentrations which gives rise to a nonexponential time dependence.

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59 The Diffusion of the Chlorine Ion in Potassium Chloride

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The diffusion coefficient of the chlorine ion in Harshaw potassium chloride crystals and in potassium chloride crystals doped with strontium

chloride has been measured. The measurements were made using radioactive chlorine 36 and sectioning techniques. The chlorine ion diffusion coefficient of the Harshaw single crystals is well represented by

$$D = (61^{-27}_{+49}) \exp[-(2.12 \pm 0.05 \text{ eV})/kT] \text{ cm}^2/\text{sec} \qquad (1)$$

from 560°C to 760°C. Below 560°C the log D versus 1/T curve has a positive curvature. Similar effects were observed in KCl by Barr, Hoodless, Morrison, and Rudham,[1] and in NaCl by Barr, Morrison, and Schroeder.[2] Their annealing experiments indicated that dislocations enhance the diffusion at low temperatures.

The diffusion data for the single crystals doped with strontium exhibited three main features.

1. The diffusion coefficients for the crystals containing 21 parts per million (atomic) Sr and 44 ppm Sr were equal to the Harshaw values for temperatures above 720°C. The high temperature diffusion mechanisms are intrinsic.
2. The diffusion coefficients for the doped crystals containing 237 ppm Sr and 469 ppm Sr were the same for temperatures above 650°C. An intrinsic diffusion mechanism, such as vacancy pairs, which is independent of the cation impurity concentration is dominant in these heavily doped crystals at high temperature.
3. The log D versus 1/T curves for the heavily doped crystals have a positive curvature for temperatures below 625°C.

The analysis of the data was carried out by assuming anion vacancy diffusion and vacancy pair diffusion,

$$D = D_{\text{anion}} + D_{\text{pairs}}. \qquad (2)$$

The following results were obtained from this analysis:

$$D_{\text{anion}} = 36.51 \exp(-2.105 \text{ eV}/kT) \text{ cm}^2/\text{sec}. \qquad (3)$$

$$D_{\text{pairs}} = 8.561 \times 10^3 \exp(-2.654 \text{ eV}/kT) \text{ cm}^2/\text{sec}. \qquad (4)$$

This analysis also permitted the determination of the fractional concentration of vacancies in KCl, n_0, which was found to be $n_0 = 43.91 \exp(-2.313 \text{ eV}/kT)$.

In this analysis the low temperature data from the regions of log D versus 1/T with positive curvature were omitted.

† Now at the U.S. Naval Research Laboratory, Washington, D.C.

[1] L. W. Barr, I. M. Hoodless, J. A. Morrison, and R. Rudham, Trans. Faraday Soc. 56, 697 (1960).

[2] L. W. Barr, J. A. Morrison, and P. A. Schroeder, J. Appl. Phys. 36, 624 (1965).

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60 F-Center Studies in Cesium Fluoride*

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Hughes and Rabin have observed optical absorption bands in x irradiated and additively colored CsF which include a triplet structure centered at approximately 6600 Å and a band at 5700 Å (77°K). These are candidates for F-center transitions.

We have produced these bands in Harshaw and Semi-Elements CsF by coloring mechanisms ranging from γ-irradiation at 77°K to electrolytic coloration. The ratio of optical densities of the triplet components and the 5700 Å band is independent of coloring technique. Selective low-temperature optical bleaching does not alter this ratio, nor does thermal bleaching. These results indicate that these absorptions arise from a single center.

Preliminary circular dichroism measurements similar to those of Margerie and Romestain have established that the center is paramagnetic, with a g-value of the order of 2. The circular dichroism of the triplet absorption is quite similar to that of the CsCl F band and strongly suggests that the center is in fact the F center. The highest-energy component of the triplet may be assigned to a Γ_6 state and the other two to a Γ_8 state, as suggested by Moran.

The well-resolved components of the triplet permit one to excite selectively the Γ_6 and the Γ_8 states. In this way, we find photoconductivity at 77°K occurring for wavelengths in the Γ_6 component but not the Γ_8 components. Similarly the triplet may be bleached at 77°K by light in the Γ_6 component but not the Γ_8 components. This suggests that the excited state after lattice relaxation differs markedly for Γ_6 and Γ_8 excitation.

For temperatures below 10°K the Γ_6 and the higher-energy Γ_8 component show a doublet structure whose origin is a current subject of investigation.

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61 Temperature Dependence and Stark Effect of the Absorption Bands in Silver Doped Potassium Chloride

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The change of the optical absorption of KCl:Ag$^+$ single crystals by high electric fields applied in [100], [110], and [111] — direction is described. The four absorption bands, known as the A, B, C and D bands, arise from the parity forbidden transition $(4d)^{10} \rightarrow (4d)^9\,5s$ and show a small temperature dependent oscillator strength caused by lattice modes of odd parity. From a plot of the oscillator strength in the form

$$(f(T) - C)/(f(0) - C) = \coth(h\omega/4\pi\kappa T)$$

an effective frequency ω can be derived. Similar to this mechanism, the external field destroys the inversion symmetry of the Ag$^+$-center and mixes $\psi(\Gamma_4^-)$ to the ground state (Γ_1^+) and the excited state wave functions $(\Gamma_3^+, \Gamma_4^+, \Gamma_5^+)$. From a qualitative group theoretical analysis assuming O_h-symmetry we find the following symmetries for the excited states:

KCl:Ag$^+$	peak energy (eV) at 79.5°K	symmetry
A	5.460	$\Gamma_3^+ + \Gamma_5^+$
B	5.655	Γ_3^-
C	5.938	Γ_5^+
D	6.435	$\Gamma_4^{\prime}$

These assignments are in variance with the calculations of Knox.[1] Even by a variation of both the crystal field parameter and the spin orbit coupling constant the peak energies cannot be fitted. The consequences of these results for the model of the Ag$^+$-center is further discussed.

[1] R. S. Knox, J. Phys. Soc. Japan 18, Suppl. II, 218 (1963).

62 An Interpretation of Some Optical Properties of the V_K Center*

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The optical absorption bands for an isolated Cl_2^- molecule-ion have been calculated for the ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ (UV band) and ${}^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ (IR band) transitions.[1] The optical density, $d(\lambda) \equiv \log[I_o(\lambda)/I(\lambda)]/\log[I_o(\lambda_{max})/I(\lambda_{max})]$, is given by $d(\lambda) = (\lambda/\lambda_e) \exp[-\gamma^2 \log^2(\lambda/\lambda_e) - 1/4\gamma^2)]$ where $\lambda_e = \lambda_{max}\, e^{-1/(2\gamma^2)}$ is the wavelength corresponding to the electronic excitation energy at equilibrium internuclear distance, λ_{max} is the wavelength for peak absorption, and $\gamma^2 = \alpha/\beta^2$ where β is a constant which characterizes the dependence of the excitation energy on internuclear distance $(E({}^2\Sigma_g^+ \text{ or } {}^2\Pi_g; R) - E({}^2\Sigma_u^+; R) = \triangle E(R_e)\, e^{-\beta(R-R_e)})$ and $\alpha = 4\pi^2\mu c\omega_e/h$ characterizes the ground vibrational state (in the harmonic approximation) of the molecule-ion with reduced mass μ and ground vibrational frequency ω_e (= 260 cm^{-1} for Cl_2^-).

If the two parameters λ_e and γ are suitably chosen, the same expression for $d(\lambda)$ gives a good fit to the observed optical absorption bands for the V_K center. The values for the parameters for Cl_2^- and for the V_K bands in a sequence of host crystals (obtained from the optical data of C. J. Delbecq and P. H. Yuster)[2] are tabulated below.

	UV Band					IR Band	
Host Crystal	LiCl	NaCl	KCl	RbCl	Cl_2^-	KCl	Cl_2^-
λ_e	384	372	362.$_4$	361.$_5$	321	744	663
γ^2	11.9	20.5	44.1	51.4	72.6	50.8	89.0

These observed trends, and also the trends observed in the ESR measurements of W. Hayes on the same crystals,[2] have been interpreted in terms of lattice energy diagrams in configuration space. We infer that the ${}^2\Sigma_u^+$, ${}^2\Pi_g$, ${}^2\Pi_u$ and ${}^2\Sigma_g^+$ states of the V_K center all lie below the valence band (in a lattice energy diagram — the picture is reversed in a one-electron excitation energy diagram) and that, at least for the UV band, the observed trends in the optical band parameters are primarily due to an interaction between the valence band and the excited electronic state of the V_K center.

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] A. C. Wahl and T. L. Gilbert, to be submitted to Phys. Rev.

[2] C. J. Delbecq, T. L. Gilbert, W. Hayes, and P. H. Yuster, to be submitted to Phys. Rev.

63 α Center Production in Potassium Chloride

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The following results, obtained on KCl x irradiated at various temperatures, will be presented and discussed:

1. At 5°K intrinsic α centers are created which decay between 20° and 40°K. Preliminary results of measurements now in progress, show that the capture cross section for electrons of these α centers is negligible;

2. At any temperature between 5° and 230°K, the presence of divalent impurities (Sr^{++} or Pb^{++}) leads to the formation of extrinsic α centers easily distinguishable from the intrinsic ones because of their larger thermal stability. The capture cross section for electrons of these extrinsic vacancies is negligible; otherwise one would see a dependence of F centers production on the purity of the sample, which is not observed;[1]

3. Points 1) and 2) strongly suggest that intrinsic and extrinsic α centers are created in pair with interstitial negative ions[2] (whose energy of formation may be lowered and whose thermal stability may be enhanced by the attractive electric field of isolated divalent impurities) and that the thermal bleaching of the α band is due to the recombination of these pairs of defects. It seems therefore interesting to study the thermal stability of isolated anion vacancies in the absence of interstitial negative ions (and of F′ centers). Measurements of this kind are now in progress;

4. At 77°K, together with extrinsic α centers due to divalent impurities which decay between 180° and 230°K, extrinsic α centers are created which decay between 105° and 140°K. The defects controlling the production of these α centers must still be determined.

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[1] H. Rabin and C. C. Klick, Phys. Rev. 117, 1005 (1960).

[2] F. Lüty, Z. Physik 153, 247 (1958).

64 EPR of Co^{++} in Magnesium Fluoride

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The complex hyperfine and fluorine superhyperfine structure of the X-band EPR spectra of Co^{++} as a dilute substitutional impurity in a single crystal of MgF_2 has been assigned. The spin-Hamiltonian parameters are similar to the earlier incomplete data for the isomorphous ZnF_2 host lattice.[1] The values of the spin-Hamiltonian tensors along the crystal's [110], [1$\bar{1}$0], and [001] directions are: for the gyromagnetic ratio, (6.033, 2.297, 4.239); for the cobalt hyperfine interaction, (637, 123, 210) Mc/sec; for the shfs of the two equivalent F^{19} nuclei along the ⟨110⟩ direction, (308, 59, 76) Mc/sec; for the four equivalent F^{19} nuclei in the {110} plane, (92, 90, 169) Mc/sec. In the last case, principal axes are not symmetry-determined; the values quoted are the projections on the Cartesian axes, since insufficient resolution made determination of the off-diagonal component difficult.

Since high-order perturbations in the cobalt hfs are important, assignment and analysis of the spectra was tractable only with the aid of a pair of computer programs, one to predict line positions as a function of magnetic-field direction by diagonalizing the spin Hamiltonian, and the second to fit observed line positions by adjusting the Hamiltonian parameters. First-order perturbation theory for the F^{19} shfs predicts splittings independent of the cobalt nuclear-spin number. However, even though the F^{19} interactions are two orders of magnitude smaller than the Zeeman effect for some magnetic-field orientations, the observed splittings vary as much as 50 percent across the spectrum. Complete diagonalization of the 32×32 Hamiltonian for a hypothetical species, CoF, quantitatively reproduces the effect, which may be traced to fourth-order perturbations (squared in both the Co hyperfine and F^{19} hyperfine interaction) between nearly degenerate states.

The interpretation of the reported data within a ligand-field model is presently being pursued and will be reported in the near future.

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[1] M. Tinkham, Proc. Roy. Soc. (London) A236, 549 (1956).

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65 F-Center Formation in Alkali Halides with Ultraviolet Light*

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The process of F-center formation with ultraviolet light absorbed in the fundamental band edge of mixed and pure alkali halides is presently being studied. In KCl(KI) and KBr(KI) it is found that excitation of the iodine ions to bound exciton states will, given sufficient thermal energy, lead to formation of a high concentration of F centers. This process of formation is felt to be more generally valid in the ultraviolet coloration of pure alkali halides since it requires the formation of anion vacancies in an otherwise perfect lattice by ~ 6eV excitation.

In KCl(KI), irradiated at room temperature, the F coloration decays exponentially into the crystal with a decay constant that scales with I^- concentration. Growth of the F band is accompanied by a non-reversible decrease in the I^- band and the appearance of a new absorption band somewhat obscured (even at 7°K) in the long wavelength tail of the I^- band. This new absorption band is thought to be associated with interstitial halide atoms.

The growth of the F band obeys a rather unique relation (quite different from later stages of x-ray coloration): $N_F \propto (It)^{1/2}$ where N_F is the total number of F centers within the crystal and the product (It) is the "exposure," a quantity proportional to the total number of ultraviolet photons incident (I is the ultraviolet intensity and t is the irradiation time in seconds). This relation holds over a tested range of 4½ orders of magnitude in t, 1½ orders in I, and 2½ orders in N_F. For constant "exposure" N_F is independent of the iodine concentration in the range 10^{17} to 10^{19} I^-/cm^3, whereas for 10^{20} I^-/cm^3, N_F is smaller and the relation breaks down at $t \sim 10^2$ seconds as F-saturation sets in. This saturation suggests a limiting F-center density of $\sim 3 \times 10^{18}$ F/cm^3 near the crystal surface.

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66 The Effects of Pre-Irradiation Annealing on the Thermoluminescence, Dielectric Loss, and Optical Absorption of Magnesium Doped Lithium Fluoride*

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The characteristics of the radiation-induced thermoluminescent glow peaks in LiF:Mg (70 ppm Mg)[1] are affected by pre-irradiation isothermal annealing. The effects were studied at temperatures between 55°C and 116°C. The pre-irradiation annealing kinetics of one of the glow peaks has been correlated with the annealing kinetics of quenched-in Mg^{++}-cation vacancy complexes as measured by dielectric loss techniques. An optical absorption band appearing at 380 mμ after irradiation of a 1/2 mm thick crystal to 1.2×10^5R has been correlated with this same glow peak. It is suggested that the trap responsible for this peak and absorption band may be a F_2^- molecule ion stabilized by and combined with a Mg^{++}-cation vacancy complex. Pure LiF[1] does not exhibit dielectric loss within the sensitivity of the apparatus used. The thermoluminescence of this latter material does not show pre-irradiation annealing effects, and in general has characteristics different from LiF:Mg. Changes in the optical absorption spectrum of LiF:Mg which occur during peak by peak readout of the thermoluminescence suggest a complex interaction between two or more color centers.

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[1] Obtained from the Harshaw Chemical Company, Cleveland, Ohio.

67 Investigation of Color Center Transformations with Pulse Bleaching Methods

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We are investigating optically-induced color center transformations in KCl with high intensity light pulses and kinetic spectrophotometry. The method makes it possible to obtain temporary absorption spectra within 10 μsec of excitation and to determine the kinetics of the interconversions. The objective is to obtain information on the electron-excess color centers by studying the fast transformations between centers of known and unknown structures. Previous work[1] has shown that illumination of colored KCl at 78°K establishes a photoequilibrium between F and F′ centers and that the presence of M centers, from prior "F light" bleaching at 25°C, alters the rate-controlling processes. A more detailed investigation has shown that the efficiency of the F-to-F′ conversion at 78°K decreases in the early stages of M band growth, which can be explained by the condensation of F centers proposed by Delbecq.[2] During the later stages of M band growth the incident "F light" is utilized preferentially to ionize M centers, the net effect being a decrease of F-center temporary bleaching and an increase in the non-equilibrium F′ center yield. In other work, pulse bleaching was applied to study the "T bands," produced by optical bleaching of colored KCl at 100°C with combinations of "F light" plus light absorbed by higher aggregate centers.[3] It was found that the T_2 (894 mμ) and T_3 (992 mμ) bands are readily interconverted by light-induced processes at 78°K, indicating that they are due to distinct, closely related centers. The T_1 band (839 mμ) is stable to optical bleaching and represents a third center.

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* This work was supported by the U.S. Atomic Energy Commission.

[1] A. R. Reinberg and L. I. Grossweiner, Phys. Rev. 122, 1734 (1961).

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[3] J. G. Ring and L. I. Grossweiner, J. Appl. Phys. 35, 2257 (1964).

68 Electron Spin Resonance of Sulphur and Selenium Centers in Potassium Chloride

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Single crystals of KCl are grown under an atmosphere of H_2S or H_2Se. In these crystals HS^- and HSe^- ions are believed to exist in negative lattice positions. U_2 centers (interstitial hydrogen atoms) are produced by irradiation with ultraviolet light at 20°K. After annealing to 120°K for some seconds and recooling to 20°K these crystals show the resonance spectra of sulfur and selenium centers which are ascribed to S^-, H_2S^-, and

Se^- ions. The resonance lines have an angular dependence with a g-tensor of axial symmetry along the body diagonals of the lattice.

(S^-: $g_{\parallel} = 1.986$, $g_{\perp} = 2.211$; H_2S^-: $g_{\parallel} = 1.987$, $g_{\perp} = 2.206$; Se^-: $g_{\parallel} = 1.769$, $g_{\perp} = 2.542$). The H_2S^- spectrum has a well resolved hyperfine structure caused by interaction with two equivalent hydrogen nuclei. For verifying the nature of the centers, crystals are grown under an atmosphere of D_2S as well as H_2S, the sulfur being enriched by S^{33} isotope. The HFS of the natural isotope Se^{77} also can be resolved.

Furthermore, crystals doped with sulfide are investigated. In contrast to oxygen doped crystals which reveal the ESR of O_2^- ions, no ESR-signals of S_2^- ions could be detected. However, introduction of F centers followed by irradiation with ultraviolet light of longer wavelength at about 370°K produces two new types of paramagnetic centers. Type 1 has orthorhombic symmetry along face diagonals ($g_x = 2.143$, $g_y = 2.081$, $g_z = 2.009$), whereas type 2 shows axial symmetry along the principal axis ($g_{\parallel} = 1.995$, $g_{\perp} = 2.060$). Both are believed to be sulfur centers. Experiments with S^{33} as well as with selenide are to follow.

69 Ultra-Purification of Alkali Halides

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The extreme sensitivity of color centers and related phenomena to trace impurities has stimulated considerable research on the preparation of ultra-pure crystals. Since membrane filters with pore diameters on the order of millimicrons have become available, some impurities can now be precipitated from solution chemically and removed by filtration, where previously they have escaped into the filtrate. Reducing the number of impurities that can act as nucleation centers permits growth of sizeable crystals from aqueous solutions. Lower temperatures and slower growth rates involved in solution growth yield crystals that approach the perfect lattice more nearly so than crystals grown from the melt. NaCl has been grown in this way, but results thus far with KCl and KBr have been less satisfactory. Recent work[1] on the formation of F centers by x-ray irradiation of aqueous-grown NaCl verifies that the growth curve is not linear. It is not possible to separate the "first stage" from the "second stage" of coloration. Conductivity measurements show a transition from extrinsic to intrinsic conductivity at 350°C as compared to "pure" melt-grown crystals that typically have a knee above 500°C.

[1] P. M. Gruzensky, to be published.

70 The Quantum Yield for the Photochemical Decomposition of O^{--} Centers in Potassium Chloride

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Potassium chloride crystals containing various amounts of O^{--} centers are irradiated with ultraviolet light into their bands at 2.92 eV, 4.25 eV, and 5.85 eV. It is shown that the photochemical reaction

$$O^{--} + \square \rightarrow O^{-} + F$$

is the only one, which takes place. From the strong linear relation between the decrease of the O^{--} bands and the increase of the F band, the concentration of the O^{--} centers can be derived. When K means the absorption constant in the maximum of the 4.25 eV band at 20°C, the concentration $N(O^{--}) = (2.6 \pm 0.1)\ 10^{16}\text{cm}^{-2}\ K$.

Irradiation into the long wavelength band yields no decomposition. Irradiation into the shorter wavelength bands above 220°K results in the thermal activated ionization of the O^{--} centers. At higher temperatures the quantum yield for decomposition of the O^{--} centers converges to 0.36 and not to one. This can be interpreted in such a way that immediately after the ionization there is a high probability for radiationless retrapping of the electron by the same center into its ground-state. The thermal activation energies are 0.60 ± 0.1 eV for the 4.25 eV band, and 0.3 ± 0.1 eV for the 5.85 eV band.

Long time irradiation shows that an equilibrium is reached after about 60% of the O^{--} centers have been decomposed. This is interpreted as coming from the inversion of the reaction given by the above relation: F centers are ionized simultaneously with the O^{--} centers by absorbing light in the L band region.

71 Storage Centers in Potassium Iodide (Thallium)

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Heavy metal impurities such as thallium, lead and silver greatly enhance the x-ray colorability of alkali halides at low temperatures. It is known that silver ions in KCl may act either as hole traps or as electron traps. A detailed study of x irradiated KI:Tl was undertaken to establish whether thallous ions may behave in the same way.

At 77°K, KI:Tl stores energy upon x irradiation. Near-infrared or visible irradiation of the charged material produces stimulated emission and, at the same time, removes the absorption bands of the storage centers. The stimulation spectrum corresponds to some of the absorption features in the visible and infrared, but definitely not to the known I_2^- absorption band at 800 mμ. Furthermore, removal of the I_2^- centers in the first thermal glow changes the stimulation spectrum only slightly. Therefore, the stimulation centers must be electron centers, presumably neutral thallium atoms. In stimulated emission, trapped electrons are raised to the conduction band whereupon recombination occurs at the site of the trapped hole.

The stimulated emission spectra indicate that most of the trapped holes are I_2^- centers after x irradiation at 77°K. During the first glow, some holes recombine with trapped electrons, while others are retrapped at more stable sites. Stimulated emission after the first glow looks exactly like the fluorescence of uncharged KI:Tl. This indicates that the retrapped holes are Tl^{++} centers since recombination at these sites would be expected to produce excited Tl^+ ions.

X-ray exposure sufficient to saturate storage in KI:Tl at 77°K produces too small a number of F centers to see either in absorption or in stimulation. If a sizeable F band is produced by greater exposure to x rays or by a higher irradiation temperature, it shows up clearly as a stimulation band. When only Tl^0 electron centers are present, bleaching at any wavelength fails to change the shape of the stimulation spectrum. By contrast, selective bleaching with F centers present does change the stimulation spectrum in a manner consistent with the existence of two or more kinds of trapped electrons. This result confirms the identification of the stimulation center as an electron center. It also shows that the F center is not a major storage center in KI:Tl.

72 Concentration Dependence in Potassium Iodide (Thallium) Storage

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Samples of KI:Tl ranging in composition from about 1×10^{-4} to 1×10^{-1} mole percent have been studied. All samples were charged at 77°K with 125 KVP x rays and the storage determined by a light-sum method. In addition, thermal glows, absorption spectra, emission spectra, and stimulation spectra were observed for each sample.

Stored energy increases with thallium concentration, but there are other trends with concentration as well. At the lowest concentrations, infrared stimulation produces only exciton emission, that is, emission characteristic of an electron combining with an I_2^- center. Thallium emission becomes more important in stimulation at higher concentrations. Removal of the first thermal glow with its destruction of I_2^- centers leaves some storage, but stimulation in this state gives only thallium emission at all concentrations. The ratio of the second glow (175°K) to the first glow (110°K) light sums also increases with thallium concentration.

Deducing the quantitative dependence of energy storage on thallium concentration is difficult. The lower thallium concentrations were estimated from the data of Yuster and Delbecq, but at the higher concentrations the optical density in the thallium absorption bands was too great for this method of analysis. In the lower concentration range, it is known that plastic deformation may increase the capacity for storage. Therefore, not only the composition but also the history of a sample determine its storage capacity. It is not possible at present to state whether storage is directly proportional to thallium concentration or is some more complex function.

73 F Center Production in Alkali Halides by Ultraviolet Irradiation

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It has proved possible to produce F centers in potassium iodide by ultraviolet irradiation in the region of the long wavelength tail of the exciton band.[1] The process is non saturating even at F center concentrations as high as 2×10^{-4}, and the effect cannot be ascribed to OH^- or H^- impurities.

It has been found that the F-center production rate rises with increasing F center concentration, toward a saturation rate depending linearly on radiation intensity. This behavior, and the dependence on the energy of the ultraviolet photons, is indicative of a process depending on the absorption of energy into the β band. However, the large coloration rate by ultraviolet irradiation at zero F center concentration suggests that absorption which is actually in the long wavelength tail of the exciton band itself may also lead to F center production. A possible explanation for the ultraviolet F center production process may be provided by the exciton decay model described in another paper, which includes a possible explanation for the creation of a vacancy distant from the original excitation, which is a necessary part of a β-band process.

The ultraviolet coloration of KI has a temperature dependence very similar to that of x-ray coloration.[2] It is also very sensitive to the presence of impurities in the crystal, which perturb the exciton band edge, causing it to move toward the visible and to mask the β band.

A search for ultraviolet coloration of other alkali iodides and bromides, where the exciton bands are relatively easily accessible, has shown that RbI behaves similarly.

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74 The Production of F-Aggregate Centers in Potassium Chloride and Sodium Chloride

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The conversion of F centers to F-aggregate centers in the temperature range −20° to +30°C has been studied. F centers were initially created either by x irradiation or additive coloration. In the case of NaCl part of the F centers could be converted to F′ centers by pulse irradiation techniques (both optical and x ray) without altering the density of F-aggregate centers initially present in the crystal. The dark decay of the F′ centers was then studied as a function of temperature. In general, the dark decay resulted in partial restoration of the F band along with growth of F-aggregate centers. The net effect of the pulse irradiation and the dark decay was to convert F centers to F-aggregate centers. On the basis of comparisons between NaCl and KCl it was concluded that the rate of aggregation depends on the density of F′ (or α) centers present in the crystal and their mobility. For aggregation to occur by the pulse technique the F′ (or α) centers must have an appreciable lifetime at temperatures at which they are mobile. NaCl fulfills this requirement; KCl does not. The aggregation produced by continuous irradiation of the crystal appears to follow the same mechanism as that produced by pulse irradiation. The continuous irradiation simply increases the density of F′ (or α) centers by continually creating new centers to compensate for their decay.

75 Paraelastic Alignment of OH^- Centers in Alkali Halides

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Besides the possibility of aligning OH^- centers because of their electric dipole moment by electric fields,[1] the same should hold in an applied stress field because of their "elastic dipole moment." This was observed by measurement of the stress-induced dichroism in the electronic OH^- band at low temperatures; it is found that the absorption increases for light polarized parallel to the applied ⟨100⟩ stress, decreases for the light polarized perpendicular to it. This observed stress dichroism is in full agreement with the model derived from the paraelectric measurements:[1] Application of ⟨100⟩ stress lifts the degeneracy of the six equivalent ⟨100⟩ orientational levels and splits them into a doublet: one low energy 4-fold degenerate state (centers oriented perpendicular to stress) and one high energy 2-fold degenerate state (centers oriented parallel to stress direction). Boltzmann occupation of this doublet together with the anisotropy of the electronic OH^- transition (as evaluated from the paraelectric measurements) explains quantitatively the observed stress dichroism. From these measurements the "shape factor" (ellipticity) of the OH^- center can be evaluated. For cases where dilatation measurements are available (as in KCl + KOH)[2] the combination of both measurements allows a quantitative determination of the components of the tetragonal elastic dipole. The stress dichroism disappears for stress applied in ⟨111⟩ direction in agreement with the model. Experiments to observe paraelastic heating and cooling — in parallel to the corresponding paraelectric effects[3] — are under way.

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[2] F. Lüty and H. Paus, See Abstract No. 123.
[3] U. Kuhn and F. Lüty, Sol. State Comm. 4, 31 (1965).

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76 V Bands in Potassium Chloride Crystals Containing Halide Ion Impurities

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New V-type bands have been observed in KCl crystals containing small amounts of halide ion impurities which have been irradiated with X-rays at room temperature. The crystals were grown from melt in air by the Kyropoulos method. Starting material of the melt was KCl powder added with small amount of KBr, KI and KF, respectively. Here the powder was prepared from $KHCO_3$ and HCl to avoid the undesirable Br^- impurity contained in ordinary reagent grade materials.[1] All the crystals thus obtained showed no absorption in the spectral range studied: 200 ∼ 800 mμ except for a small OH^- band ($\sim 1\ cm^{-1}$) as in nominally pure ones.

Now, crystals containing Br^- impurity, when they were X-ray irradiated at room temperature, showed in the ultraviolet region the V_3 and a trace of the V_2 bands as in ordinarily pure samples and an additional new band located at 240 mμ. The size of this band increased as the amount of added Br^- was increased, for the same dose of X-ray irradiation. These suggest that Br^- should incorporate in some way with the center. We shall denote this V_{Br}. The optical and thermal nature of V_{Br} centers resemble those of V_2, being bleached by F-band illumination or by thermal treatment near room temperature (e.g. at ∼80°C). The growth of the V_3 band was little affected by the presence of Br^- so long as the bromine content was small (less than 1 mol %). A corresponding band, V_I, was found in the ultraviolet absorption spectrum of KCl containing I^- impurity, the peak of which was at 250 mμ. We could not find any band which might be ascribed to a fluorine ion in the range of spectrum studied for KCl containing F^- impurity.

Further studies for the determination of the models of these centers are under way.

[1] K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan 15, 1982 (1960).

77 Dose Dependence of F Center Production by Fast Neutrons in Magnesium Oxide

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Parallel electron spin resonance and optical absorption studies of magnesium oxide, neutron irradiated to six different doses in the range 10^{17} to 10^{19} nvt $>$ 1 MeV, have made possible a detailed correlation of the F center with the optical band centered at 4.95 eV. Thermal bleaching experiments at 310°C for periods between 5 minutes and 2 days confirm this correlation as well as the earlier less detailed experiments of Wertz et al.[1] The results are consistent with an oscillator strength of $f \doteqdot 0.8$ for the F band in magnesium oxide.

At doses $< 3 \times 10^{19}$ nvt, the curve of F-center concentration versus dose may be represented mathematically as the sum of a saturating exponential and a linear increase. This behavior is predicted by a simple theory which assumes that F centers are,

(a) formed by the trapping of electrons at vacancies present prior to irradiation, and

(b) increased in number by the formation of F centers from vacancies produced only by the irradiation process.

The F-center concentration reaches a maximum value of 6×10^{18} F/cm^3 at 8×10^{19} nvt, after which dose it decreases. This effect is not accounted for in terms of the simple model above: it is probably associated with the clustering of defects caused by irradiation induced diffusion at the ambient pile temperature of 150°C.

[1] J. E. Wertz, G. S. Saville, L. Hall, P. Auzins, Proc. Brit. Ceram. Soc., 1, 59 (1964).

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78 Deformation Splitting of Zero-Phonon Lines in Neutron Irradiated Magnesium Oxide

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Many zero-phonon lines have been observed in the optical absorption spectrum of both annealed and unannealed neutron irradiated magnesium oxide single crystals.[1] The orientations and symmetries of the defect centers giving rise to some of these sharp lines have been investigated by the application of uniaxial stress and polarized light techniques using a Cary 14 spectrophotometer. Stresses of up to 55 kg/mm^2 have been applied along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$ crystal directions. The 14,925 cm^{-1} and 21,320 cm^{-1} lines in crystals irradiated to 5×10^{19} nvt $>$ 1 MeV and annealed for several days at 400°C as well as the 15,408 cm^{-1} and 15,576

cm^{-1} lines in crystals irradiated at 600°C to a dose of 4.3×10^{20} nvt, were chosen for the initial experiments. Preliminary analysis of the observed splitting patterns indicates that:

(i) Lines at 14,925 cm^{-1} and 15,408 cm^{-1} are associated with centers having $\langle 111 \rangle$ orientation and trigonal symmetry.

(ii) The splitting patterns for lines at 15,576 cm^{-1} and 21,320 cm^{-1} cannot be interpreted in terms of defects having simple orientational degeneracy.

Centers having the requisite orientation and symmetry properties noted have been observed by Wertz and his associates in electron spin resonance experiments.[2] Definitive correlations between these defects and the zero phonon lines investigated by the present authors have not so far been made.

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[1] J. E. Wertz, G. Saville, P. Auzins, and J. W. Orton, J. Phys. Soc. Japan, 18 (Supp.II), 305 (1963).

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79 Magneto-Optic Experiments on the F Center and F_A Center in Potassium Chloride*

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We report the measurement of the magnetically induced circular dichroism in the optical absorption bands of the F center and F_A center in KCl performed to test theoretical predictions of Henry, Schnatterly, and Slichter based on the method of moments. It is found that a magnetic field can alter the area of an optical absorption band, but only at the expense of other optical absorption bands of the center; the total area due to all the optical absorption bands of the center remains constant. The magnetic field causes the F band to shift in energy. The shift is found to be greater in the peak than in the tails of the F band. Depending upon the orientations of the F_A centers, the magnetic field causes either a shift in the F_{A2} band, or an increase in the area of the F_{A2} band with an equal and opposite decrease in the area of the F_{A1} band. These results are in good agreement with the predictions of Henry, Schnatterly, and Slichter.

We show that the paramagnetic circular dichrosim signals in the K band and F band occur with the same spin-lattice relaxation time, confirming that the K band is an excited state of the F center. The ratios of the coupling to the cubic and non-cubic lattice modes of the F center and the ratios of the spin-orbit coupling constants of the F_A center are also evaluated.

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* Now at Bell Telephone Laboratories, Murray Hill, New Jersey.

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80 Crystallographic Orientation of the Thallium Dimer Center in Sodium Iodide*

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An investigation of the crystallographic orientation of the thallium dimer center in NaI is being conducted. Assuming random thallium substitution for sodium, the pair of thallous ions in near neighbor positions[1] (dimer center) should have a ⟨110⟩ orientation in NaI crystals. Use is made of a continuous, high-intensity deuterium ultra-violet source reflected from a single LiF plate at Brewster's angle to achieve 100% plane polarized light which illuminates the NaI:Tl sample through a monochromator. Wavelengths in the dimer excitation bands[2] are incident on the sample with the plane of polarization oriented in principal crystallographic directions. The resulting dimer luminescence is monitored by a phototube through appropriate filters and the degree of polarization is analyzed in the usual way.[3] These investigations are initially conducted at 77°K, however we intend to go down in temperature to 4°K shortly. NaI samples whose thallium impurity concentration is above 0.05 mole% are used to insure a good dimer/monomer population ratio.[4] We also plan to investigate the luminescence of the dimer center when plane polarized light whose wavelength is in the exciton absorption band of the host NaI crystal is incident on the sample.

* Work supported in part by U.S. Atomic Energy Commission.

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81 A Chemical Approach to V Centers in Alkali Halides

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At the Argonne Color Center Symposium it was suggested that halogen molecules of different kinds are formed in irradiated alkali halides and that these could be identified with the various known V centers. This has been amply confirmed in the case of the X_2^- center, verifying the general idea that covalent bonds can form in ionic crystals. In this paper, in the absence of sound theoretical concepts of V centers in general, a heuristic approach is presented which provides an overall viewpoint for developing models of V centers (especially diamagnetic ones).

The study deals with the following aspects, leading to insights into the nature of V centers and V-center formation in alkali halides: (1) spectra of halogen in various media, (2) properties of solid polyhalides, (3) interactions of halide ions and halogen atoms and molecules, (4) the photo-chemistry of X^- in solution, and (5) the similarities in the optical absorption spectra of certain halogen molecules and certain V centers.

By assuming that an alkali halide crystal (AX) represents a solid matrix in which photochemical reactions involving halide ions can occur, it is possible to compare solid state color center phenomena involving V centers with photolysis in solutions involving halogen molecules and ions. From a chemical point of view the products of photolysis (X_2^-, X_2 and X_3^-) of an irradiated glass or aqueous solution containing an alkali halide are the same as the V centers V_K, V_1 and V_2 (or V_4) in irradiated crystals. Since only the molecular model (X_2^-) for the V_K and H centers is known with certainty (because it is one of the few paramagnetic V centers) this chemical approach serves to support X_2 and X_3^- models for the V_1 and V_2 or V_4 centers, and also leads to the correct model for the V_K center (see table below).

TABLE

Absorption peak wavelength (in mμ) of trapped hole centers and various kinds of halogen molecules; V center models based on chemical concepts.

Absorption bands	V_K	X_2^-	H	$X_4^=$	V_1	X_2	$V_2(V_4)$	$X_3^-(1)$	V_3	$X_3^-(2)$
KCl.	364	354	345		356	335	233	230	218	
KBr.	385	375	380		410	400	275	270	232	(230)
KI.	404	387	540		570	520	355	355	290	290
			450		470	460				
General Conclusion	V bands in alkali halides arise from center which may be described as linear arrays of halogen atoms and ions involving *molecular bonds*; the crystallinity of the salt plays only a minor role.									
V center models based on solution spectra	$V_K = X_2^-$		$H = ?$		$V_1 = X_2$		$V_2 = X_3^-$		V_3 band in KI (and possibly KBr) due to excited state of V_2 center. V_3 center in KCl is *not* a halogen center.	

82 The Mechanism of V_K-Center Formation

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The mechanism usually assumed for formation of V_K centers by x rays is as follows: x rays produce free electrons and holes which recombine with each other in pure crystals; in crystals containing impurities such as

Tl^+ and Ag^+, the electrons are quickly trapped thereby increasing the lifetime of holes; the formation of the X_2^- center is then pictured as naturally arising from the increased density of free holes by a chemical bonding of the resulting X atom with an adjacent X^- ion.

Recent work has indicated that when free electrons and holes recombine they do so through nonconducting exciton states; these states may be described as an X_2^- plus a bound electron, i.e., and $X_2^{=*}$ molecule. There are thus two ways in which X_2^- can form: (1) from the direct self-trapping of a free hole, or (2) from the ionization of an $X_2^{=*}$ molecule which is produced during irradiation with ultraviolet light or x rays. By using radiation which does not produce free holes, and KI crystals containing such efficient electron traps as Tl^+ and lattice imperfections, it is possible to distinguish between these mechanisms. When such crystals are irradiated with radiation from a Cd lamp on the long wavelength side of the first exciton band, they emit $X_2^{=*}$ luminescence during irradiation. After the ultraviolet light is turned off, studies of (a) induced photoconductivity, (b) optically and thermally-stimulated luminescence, and (c) recombination luminescence demonstrate the presence of V_K centers and extrinsic electron centers. Irradiation in the electron center band causes a parallel and simultaneous decrease of the V_K and the electron center band and a release of light characteristic of $X_2^{=*}$ luminescence as a result of the mobile electrons combining with V_K centers.

Since V_K centers may be formed with non-ionizing radiation, it is concluded that they are not necessarily produced through the generation of free electrons and holes, but through the agency of a relaxed exciton. The following mechanism is proposed for this process: (1) $X^- + h\nu_{UV} \rightarrow X^{-*}$; (2) $X^{-*} + X^- \rightarrow X_2^{=*}$; (3) $X_2^{=*} \rightarrow 2X^-$ + (recombination) luminescence, or (4) $X_2^{=*}$ + trap $\rightarrow X_2^-$ + trapped electron (no vacancy). It is implicit in the mechanism that stable X_2^- cannot be generated in a pure perfect crystal (i.e., defects or impurities are absolutely necessary, notwithstanding the intrinsic nature of the center or the fact that it is observed in supposedly pure crystals). The experiments of Teegarden and Weeks which show a slight storage of energy after ultraviolet-light irradiation at low temperature can be explained by the above mechanism.

83 Possible Mechanism of Vacancy and Interstitial Halogen Generation in Alkali Halides

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The major process observed during the x irradiation of an alkali halide crystal, A^+X^-, at low temperatures is luminescence due to the radiative decay of $X_2^{=*}$ (X_2^- plus a bound electron) molecules which are formed during the irradiation. Even at higher temperatures where the luminescence drops off, it is likely that these diatomic molecules are temporarily present while the crystal is being irradiated. A mechanism for vacancy generation in perfect crystals is proposed in which it is assumed that the progenitor for color center formation is a dissociating $X_2^{=}*$ (excited) molecule: if this molecule is initially created, or subsequently placed, in an excited vibronic, predissociative, or repulsive state, it may dissociate into a normal halide ion and an uncaged atomic halogen fragment, X, moving into an interstitial position and leaving behind a vacancy, according to the reaction $X_2^{=}** \rightarrow X_{\mathrm{int.}} + \square + X^- + e$. The probability that the halogen atom would be caged or move into an interstitial site is limited by crystal geometry. Subsequent capture of the electron and motion of the interstitial halogen atom results in the formation of F centers and H or other V centers depending on the temperature.

The key part of the suggested mechanism is the molecular dissociation of diatomic molecules which can (1) provide the momentum needed for the generation of the Schottky and Frenkel defects noted *after* irradiation, and (2) account for the $X_2^{=}*$ luminescence (major process) noted *during* irradiation.

A related molecular mechanism using the energy released from the chemical interaction of two $X_2^{=}*$ (or X_2^-) molecules to form a vacancy and an interstitial halogen pair is considered.

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84 Mechanism of Color Center Formation in X Rayed Imperfect Crystals at Low Temperatures

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During x irradiation at low temperatures, molecule-like entities, $X_2^{=}*$, are temporarily formed by a major process and disappear with accompanying luminescence, according to the following schematic equation: (I) Perfect crystal $\underset{\text{C. L.}}{\overset{\text{x-rays}}{\leftrightarrows}}$ $X_2^{=}*$, where C. L. is characteristic luminescence. If the crystal contains Tl^+ or Ag^+, some X_2^- centers can be found after the radiation is turned off. This can be explained by the process: (II) $X_2^{=}*$ + electron trap $\rightarrow X_2^-$ + trapped electron, where the cationic impurity acts as the electron trap. The recombination process: (III) $\vec{e} + X_2^- \rightarrow X_2^{=}*$, would restore the crystal to its original state with the emission of C. L.

The purpose of the present study was to test the general validity of process II as a possible mechanism, by substituting different kinds of electron traps and attempting to detect X_2^- and the trapped electron. Alkali halides containing (1) Tl^+, (2) lattice defects resulting from plastic deformation, and (3) F centers, were irradiated at 77°K and stimulated luminescence and photoconductivity measured. In the case of KI, using all three types of electron traps, process II was verified by optical absorption measurements, and process III was verified by (a) characteristic stimulated luminescence (emission at 370 and 302 mμ) and (b) photoconductivity. The photoconductivity spectrum and stimulated emission spectrum were identical in the 2 to 0.6 eV region; analysis indicated that the centers responsible for absorption and photoconductivity were electron centers. No photoconductivity could be detected from the X_2^- center. Similar experiments, but less detailed, have been done with KCl and KBr with the same conclusions. In the case of F centers, the verified process II in additively colored crystals is: $X_2^{-*} + F \rightarrow X_2^- + F'$. KI is particularly convenient for study because the X_2^- (V_K) can be observed in optical absorption without interference from the V_1. All these experiments provide support for the proposed mechanism of electron-hole storage in imperfect crystals at low temperatures as given by equation II.

Although the x rays generate free electrons and holes, it is not necessary to assume that the free carriers play a direct role in color center formation; the relaxed exciton, X_2^{-*}, formed as an intermediate in electron-hole recombination is sufficient for this purpose. A subsequent study of the effects of ultraviolet light which produces X_2^{-*} but not free electrons supports this contention.

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85 Temperature Dependence of Halogen Center Formation in X-Irradiated Potassium Iodide

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In the temperature range 78-300°K the major centers produced by x rays in KI are the F center and a halogen (V) center identified as an interstitial I_3^- center having absorption peaks at 335 and 280 mμ. An experimental investigation of the temperature dependence of the rate of formation of the V centers shows the same acute increase in the 80-110°K range as for F centers, being negligible at 78°K, reaching a maximum at 130°K and then slowly falling off. Two processes having somewhat similar dramatic temperature dependences also occur in the same temperature region: (1) the 370 mμ luminescence due to an I_2^{-*} center suddenly decreases, and (2) the thermal mobility of I_2^- centers increases. Since the color center formation is probably related to only one of them, two alternative mechanisms are proposed, one involving the molecular dissociation of I_2^{-*} and the other, the chemical reaction of two thermally mobile I_2^- centers.

Assuming that the temperature dependence of the 370 mμ emission is similar to that of the halogen-center formation, the decrease in luminescence would be due to the fact that some of the I_2^{-*} emission centers formed during the irradiation are decomposing (to form color centers) rather than decaying (radiatively or non-radiatively). Molecular dissociation of the $I_2^{=*}$ via a thermally activated process would result in a negative ion vacancy and an interstitial iodine fragment; subsequent motion of the halogen atom is assumed to result in the formation of an interstitial I_3^- V-center via reactions such as $\vec{I} + \vec{I} \rightarrow I_2$, followed by $I_2 + I^- \rightarrow I_3^-$. Since ultraviolet radiation can produce $I_2^{=*}$, it is expected also to result in F and I_3^- (int.) formation, at least at special lattice sites; this is apparently the case from the experiments of Hall, et al., who studied only the ultraviolet-produced F center production.

The alternative mechanism is that two thermally mobile I_2^- (or $I_2^{=*}$) centers will react chemically with the release of kinetic energy according to a process such as $I_2^- + I_2^-$ (occupying 4 lattice sites) $\rightarrow I_2$ (occupying 1 lattice site) $+ 2\,I^- +$ vacancy.

Similar mechanisms can explain the formation of F (and V) centers in ultraviolet irradiated KCl(I) reported by Goldberg and Mahr where the progenitor would be a $ClI^{=*}$ or ClI^- molecule.

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86 Thermal Growth of M Centers in Additively Colored Potassium Chloride Crystal

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This report concerns an experiment to check if F′ centers contribute to the formation of M centers. A KCl crystal containing F centers was illuminated with F light at $-100°C$ to produce F′ centers, and then warmed to a particular temperature in the dark. This process was repeated several times to accumulate M centers. The height of the M band was then measured at liquid nitrogen temperature. More than ten particular temperatures were chosen for the warm-up between $-50°C$ and $+100°C$. As the crystal was warmed up to a temperature above $-40°C$, where F′ centers were almost gone, the M band growth was observed; and it reached a maximum value at $+70°C$, where F′ centers disappeared completely. An absorption band that was observed at about 600 mμ as the crystal was warmed up, started to decrease at $-40°C$ as if the centers responsible for this band were converted to M centers. The thermal instability of the 600 mμ absorption indicated that it was not the result of F_A centers. The band may be related to OH^- ions, as the crystal with OH^- ions showed an enhancement of the band. Thus, OH^- ions may contribute to the formation of M centers in this case. In the crystal showing a small absorption at 600 mμ, the M band grew slightly.

The results suggest the following process. Electrons released thermally from F′ centers are trapped at some electron traps at temperatures where

F′ centers become thermally unstable. As the crystal is further warmed above −40°C, the traps become unstable and electrons are released from these traps to form M centers.

87 Color Center Production in Alkali Halides Under Pulsed High Energy Irradiation*

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An electron linear accelerator has been used to produce color centers in alkali halide crystals. The production takes place and is observed during a single, five microsecond pulse at an energy deposition rate of 4×10^{24} eV/sec in a crystal approximately 0.6 cm thick. The method of observation utilizes a grating monochrometer providing F-band light, suitable optics, and photomultiplier to detect the transient change in optical absorption during the accelerator pulse. The transient signal is displayed on an oscilloscope with the sweep triggered by a pulse from the accelerator.

A composite signal is observed and results from the combined processes of luminescence and color center production in general agreement with similar experiments by Schulman and Boag[1] and Compton and Bryant.[2] The contribution due to the luminescence alone is determined by turning off the F light. This signal is then subtracted graphically from the composite signal to obtain the time dependence of the color center build-up. Experiments were carried out with Harshaw NaCl and KCl crystals, with zone-refined and lead doped KCl.[3] The F-center density reached a steady state during the accelerator pulse in the Harshaw crystal; a build-up of color centers occurred in the zone refined and lead doped KCl, but it was not clear whether a steady state was reached. In all cases the density remained constant after cessation of the pulse out to times of at least milliseconds.

It is concluded that the observed results are due to a "first stage" coloration process[4] in the sense that the observed saturation is due to the filling of existing vacancies or clusters. This conclusion is also borne out by the fact that the energies to form the F center during the process are 183 and 83 eV, respectively, for NaCl and KCl. The first stage coloration observed on the present time scale, will differ, however, from that carried out at the usual rates in that a relatively slow diffusion process as a necessary step in the formation of an F center is apparently ruled out.

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88 Stress Spectra of Zero-Phonon Lines in Lithium Fluoride

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A general theoretical study has been made of the possible types of stress spectra which can occur in cubic crystals. There are seventeen types of spectra which occur in three main groups dependent on whether orientational and/or electronic degeneracy is removed by stress. These results have been applied to the analysis of stress spectra in diamond, magnesium oxide and lithium fluoride.

Uniaxial stresses of up to 16 kg/mm^2 have been applied to crystals of LiF at 4.2°K along the crystalline symmetry directions [100], [111], and [110]. The centers have been produced by irradiation with 4 MeV electrons at dose rates at 10^6 rads/min for one hour. In some cases lines were enhanced by subsequent optical bleaching. High resolution measurements have been made using a 3-meter Baird concave grating spectrograph of the eight most prominent lines produced which have air wavelengths of 3599, 3909, 3932, 4747, 4874, 5234, 5612, and 6009Å. All the lines show splittings into several components on the application of stress, the maximum observed splitting being about 40 cm^{-1}.

The spectra have been investigated using polarized light, and the results interpreted in terms of the general theory of stress spectra. The most interesting results were obtained for the 3909 Å line associated with the R_2 band. The present results support the $\langle 111 \rangle$ orientation of this center; however the intensities of the components are stress dependent leading to an overall stress-induced dichroism. These results suggest that the ground state is ideally orbitally degenerate, but that this degeneracy is removed either by the stress or by the dynamical Jahn-Teller effect. The 4747 and 5234 Å lines are attributed to centers having monoclinic symmetry, and may result from two transitions within the same center. The Pick N_1 center has the appropriate symmetry and transition $A_g \rightarrow A_u$ and $A_g \rightarrow B_u$ could account for the two observed lines.

89 D Band in Potassium Chloride Crystals Containing Ag$^+$

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It is said that the D band which had been observed by Etzel et al., in KCl:Ag$^+$ crystals colored by x irradiation at room temperature is due to the Ag_{III} center proposed by Delbecq et. al. On the other hand, from F → D optical conservation and the dichroic properties of this band, the origin of this band has been thought to be an electron trapped complex center. According to our recent EPR and optical studies of this band, it seems that the D band consists of two absorption bands overlapping each other; the absorption bands due to Ag_{III} center and the electron trapped complex center (338 mμ, ~ 342 mμ, respectively).

90 V Centers in Potassium Bromide Crystals

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The nature of V centers stable at room temperature in KBr crystals has been investigated by means of preferential bleaching with polarized light. V centers were produced by ionizing radiation, by electrolysis with a pointed anode, or by additive coloration with bromine at high pressure.

In KBr crystals doped with alkaline earth impurities an absorption band, which did not depend on the method used to introduce V centers, was obtained at 262 mμ in KBr (Ca), 261 mμ in KBr (Sr) and 267 mμ in KBr (Ba). This band has ⟨100⟩ - type dichroism at 77°K. Optical bleaching of this band at room temperature produced two overlapping absorption bands which arise from a common center and have ⟨111⟩ - type dichroism at 77°K. These three bands, although located near the V_2 and V_7 bands produced in pure crystals, have quite different optical properties from the V_2 and V_7 bands.

In pure KBr crystals no V center was found which was independent of the method of production of V centers. Two bands of ⟨100⟩ - type symmetry were produced at 253 mμ and 270 mμ both by electrolysis and additive coloration, but there was no corresponding band in irradiated crystals. The intensity of these bands varied from crystal to crystal and it is suggested that these bands are related to impurities. The main product of additive coloration is a broad band extending from 350 mμ to the fundamental absorption edge, which is independent of impurities and is attributed to precipitated bromine. The broad band usually obtained by prolonged irradiation with ionizing radiation and referred to as the V_2 and V_3 bands may also be due to precipitated bromine.

91 The Formation, Bleaching and the Stress Effects in Some of the V Bands in Potassium Chloride and Potassium Bromide

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Optovac crystals of KCl and Hilger and Watts crystals of KCl and KBr were irradiated with 2 MeV electrons at room temperature and at liquid nitrogen temperature.

In KCl, the V_2 band is the major band that bleaches at room temperature. Using this fact, the exact peak position and the half width of the V_2 band have been obtained to be, respectively, 5.35 eV and 1.0 eV at room temperature, and 5.42 eV and 0.75 eV at liquid nitrogen temperature.

The V_1 band is bleached and the V_2 band is produced by illuminating the crystal with 365 mμ light at not higher than 130°K, following irradiation at liquid nitrogen temperature. The V_K and the V_4 bands disappeared during the subsequent warm-up to room temperature.

In KBr, the V bands formed at room temperature are very stable. In both KCl and KBr, no preferential bleaching of the V_2 or V_3 band by polarized light has been obtained at either room or liquid nitrogen temperatures.

The effect of stress on the V bands (especially the V_2 and V_3 bands) has been studied in crystals of KBr. Stresses were applied in most cases along the [001] direction and in our specimen holder macroscopic slip usually occurred on only one of the (101), $(\bar{1}01)$, (011), and $(01\bar{1})$ planes. Optical absorption measurements were made at room temperature with polarized light incident along the [100] and [010] directions.

In crystals irradiated with 2 MeV electrons and then subjected to an applied stress below the elastic limit, no appreciable changes in absorption and no anisotropy were observed. Beyond the elastic limit an uniaxial [001] stress giving slip on the (101) planes gave the following results:

(a) An increase in the total absorption in the V_2 band.
(b) A decrease in the total absorption in the V_3 band.
(c) An anisotropic absorption in both the V_2 and V_3 region such that the absorption with $E||$ [001] is larger than that with $E||$ [100].

In unirradiated crystals, an applied stress above the elastic limit does not produce the V_2 and V_3 bands, neither is there any anisotropy in the absorption in this region (the 6.2 eV band present in samples before any treatment is increased in strength).

Electron irradiation of plastically stressed crystals gave the same results as under (a), (b), and (c) above.

These effects may be interpreted in terms of the interaction of V_2 and V_3 centers with dislocations. The results will be discussed in terms of the possible symmetries of the centers. One model for the observed changes favors the symmetry ⟨100⟩ for both V_2 and V_3 centers.

92 Electron Capturing by the U Center

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M, R and N centers have been found to capture an electron and generate the F′ type centers.[1] These centers will play an important role in the formation of the F-aggregate centers. The U center has been found to have higher excited states and its optical absorption and photoconductivity spectrum closely resemble those for the F′ center.[2] The U center has the possibility of conversion to U′ center, i.e. U + e in analogy with the F′ center. The thermal stability of the possible U′ center is low and the efficiency for the generation of free electrons from U centers is very small at low temperature. Therefore, the U to U′ conversion by light can not be expected. We have used X rays to generate the free electrons. The trapping of the electron by the U center has been studied through photoconductivity measurements.

The rapid decrease of the photoconductivity in KCl containing U centers with a concentration of $5 \times 10^{17}/\text{cm}^3$ has been observed between the temperature range of 100-120°K and the nature of the photocurrent was the secondary one. Below 120°K, the photoconductivity increases slowly with decreasing temperature to 20°K. The same crystal, but with the U center removed, or pure and additively colored crystals have been found not to show the rapid decrease of the photoconductivity. These facts indicate that the free electron can be trapped by the U center and the trapped state is unstable above 120°K. The formation of the U′ center occurs below 110° and 90°K in KBr and NaCl crystals, respectively.

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93 Formation of F and V Centers in Ca^{++} Doped Alkali Halides

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It is well known that the production of F centers by x rays around room temperature is enhanced by the addition of divalent cation impurities. Crawford[1] suggested that an isolated positive ion vacancy is converted to Cl_2^- and a negative ion vacancy by hole capture. Recently it was shown[2] that the enhanced coloration by divalent impurities is nearly equal to the concentration of isolated positive ion vacancies. The purpose of this paper is to present the results of further studies on this conversion and its relation to the production of V centers.

Measurements were made on the change of the ionic conductivity by x irradiation near room temperature in NaCl doped with Ca^{++}. The decrease in the number of isolated positive ion vacancies calculated from the conductivity decrease was nearly equal to the number of F centers produced in the early stage of coloration. In pure crystals, however, x irradiation increased the ionic conductivity. In another experiment the initial formation rate of F centers in NaCl doped with Ca^{++} was measured at various temperatures and plotted as a function of $1/T$. A straight line was obtained between −80°C and room temperature giving an activation energy of 0.08 ± 0.01 eV. This result suggests that a unique process, presumably the Crawford conversion, is taking place in this temperature range. Also the production of V centers was measured in Ca^{++} doped alkali halides at −80°C. The strength of the V band in KBr makes it most appropriate for a quantitative comparison. Similar qualitative results were obtained in NaCl. From the relation between the growth of the F and V bands it was concluded that the V center found by Hayes et al.,[3] is associated with a positive ion vacancy. On the other hand the V_4 center is not correlated with the positive ion vacancy. A recent photochemical study[4] made in conjunction with these measurements indicates that it is more likely a di-interstitial center.

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94 Recombination of Point Defects in Alkali Halides at Low Temperatures

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Frenkel pairs consisting of alpha centers and their anticenters, the interstitial ions, are produced in alkali halides at low temperatures by low energy x rays. Experiments have been performed in which the thermal stability of these defects is studied in both pure and Cl^- doped KBr. In the pure material three annealing stages between 6 and 16°K obeying first order kinetics are attributed to correlated recombinations between the vacancies and interstitials and a second order process at 22°K leads to the recombination of more distant vacancy-interstitial pairs through the free migration of an interstitialcy. In the doped specimens the above annealing stages are partly or totally suppressed and many interstitials remain stable until circa 100°K. Observation of an absorption band at 5.4 eV indicates that the enhanced stability of the α center is due to the replacement of a Br^- interstitial by a Cl^- interstitial in the doped specimens. Presumably the smaller mass and size of the Cl^- interstitial makes it more difficult for it to initiate interstitialcy migration.

The stability of the interstitial should play an important rôle in determining the efficiency of radiation damage processes. Measurements on pure and doped materials at both 16°K and 22°K indicate that this is the case: a large change in efficiency being observed in the pure material when the free migration of the interstitial is permitted at the temperature of irradiation. In 8 mole% Cl^- doped KBr, on the other hand, the Cl^- interstitials are stable at both irradiation temperatures and no change in the efficiency of α center formation is observed.

The stability of the interstitial should be important in the formation of divacancy centers by two separate ionizing events since the second ionization perturbs the configuration produced by the first ionization. It is shown that if the first defect created is an α center, the subsequent formation of any other vacancy on a neighboring site will very likely result in the recombination of the α center and its interstitial. This would not be the case if an F center were the first defect to be created. These conclusions are in accord with observations.

95 Formation of F Centers by X Rays in the Proximity of Absorption Edges

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It has been variously suggested[1, 2] that multiple ionization of the halide ions in alkali halides will result in the production of Frenkel defects. The effect of the multiple ionization produced by an Auger cascade on defect production was studied by Sharma et al.,[3] using monochromatic x rays having energies in the vicinity of the K edge in chlorine and bromine in KCl and KBr respectively. The measurement in KBr was extended to lower temperatures by the present authors and measurements also made in the proximity of the K edges of bromine and rubidium in RbBr and RbCl. Appreciable edge effects were observed in all cases including the K edge of rubidium. It became apparent, however, that the interpretation of the results is not as simple as one has expected because the energy distribution of the secondary photoelectrons changes considerably as the energy of the incident X ray photon crosses the K edge of an ion. It is conceivable that this change could be responsible for the observed edge effects, especially when the energy of the incident photons is high, as in the case of the bromine and rubidium edges. A Monte Carlo calculation was therefore made to obtain the total number of the inner shell ionizations produced by an incident electron with various energies. The classical ionization cross section obtained by Gryzinski[4] was used. This cross section is known to give quantitative agreement with various experimental results in atomic physics. It turns out that in KBr the M shell ionization of bromine has such a high efficiency that it could account for the experimental rate of defect formation at the lowest temperature if one assumes that each M shell ionization will produce one defect. In KCl the higher ionization energy of the inner shell of chlorine makes the inner shell ionization by low energy electrons less probable. Therefore for the edge effect at the K-edge of chlorine in KCl observed by Sharma et al., the contribution from the change in the energy distribution of photoelectrons is not very important. The effect of double ionization produced by the direct process and single ionizations at the neighboring halide ions[5] are also being considered.

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96 Some Optical and Electrical Properties of Color Centers in Cesium Bromide Crystals

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The thermal bleaching of color centers in CsBr crystals irradiated with X rays at liquid helium temperatures has been examined. A new absorption band at 320 $m\mu$ was found. Efforts were made to find a relationship between the bleaching properties of the different bands. Electrical glow curves were made in parallel.

Further experimental evidence was found to support the idea that the F-band complex contains absorption bands due to other centers than the F center. This is confirmed by photoconductivity measurements in the F band made between liquid helium temperature and liquid nitrogen temperature.

The curves of $\eta\omega$ as a function of the wavelength show a high quantum yield at 580 $m\mu$, due to centers giving rise to a small optical absorption. After an adequate treatment of the samples no difference in quantum yield can be found in the two main bands of the F complex. $\eta\omega$ curves were determined as a function of the temperature at the wavelength of 580, 620, 640 $m\mu$.

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97 Electrical Conductivity Due to M and Colloidal Centers in Additively Colored Zone Refined Potassium Chloride and Potassium Bromide Crystals

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In the usual plots[1] of the ratio σ_c/σ_n (σ_c is the conductivity of the colored crystals and σ_n of the uncolored crystal) versus temperature, two maxima have been observed, the first between 30° and 100°C for zone refined KCl and between 100° and 200°C for zone refined KBr and the second between 350° and 500°C for KCl and between 250° and 450°C for KBr. However, if the work is done with great care to avoid exposure of the crystals to light, the M center concentration is small, the first maximum is practically absent and the ratio remains nearly unity up to 300°C in KCl. On the other hand, if the crystal is irradiated with F or white light to convert some of the F centers to M centers, the value of σ_c/σ_n at the first maximum increases. The larger the initial concentration of M centers, the greater is the height of the first maximum of σ_c/σ_n. This indicates that most of the excess conductivity in the region of first maximum is due to the electrons from the ionized M centers. The second maximum in KBr has the same properties as those found for KCl earlier[1] and is attributed to the presence of metallic colloids. The electron affinity is found to be 0.6 eV for KBr. The background divalent impurity was less than 1 ppm in these crystals. The effect of larger background impurity or deliberately introduced impurity was to reduce the formation of M centers and colloids and to suppress the values of σ_c/σ_n at both the maxima. If the impurity concentration is comparable or larger than the F concentration, the value of σ_c/σ_n becomes much smaller than unity above 300°C. This is presumably due to the formation of aggregate centers consisting of F center, cation vacancy and divalent impurity.

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98 Thermoluminescence and Two Stage Coloration in X-Irradiated Zone Refined Potassium Chloride Crystals

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If the background divalent metal impurity concentration is reduced to less than 1 ppm, KCl crystals X irradiated at room temperature show only two thermoluminescence peaks at 135°C and 190°C for 40°C/min rate of heating. The rates of growth of the areas of these two peaks with time of X irradiation obey the equations developed by Mitchell, Wiegand and Smoluchowski[1] for the first and second stage colorations respectively. Further, the areas under the two peaks are found to be proportional, separately, to the initial concentrations of the two types of F centers. It is concluded that the first peak is due to the thermal bleaching of the first stage F centers and the second peak due to the thermal bleaching of the second stage F centers. These investigations provide an experimental method of measuring the concentrations of the two types of F centers separately.

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99 Theory of the Magnetic and Optical Properties of the Self Trapped Hole in Ionic Crystals

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Using a semi-phenomenological method, the energy of the self-trapped hole in several of the alkali halides and CaF_2 is obtained as a function of the separation of the two halogen ions at which the hole is assumed trapped. The lattice distortion energy, due to changes in the Madelung, repulsive and polarization energies, is calculated as a function of the totally symmetric displacement of the two participating halogen ions and the ions adjacent to the halogen ions which trap the hole. The wave functions and energies of the Σ_u and Σ_g states of the F_2^- molecule ion are calculated as a function of internuclear distance. The lattice energy calculations are combined with the electronic energy calculations. For Cl_2^-, the wave functions and energies were taken from an article, to be published by A. C. Wahl and T. L. Gilbert. In all cases, it was found that only the Σ_u state exhibited a minimum. From the resulting configurational coordinate curves the optical absorption energy and width are computed. The isotropic and anisotropic hyperfine constants are calculated as a function of internuclear distance between the nuclei of the halogen ions that trap the hole.

100 Bleaching of Nascent Color Centers by Recombination Luminescence during Low Temperature X-ray Irradiation

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The existence of intense electron-hole recombination luminescence during 4°K x-ray irradiation of alkali halide crystals has recently been established.[1] This luminescence tends to bleach color centers which are being created by the irradiation. It has proven possible to determine the magnitude of this bleaching process experimentally by a geometrical manipulation which, at a given state of the irradiation, increases the effective luminescent intensity by increasing the volume of crystal being irradiated without changing the x-ray intensity. Further irradiation rapidly diminishes the concentration of F, V_K and H centers relative to α centers through electron redistribution due to the enhanced F-center bleaching. The measured growth rate change, when multiplied by a calculated geometrical factor, gives the bleach rate under normal conditions. For F centers in KBr this bleach rate was found to exceed the net F-center growth rate by a factor of roughly 10 at moderate concentrations. Under normal circumstances the bleaching process is overbalanced by a process which may be presumed to involve the trapping of electrons by α centers. An upper limit for this trapping rate was obtained by observing the regrowth of F centers after having bleached with an external light source. These experiments indicate that the measured F-center growth rate at a given stage of irradiation is adequately represented as the difference between a trapping rate and a bleaching rate, each of which is an order of magnitude greater than their difference.

Electron redistribution by the intrinsic luminescence is also illustrated in another experiment, beginning with x-ray irradiation at 77°K (where the luminescent intensity is very low) to produce F, α, F′, and various V centers. The net effect of subsequent irradiation at 4°K is to rapidly convert F′ and F centers into α centers.

[1] M. N. Kabler, Phys. Rev. 136, A1296 (1964).

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101 F Centers in Gamma-ray Irradiated Potassium Chloride: I. Growth at Low Dose Rates*

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The coloring of KCl single crystals (Korth) by Co^{60} gamma rays has been studied by measuring the F-center absorption, at closely spaced intervals of time, while the crystal is being irradiated. Typically, the F center vs. dose curve resembles a saturating exponential but definitely *cannot* be described by one single exponential expression. Both the curve shape and saturation level are dose rate dependent in the range 200 to 3000 R/hr. Saturation levels around 5×10^{15} F centers/cm^3 were obtained. Due to the low radiation levels used, it is thought that only the first stage F-center growth mechanism is operating. Any particular sample can be colored to saturation or below, then annealed at 200°C and when recolored, the original growth curve is very nearly reproduced. This alternation of coloring and annealing can be repeated many times with little effect on the growth curve. Also, the growth curves are influenced by plastic compression prior to irradiation. The saturation coloring increases with increasing strain. For example, it is increased twenty percent by a two percent strain. An attempt was made to determine if the coloring curves contain an induction stage near the origin. If such a stage is present it is less than two or three minutes in time or 10 R in dose. This indicates that the growth mechanism does not involve the diffusion of certain types of structural defects. The kinetics of the F-center coloring were studied. The results cannot be adequately summarized in a few sentences.

* Research performed under the auspices of the U.S. Atomic Energy Commission.

† On leave from Max-Planck Institut für Kernphysik, Heidelberg, Germany.

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102 F Centers in Gamma-ray Irradiated Potassium Chloride: II. Annealing Kinetics above Room Temperature*

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The annealing of F centers in KCl single crystals (Korth) colored by Co^{60} irradiations at dose rates of $1 - 3 \times 10^3$ R/hr has been studied by making absorption measurements while heating the sample. The crystals were contained in a controllable oven installed in the facility used to study coloring during irradiation. Samples were irradiated until the F-center growth curve reached saturation at approximately 5×10^{15} centers/cm^3.

At F-center saturation the V-band region contains a broad (single?) absorption band. Because of the low dose rate and saturation level obtained, it is thought that only stage I coloring is present when annealing was commenced. During annealing runs, F-center measurements could be made at all temperatures of interest. However, it was necessary to lower the crystal to room temperature to make absorption measurements at other wavelengths, between 0.19 and 2 microns, with a separate spectrophotometer. It was found that any decrease observed in the F-center concentration is paralleled by a proportional decrease in the V-band region. Heating to 200°C completely removed all coloring. Isothermal annealing data could be fitted by bimolecular kinetics described by the equations $(-dF/dt) = F\Sigma V_i$ and $F = V = \Sigma V_i$ where F is the F-center concentration, V_i is the concentration of the i^{th} type of hole center having recombination coefficient k_i. Linear heating studies above room temperature indicate that the annealing occurs in three prominent stages. The room temperature annealing is described in III. Also, the linear heating data are closely fitted by the bimolecular kinetics. Activation energies for each of the three prominent stages were obtained from annealing curves by computing the contributions of each stage to the observed curve. The energies obtained were 0.65, 1.15 and 1.8 eV with an error of about ten percent.

* Research performed under the auspices of the U.S. Atomic Energy Commission.

† On leave from Max-Planck Institut für Kernphysik, Heidelberg, Germany.

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103 F Centers in Gamma-ray Irradiated Potassium Chloride: III. Room Temperature Annealing*

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The room temperature annealing, i.e., the stability, of the Co^{60} gamma-ray induced F centers in single crystal KCl (Korth, Harshaw) was studied with the facility for making optical absorption measurements during irradiation. Samples were colored, using dose rates from 200 to 3000 R/hr to F-center concentrations up to $5 \times 10^{15}/cm^3$. After coloring, the gamma-ray field is "turned off" but F-center absorption measurements are continued. Immediately after irradiation a small fraction of the total absorption decays with a half-life of approximately one hour. After this component has decayed away, the remaining coloring is also found to be unstable. It has a half-life on the order of days. This slowly decaying component can be explained by the linear heating results, reported in II, which indicates that the lowest temperature annealing stage is operable at room temperature. Some additional observations on only the fast component are as follows: By varying the irradiation time it was found that this component reached saturation after an irradiation of only twenty minutes and remains essentially constant for longer irradiations. At the maximum dose rate the saturation concentration is roughly 3×10^{14} F centers/cm^3. Decreasing the dose rate also decreases the saturation level. Subjecting the crystals to plastic compression prior to irradiation causes the rapid component to decrease. The saturation concentration is the same in both thin (0.8 cm) and thick (2.0 cm) crystals. Also, it is possible to split the decay curve into two simple exponentials. However, for a variety of reasons, it is most likely that the rapid component must be attributed to a mechanism that cannot be described so simply. Surprisingly, all of the results obtained so far suggest that the rapid component should be attributed to surface, not volume, effects.

* Research performed under the auspices of the U.S. Atomic Energy Commission.

† On leave from Max-Planck Institut für Kernphysik, Heidelberg, Germany.

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104 Ionic Conduction in Sodium Chloride Doped with Calcium

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Several controversies existed on the association of divalent impurity ions with positive ion vacancies in alkali halides, especially among various experimental results on NaCl containing Ca^{++}.[1]

In the present work, the following important improvements were achieved in the experimental procedures: (a) analysis of Ca content in the crystal by Ca^{45} tracer method, and (b) special precautions in growing crystals to get rid of anion impurities, such as hydroxide and oxide. Ionic conductivity results as a function of Ca concentration at 300 and 400°C showed clearly the occurrence of predominant association for NaCl containing $1 \sim 20 \times 10^{-4}$ Ca^{++}. The value of association energy at 400°C is estimated to be 0.48 eV by using simple association theory. The value of free vacancy mobility at 400°C is close to that obtained by Etzel and Maurer on NaCl containing Cd^{++}.[2]

[1] A. B. Lidiard, *Handbuch der Physik* (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246, and J. Itoh and M. Satoh, J. Phys. Soc. Japan 18 Suppl. II, 57 (1963).

[2] H. W. Etzel and R. J. Maurer, J. Chem. Phys. 18, 1003 (1950).

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105 Paring of Electron and Hole Centers in Irradiated Potassium Iodide (Thallium) at 78° K

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The x irradiation of KI:Tl at 78°K produces Tl^0 and I_2^- as the electron and the predominant hole center. Warming past 106°K mobilizes I_2^-

which either combines with Tl^0, producing the first glow peak, or retraps at Tl^+. Warming past 178°K stimulates the combination of the remaining electron and retrapped hole centers producing the second glow peak. These processes are followed by both the recombination light sums and the changes in optical absorption.

The question at point is, does the moving I_2^- combine with its original electron, or are there several electrons available? The following results suggest that the former is true, that the electron and hole centers are paired rather than randomly distributed.

The ratio of recombination to retrapping, as the first glow is removed by parts, is constant throughout the glow peak. In addition the ratio is independent of x-ray dose and the level of storage. These results indicate that I_2^- has the same probability of recombining or retrapping in a crystal with a high concentration of electron and hole centers as in one with a low concentration. Since the concentration does not affect the ratio the centers must *not* be randomly distributed. It is suggested that electron and hole centers are produced, one pair to each "active" volume, with a distribution of electron-hole distances, but with very few distances so great as to overlap another pair's volume. In any one volume the hole either recombines or is retrapped depending on how far it is from its electron. The same model may be extended to the case where electrons are moving. They may either recombine with holes or retrap at Tl^+.

106 Theory of Optical Pumping in the F_t Center in Calcium Oxide*

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We recently reported optical pumping of the triplet state ESR lines of the CaO F_t center.[1] The latter is pictured as a coupled F-center pair along ⟨100⟩ directions, with possibly an intervening Ca vacancy. The ground singlet and low spin triplet are separated by 4×10^{-3} eV, thus at helium temperatures the triplet is thermally vacant. Relaxation times are such that pumping into the triplet via higher excited states is easily done. It was shown that unpolarized broadband light induces a tensor-type polarization of the triplet, meaning that only the $M_S = \pm 1$ states become populated, or alternatively only the $M_S = 0$ state, according to whether the magnetic field is parallel to or normal to, respectively, the F_t center axis. A simple theory of this effect, indicated briefly in reference 1, is presented in somewhat more detail.

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* Supported by the U.S. Air Force.

[1] D. H. Tanimoto, W. M. Ziniker, and J. C. Kemp, Phys. Rev. Letters 14, 645 (1965).

107 Structure in the Luminescence Emission of the S_2^- Ion

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We have previously reported[1] a luminescence emission from sulfur-activated alkali halides at 77°K consisting of a series of over a dozen nearly equally spaced narrow bands (separation ~ 600 cm^{-1}) between 5000 to beyond 7000Å, and have ascribed this emission to the S_2^- ion by analogy with a similar luminescence reported by Rolfe for O_2^- at 77°K.[2] Measurements of this emission have now been made near liquid helium temperature, revealing fine structure which again resembles that found for O_2^- at 4°K.[3] Specifically, each of the previously reported emission bands in sulfur-activated KCl and KBr is resolved into a sharp peak of relatively high intensity and three or more satellites on both the high and low energy sides of this main peak.

The main features of the spectra are believed to be due to a transition from an excited electronic state to the electronic ground state, the transition being modified primarily by quanta of the main vibration of the S_2^- molecule in the ground electronic state. The frequency of the vibration is found to be $\omega_e = 636$ cm^{-1} in KBr and 655 cm^{-1} in KCl, and the anharmonicity $\omega_e\chi_e \sim 3$ cm^{-1} in either (the last digit being quite uncertain in each case). Of the fine structure, several lines on the low energy side of the main peak can be identified as lattice virbations[4] and others presumably as combinations of them (two-phonon lines). These also appear in the O_2^- spectra,[2, 3] but much less prominently. One line on the high energy side can be attributed to the isotope S^{34}. Other details are not fully understood and may result from perturbation by the crystalline field.

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[2] J. Rolfe, F. R. Lipsett, and W. J. King, Phys. Rev. 123, 447 (1961).
[3] J. Rolfe, J. Chem. Phys. 40, 1664 (1964).
[4] A. D. B. Woods, B. N. Brockhouse, R. A. Crowley, and W. Cochran, Phys. Rev. 131, 1025 (1963).

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108 Thermal Conductivity of Hydroxide Doped Alkali Halides

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Several years ago[1] it was discovered that NaCl grown from NaOH-doped melts revealed an anomalously low thermal conductivity below 10°K. This work has been repeated on NaCl crystals grown under more controlled conditions and has been extended to several other alkali halides. The new results on NaCl:NaOH are consistent with those in Ref. 1. The low temperature depression in thermal conductivity scales quite well with the strength of the "OH" band at 185 mμ for concentrations of 4 parts per million to 430 ppm. (The maximum absorption has been calibrated against chemically determined alkalinity to yield 1.4 ppm mole fraction NaOH per cm^{-1} absorption.) All the curves show a dip at 5°K independent of concentration. The $CO_3^=$ ion cannot be the active scatterer of phonons since crystals with widely different infrared absorption bands at 7.1μ but with the same 185 $m\mu$ band have the same thermal conductivity.

The conductivity depression in KCl:KOH is not as great as that in NaCl:NaOH. A crystal with 700 ppm alkalinity exhibits a conductivity two orders of magnitude less than that of a pure crystal, with a T^3 temperature dependence at low temperatures, a maximum at 7°K, a minimum at 14°K, and another maximum at 40°K. An electric field of 200 kV/cm causes a 150% rise in the low temperature conductivity. At small fields the conductivity decreases by about 10%; it then rises for $E > 100$ kV/cm.

Crystals of KBr:KOH, RbCl:RbOH, and NaBr:NaOH have also been studied. They do not reveal any spectacular low temperature effects.

[1] M. V. Klein, Phys. Rev. 122, 1393 (1961).

109 Origin of the L Absorption Bands

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The optical absorption spectrum of an F center due to transition from its ground state to the conduction band was investigated theoretically by using the semi-continuum approximation. The wave function of a conduction electron is warped by the presence of the anion vacancy in such a way that its amplitude in the vacancy increases with decreasing wave number of the electron. A sharp maximum of the amplitude at $k = 0$ gives rise to an absorption peak associated with the transition from the ground (ls) state to the vicinity of the Γ point in the Brillouin zone. In this respect the Γ state behaves as if it were a localized level at the F center in the conduction band.

By referring to an energy band calculation for KCl made by Oyama and Miyakawa,[1] a tentative assignment of the L absorption bands may be given as follows: The short wavelength side of the K-absorption peak corresponds to the $ls \rightarrow \Gamma_1$ transition. The L_2-peak and the L_3-peak may be caused by the $ls \rightarrow \Gamma_{12}$ transition and by the $ls \rightarrow \Gamma'_{25}$ transition, respectively, if one assumes the Γ_{12} level to be lower than the Γ'_{25} level in accordance with a result of the energy band calculation. A relatively flat and wide portion of the energy vs k curves for the lowest (sp) conduction band near the Brillouin zone boundary may be responsible for the background absorption underlying the L_2 and L_3 bands. The origin of the L_1 band is still obscure. A possible interpretation as a (localized or free) phonon assisted transition was investigated.

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[1] S. Oyama and T. Miyakawa, J. Phys. Soc. Japan 20, 624 (1965).

110 Copper Centers in Ionic Crystals

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Three types of copper centers are described and compared with the corresponding silver centers.

1. Cu^+ centers. They give rise to two absorption bands in the ultraviolet which are assumed to be due to vibrationally allowed $3d^{10} \rightarrow 3d^9 4s$ transitions. The unexpected small temperature dependence of the oscillator strength indicates a partial violation of the inversion symmetry of the center, due to the small ionic radius of Cu^+. In a matrix with smaller lattice constant the temperature dependence of the transition gets larger.

2. Cu^0 and Cu^{++} centers are prepared by X-ray irradiation of the crystals at 78°K. For the Cu^{++} centers (as in the case of Ag^{++}) the symmetry of the surrounding halogen ions is lowered by a Jahn-Teller distortion. This is shown by the dichroic behavior of the absorption at low temperature. But there are characteristic differences to the Ag^{++} center: The number of the absorption bands, the disorientation temperature of optically aligned centers and the orientation of the electric vector in comparison to the axis of the center. These differences are interpreted by the assumption that the surrounding octahedron of halogen ions is compressed by a Jahn-Teller distortion, instead of extended, as in the case of $KCl:Ag^{++}$. The number of bands and the orientation of the electric vector is in agreement with transitions predicted by the molecular orbital scheme.

111 Lattice Dynamical Aspects of the Vibronic Transitions in Impurity Centers

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The detailed interpretation and calculation of various characteristics of the vibronic spectra of impurity centers requires careful investigation of the lattice vibration modes modified by defects. The latter problem is solved for the special model of NaCl-type lattice in which the real interactions are expressed by effective parameters associated with the empirical constants. The numerical calculations are carried out for KCl lattice by means of an electronic computer. The conditions of appearance of localized modes of various symmetries, the dependence of their frequencies upon the parameters of the perturbation operator, and the asymptotic spacewise attenuation are investigated. The localized mode of A_{1g} symmetry, which is supposed to play the main role in the interaction of electronic transition with lattice vibrations, can be generated only by an essential increase of force constant (~ 3.6 times). As a result of this, such even localized modes are absent in the usual luminescence centers (mercury-like or F centers in alkali halides). Nevertheless, the lattice vibrations near these centers are essentially modified and more or less good pseudolocalized modes of required symmetry arise. Taking into account this modification, the distribution function of Stokes' shifts for KCl containing Tl^+ and F centers are calculated. These functions make it possible to investigate the temperature dependence of the half-width of vibronic spectra.

On the basis of an exact dynamical theory of non-ideal lattices, the quasimolecular model of vibrations near impurities is investigated. The point symmetry and possible number of localized and pseudolocalized modes are considered.

Using the quasimolecular model, the frequencies of odd vibrations and the temperature dependence of the intensity of the Mössbauer line for Tl^{205} nucleus (γ-transition energy 205 keV) bound in KCl are calculated. The possibility of manifestation of these vibrations in infrared spectra is discussed.

112 Localized and Resonant Phonon States for Defects in Alkali Halides*

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Over the past several years there have been a large number of computations of the defect vibrational properties of lattices based on specific models for either the unperturbed lattice spectrum, or on restricted assumptions for the defect. Usually, these have employed the Green's function method introduced by Lifshitz. From these many detailed investigations certain general features have emerged; among them are symmetry considerations, asymptotic behaviors, field-particle models, and sum rules. It is proposed to discuss each of these with particular reference to either direct lattice (optical) excitations, and with respect to electron-phonon coupling.

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113 ESR Studies of the R Center in Potassium Chloride*

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An experimental and theoretical study is being made of the g factor and the spin-lattice relaxation mechanisms of the R center in KCl.[1] Experiments have also been performed to determine the effect of the R center on the T_1 of the F center.

The g calculations employ the vibronic wave functions already published.[2]

Results, thus far, indicate that the dynamical Jahn-Teller effect plays a crucial role, producing reduction factors of about 0.1 for both the orbital angular momentum and the spin-orbit interaction. The latter is of special interest, being inverted in the manner which Smith[3] has described for the excited state of the F center. The theory also predicts a shift of the line with applied stress whose sense is in agreement with experiment. The effect of random internal strains[2] corresponding to stresses of about 1 Kg/mm^2 has been considered in estimating the g shift. It appears that random strains of such a magnitude may account for the line width for small applied stresses at 2°K.

An order of magnitude estimate has been made of the T_1 arising from an Orbach process described earlier.[1] It appears that the process envisaged does not provide a sufficiently rapid rate to produce line broadening at 2°K.

An anisotropy in the T_1 of the F center due to cross-relaxation with R centers was sought in crystals with F center concentrations of about 5×10^{16} cm^{-3} and R center concentrations of about 10^{14} cm^{-3} (all crystals used were x-ray colored). The R centers were selectively bleached[1] and the corresponding F-center T_1 anisotropy sought in the appearance of the F-center line. No effect was recorded at any stress up to 3Kg/mm.^{2} These measurements support those of Warren, Feldman, and Castle[4] who looked for changes in the F center T_1 as a function of applied stress only.

* Work supported by the U.S. Atomic Energy Commission.

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[3] D. Y. Smith, Phys. Rev. **137**, A574 (1965).

[4] R. W. Warren, D. W. Feldman, and J. G. Castle, Jr., Phys. Rev. **136**, A1347 (1964).

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114 Pseudopotential Calculations for F Centers

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Several approximations to the Hartree-Fock scheme have been used to calculate F center wave-functions in a static lattice for NaF, NaCl, and KCl. The ions neighboring the vacancy are represented by a point charge or, for 1 to 14 shells, by pseudopotential of the form given by Austin and Heine. In both cases the potential is expanded in Kubic harmonics about the center of the vacancy. The spherically symmetric part of the potential leads to a radial Schrödinger equation that is solved by numerical iteration in integral equation form. The first nonspherical term in the potential is then applied as a perturbation by means of a technique suggested by Dalgarno.

Bound states are obtained for 1s, 2p, 3d, and in some cases 4f, and 2s zero order wave functions. Optical absorption energies, oscillator strengths, and hyperfine interaction constants are compared with experiment and with the previous theory of Gourary and Adrian. The results show that the F electron is concentrated too strongly at the nearest neighbor positive ions when the nonspherical terms are included in the point ion potential. Since the pseudopotential for a positive ion has a repulsive core, the results obtained by including the pseudopotentials are in somewhat better agreement with experiment.

Calculations are in progress for the spin-orbit splitting of the first excited state and for the shift in g value of the ground state. The overall work is also being extended by taking exchange into account, introducing a modification of the free ion wave functions by the crystalline potential, and improving the calculation of overlap integrals.

115 Valence Band in Lithium Chloride*

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A study of the valence band in lithium chloride was undertaken using the tight binding method. Analytic Hartree-Fock wave functions for the 3p and 3s electrons in the free chloride ion were used.[1] The lithium potential and wave functions were obtained for the free ion case by a direct application of the variational technique. The analytic potential for the chlorine ion as given by Casella was used.[2] The nearest neighbor chlorine and lithium ions were taken into account. The 3p and 3s chlorine functions were allowed to mix. It was found that this mixing changed the energy values by about one percent. The Hamiltonian was evaluated for values of the reciprocal lattice vector k in the ⟨100⟩, ⟨110⟩, ⟨111⟩ directions of k space. The top of the 3p band was found to lie 6.20 eV below the vacuum. The bottom of the 3s band lies 14.5 eV below the vacuum. The maximum width of the 3p band was found to be 2.18 eV. It was found to have the normal band structure for a fcc crystal. Work is being carried out on KCl, NaCl and NaI. Preliminary results for KCl and NaCl indicate that the results are in good agreement with previous calculations.[2, 3] The problem of Tl centers in NaI is also under consideration. The authors wish to thank Prof. W. J. Van Sciver and Dr. H. Mullish of the N.Y.U. Computing Center for their considerable help.

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** NASA pre-doctoral fellow in physics.

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116 On the Splitting of Zero-Phonon Lines by Uniaxial Stress

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The number of components into which a zero-phonon line splits as a result of applying an uniaxial stress along different crystallographic directions determines the symmetry of the corresponding color center.[1, 2] The symmetry group O_h of an ideal alkali halide crystal is reduced to a group P of lower symmetry by stress along different directions as given in the two upper lines of the table ($n_1 \neq n_2 \neq n_3$ and $n_1, n_2, n_3 \neq O$). The symmetry group S of a color center must be a subgroup of O_h. The different cosets of this subgroup S with respect to O_h contain the transformations of a color center from one original orientation into the different possible orientations. Multiplication of a coset with the group P generates a set of cosets which contain all transformations into equivalent orientations relative to the axis of stress. The number of *different* sets of cosets as presented in the table is equal to the number of non-equivalent orientations relative to the axis of stress and may be interpreted as the number of components of the split line. Deviations from these predictions may occur. For example, in a linear approximation in stress one does not always find the full number of components for $P = C_{2h}$ and $P = C_i$. By comparison, more components may occur if degenerate levels are involved in the transition.

For the rhombic and monoclinic case of S there exist two possibilities depending upon whether the twofold axes are all parallel to ⟨100⟩ or whether there are also twofold axes parallel to ⟨110⟩.

The described method has been applied to the determination of the symmetry of the N_1 and the R center in X-irradiated NaF.[2, 3]

		Stress P					
		⟨100⟩	⟨111⟩	⟨110⟩	$\langle n_1 n_2 O \rangle$	$\langle n_1 n_2 n_2 \rangle$	$\langle n_1 n_2 n_3 \rangle$
	S	D_{4h}	D_{3d}	D_{2h}	C_{2h}	C_{2h}	C_i
Cubic	O_h O T_d	1	1	1	1	1	1
	T_h T	1	1	1	2	1	2
Tetragonal	D_{4h} D_4 C_{4v} D_{2d}	2	1	2	3	2	3
	C_{4h} C_4 S_4	2	1	2	4	3	6
Trigonal	D_{3d} D_3 C_{3v}	1	2	2	2	3	4
	C_{3i} C_3	1	2	2	4	4	8
Rhombic	D_{2h} D_2 C_{2v} ⟨100⟩	3	1	3	6	3	6
	D_{2h} D_2 C_{2v} ⟨110⟩	2	2	3	4	4	6
Monoclinic	C_{2h} C_2 C_s ⟨100⟩	3	2	4	8	6	12
	C_{2h} C_2 C_s ⟨110⟩	2	3	4	6	7	12
Triclinic	C_i C_1	3	4	6	12	12	24

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117 A Rhombic Color Center in X-Irradiated Sodium Fluoride

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The 5746 Å zero-phonon line in x irradiated NaF is split at 4.2°K into 1, 2, 3 and 4 components under uniaxial stress along $\langle 100 \rangle$, $\langle 111 \rangle$, $\langle 110 \rangle$ and $\langle 210 \rangle$ directions, respectively.[1, 2] This result suggests rhombic symmetry (D_{2h} or D_2 or C_{2v}, with at least one twofold axis along $\langle 110 \rangle$) of the color center associated with the line studied. The magnitude of the splitting, which depends linearly on pressure, can be written for different directions of applied stress P in terms of three splitting coefficients A_o, A_1, and A_2 as follows:

$$\begin{array}{llll} P \parallel \langle 100 \rangle : & A_o - 2A_1 & P \parallel \langle 111 \rangle : & A_o \pm A_2/3 \\ & A_o + A_1 & & \\ P \parallel \langle 110 \rangle : & A_o + A_1 \pm A_2/2 & P \parallel \langle 210 \rangle : & A_o + A_1 \pm 2A_2/5 \\ & A_o - A_1/2 & & A_o + 2A_1/5 \\ & & & A_o - 7A_1/5 \end{array}$$

Experimentally we obtain $A_1/A_o = 0.1 \pm 0.2$ and $A_2/A_o = \pm (5.3 \pm 0.9)$. The theoretically calculated 2 components for stress along $\langle 100 \rangle$ cannot be resolved because of the small ratio A_1/A_o. The unresolved line also does not exhibit any polarization. In contrast, for stress along $\langle 210 \rangle$ the components are resolved in spite of the small A_1/A_o ratio because of their different polarizations. From a comparison between the thermal behavior of the 5746 Å line and the M band during an annealing experiment, it follows that the line does not correspond to a transition of the M center which is known to have D_{2h} symmetry. Apart from the M center the simplest F-aggregate center of rhombic symmetry consists of 3 neighboring F centers arranged in a line along $\langle 110 \rangle$. A simple center of C_{2v} symmetry may consist of an M center perturbed by a nearest neighbor cation vacancy or impurity.

[1] G. Johannson, W. v. d. Osten, M. Schinkmann, and W. Waidelich, Physics Letters 11, 210 (1965).
[2] G. Johannson, F. Lanzl, W. v. d. Osten, and W. Waidelich, Physics Letters 15, 110 (1965).

118 Abstract Withdrawn

119 Electron Trapping Energy as a Function of Normal Modes*

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Within the framework of the "adiabatic-harmonic" approximation, there exists a unique set of normal lattice coordinates for each bound F-center electron state. The various sets of normal coordinates are related to one another by products of unitary matrices. These matrices are dependent on the lattice equilibrium configurations, which in turn are functions of the F-center electron state. We have assumed that to each bound state there corresponds a particular equilibrium configuration. With these transformation matrices, expressions for the electron trapping energies for any bound state transitions have been derived in terms of phonon eigenfrequencies and a basis set of normal coordinates. This formulation of the trapping energies includes degenerate and non-degenerate modes and does not require the solution of Feynman-Hellman integrals. This is in contrast to the work of Markham.[1] The basic ingredients that enter our development are the phonon eigenfrequencies and the transformations. From the trapping energy formula, we determine the number of phonons stored in the various modes of the lattice. Here only Frank-Condon transitions are considered. General expressions for the Huang-Rhys factors are developed in terms of the stored phonons. Only under very restrictive conditions are they equal. Although the above developments are completely formal and hence model independent, any explicit calculations will, of course, depend strongly on the choice of model. We have carried out such calculations for the tight binding model of the F-center, where O_h and D_{4h} symmetry has been associated with those states giving rise to the F bands. The results for the Huang-Rhys factor and the "peak" energies of the F bands for several alkali halides agree approximately with experiment.

* Research supported in part by the National Aeronautics and Space Administration.

[1] J. J. Markham, Revs. Modern Phys. 31, 956 (1959).

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120 Mobility of Anion Vacancies in Potassium Chloride and Potassium Chloride Containing Sodium

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In an earlier work[1] it was demonstrated that the formation of primary F-aggregate centers (as F_A or Z_1) are formed by thermal diffusion of an ionic defect with an activation energy of 0.6eV (in KCl), this defect being either the anion vacancy or the F′ center. This open question can now be answered by comparing the mobility of these two defects in question, when they are associated with an isolated Na^+ ion. A system of

F_A(Na) centers in KCl was aligned with polarized light and controlled by the dichroitic F_A spectrum. Electrons released from these aligned F_A centers at 50°K (by optical excitation plus field ionization) converts this system half into ionized F_A centers ("α_A-centers") and half into F'_A-centers, without any change in the orientation of the ionic complex Na^+/anion-vacancy. The F'_A band shows a ⟨100⟩ dichroism related to the state of alignment of the F_A centers from which they were formed by capturing a second electron. Pulse annealing of this system of aligned α_A and F'_A centers causes no change in the F'_A dichroism (demonstrating that the F'_A centers have *not* reoriented thermally), whereas — after optical $F'_A \rightarrow F_A$ back conversion — the F_A dichroism has partly disappeared, for long pulse annealing with half of its initial value. These measurements demonstrate clearly a high mobility of the vacancy and immobility of the F' center. Quantitative analysis with different pulse annealing temperatures yields an activation energy for the jumps of an anion vacancy associated with the Na^+ ion of $E = 0.45$eV. This determination makes it necessary to interpret the 0.6eV[1] as the *activation energy for the anion vacancy migration in pure KCl.* The difference in the two values for KCl and KCl:Na is reasonable in view of the small Na^+ ion and explains why migrating vacancies associate to Na^+ impurities.

[1] H. Härtel and F. Lüty, Z. Physik **177**, 369 (1964) and Z. Physik **182**, 111 (1964).

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121 Effect of Uniaxial Stress on Zero-Phonon Lines in Magnesium Oxide

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Experiments have been carried out on single crystals of magnesium oxide similar to those on lithium fluoride described by Hughes and Runciman.[1] Specimens of magnesium oxide supplied by the Norton Co. were irradiated in a high flux reactor (DIDO) with high energy neutrons (>1 MeV) to a dose of 10^{18} nvt. The average temperature of the specimens during irradiation was about 90°C.

When the absorption spectra of the irradiated specimens were examined at 4.2°K on a 3-meter Baird spectrograph, sharp lines were seen at 27650. 24520, 24200, and 13400 cm^{-1}. Only the 27650 and 24200 cm^{-1} lines were sufficiently intense to use in a uniaxial stress investigation. By supporting the specimens in a holder it was possible to apply stresses of up to 28 kg/mm^2 along the crystal directions [100], [111], and [110]. The 27650 cm^{-1} line is associated with a band at 28310 cm^{-1} and the phonon spectrum of the center can be adequately explained by taking 188. 292. and 401 cm^{-1} as the energies of the fundamental phonon modes. Two weak lines were also present on the high energy side of the 27650 cm^{-1} line at separations of 18 and 40 cm^{-1}. These may be due to the presence of impurity ions near the defect center.

Both the lines examined showed the same splitting patterns and are associated with centers having ⟨110⟩ orientation and orthorhombic symmetry. The model proposed by Wertz[2] for the V_4 center also has this orientation and symmetry.

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[1] A. E. Hughes and W. A. Runciman, 1965 (to be published).

[2] J. E. Wertz, J. W. Orton, and P. Auzins, Discussions Faraday Soc. 31, 140 (1961).

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122 F_A Centers in Alkali Halides

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Recent work on F_A centers is reviewed, emphasizing its "model character" for the F center. Special interest is focussed on the relaxation and reorientation behavior, measurable by dichroitic experiments which are not possible with F centers. Three recent results for the activation energy of reorientation of F_A(Na) centers in KCl should be noted:

1. F_A(Na) without electron $E_1 = 0.45$ eV[1]
2. F_A(Na) electron in ground state $E_2 = 1.25$ eV[2]
3. F_A(Na) electron in excited state $E_3 = 0.10$ eV[3]

The reorientation, which takes place by a jump of the halogen into the vacancy is surely favored by the adjacent small Na^+ ion ($E_1 = 0.45$ eV instead of 0.6 eV in pure KCl).[1] But obviously the presence of an electron in different states has the strongest effect on the resulting energy. For explanation one has to consider the adiabatic transition from the normal (100) lattice position of the center into the (110) saddle-point configuration necessary for the reorientation: This transforms the s- and p-type electronic state of the F_A center into the lowest symmetric and antisymmetric state resp. of the resulting double well potential, hereby considerably *increasing* the energy of the *symmetric* state, but *decreasing* the energy of the *antisymmetric* state. This change in the electronic energy adds to the ionic activation energy and brings about the total values E_2 and E_3.

In case of the "type II F_A-centers,"[3] the small Li^+ ion reduces the ionic activation energy further so that here the gain in electronic energy in the excited state *overcompensates* the ionic activation energy. Therefore after optical excitation the lattice position of the neighboring halogen becomes instable, the excited center relaxes into the *stable saddle-point configuration.* De-excitation of the electron now takes place as a radiative transition between the well overlapping antisymmetric and symmetric electronic states of the double well potential, yielding a narrow emission with large Stokes shift and short radiative lifetime. The measured reorientation rate and polarization of the emission are in quantitative agreement with this model.

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[1] E. Link and F. Lüty, See Abstract No. 120.
[2] F. Lüty and K. Seifriz, See Abstract No. 124.
[3] B. Fritz, F. Lüty, and G. Rausch, See Abstract No. 57.

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123 Density and Lattice Parameter of the System Potassium Chloride Plus Potassium Hydroxide

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The interest focussed on the OH^- center by the recent paraelectric and paraelastic work make it desirable to confirm beyond any doubts the substitutional model for the OH^- center and to obtain information about the lattice distortion introduced by this defect. Two types of measurements were done for this purpose:

1. *Density measurements* on KCl crystals with different amounts of OH^- (up to 5.3×10^{-3}), the OH^- content in the crystal being controlled chemically and optically. A sensitive flotation method was used, allowing by direct comparison of the doped and undoped probes a relative density change less than 5×10^{-6}. A linear decrease of the crystal density with OH^- content was found. Assuming a substitutional model for the OH^- (mass substitution $Cl_{35} \rightarrow OH_{17}$) the corresponding volume decrease is obtained.

2. *Lattice parameter measurements,* using x-ray diffraction techniques with single crystals and powdered probes, gave a linear decrease of $\Delta a/a$ with OH^- content, from which the volume decrease is directly obtainable.

By these two independent determinations complete agreement is found within the experimental error for the values of $\Delta V/V$, so giving the first real proof for the substitutional model of the OH^- center. From the constant ratio $\Delta V/V : n(OH^-)/n(Cl^-) = -0.21$ the size of the OH^- can be evaluated. Idealizing the crystal as a homogeneous elastic continuum and using Eshelby's theory, the sum of the dilatations around the OH^- center may be evaluated assuming the validity of the linear theory even to the immediate vicinity of the defect. The OH^- center behaves in respect to macroscopic volume change roughly like a spherical misfitting ion of 7% smaller radius than the Cl^- ion.

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124 Thermal Reorientation and Dissociation of F-Aggregate Centers

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F centers which are associated with monovalent foreign cations (F_A-center), with divalent cation/vacancy complexes (Z_1 center) or with other F centers (M centers) become mobile above room temperature. This can be observed in the case of optically aligned F_A and M centers by the decay of dichroism (thermal reorientation) and for all three centers by the back-conversion to F centers (thermal dissociation) caused by pulse annealing in the dark to higher than room temperature. Both reactions follow Arrhenius type equations and have the following activation energies in KCl (with marked deviations from older measurements):[1]

	F_A (Li)	F_A (Na)	M	Z_1 (Ca)
E(Reorientation)	0.91 eV	1.25 eV	1.56 eV	....
E(Dissociation)	0.99	1.35	1.70	0.94 eV

In all cases the reorientation rate is one to two orders of magnitude higher than the dissociation rate, demonstrating the "binding effect" of the point imperfection to which the F center is associated. Whereas the isothermal decay of dichroism goes strictly exponential with time, the dissociation rate deviates from this law. This can be quantitatively explained by a return motion of F centers before they have made one or two jumps away from the binding point imperfection. Optical reaggregation of thermally dissociated F-aggregate centers shows clearly that the F centers have diffused away only a very short distance and are still far from a statistical distribution. Generally these measurements show that an anion vacancy with an electron in the ground state has a much higher activation energy for migration than the empty anion vacancy.

[1] T. Tomiki, J. Phys. Soc. Japan 14, 1114 (1959).

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125 Destruction of F-Aggregate Centers by X Irradiation

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F-aggregate centers (M, R, F_A, Z_1, and Z_2 centers) which were formed by optical irradiation in additively colored KCl crystals are effectively destroyed by x irradiation and reconverted into isolated F centers. The "destruction-efficiency" is high near room temperature (about 20eV of absorbed x ray energy is needed to destroy one F-aggregate center at 50°C) and decreases with temperature. Three experimental results demonstrate the basic difference of this effect from thermal association and dissociation of F-aggregate centers:

1. The activation energy for x-ray destruction is small (0.14eV) compared to $E = 0.6$eV needed for the formation process by vacancy migration or $E = 1.25$eV needed for thermal dissociation (values for F_A(Na)).

2. Optically aligned F_A or M centers are never reoriented but only destroyed by x irradiation, though thermal reorientation is about two orders of magnitude more probable than thermal dissociation.[1]

3. After x-ray destruction of an F-aggregate system the resulting F centers aggregate under F-light irradiation exactly like a system of randomly distributed F centers (again in contrast to the behavior after thermal dissociation).[1]

These three points apparently rule out the interpretation that the clusters are dissolved by some kind of energy localization causing a migration of F centers (or vacancies) from the cluster into the lattice. Instead of this we propose the following: F centers and interstitials are produced with high efficiency under x irradiation; the mobile interstitials are able to recombine with other F centers and by this change mix the places of the F centers with a much higher rate than the production rate of new centers. If F centers were optically aggregated at special lattice places (forming F_A, Z, M... centers) they are effectively annihilated by the x ray produced mobile interstitials while new F centers arise — with statistical distribution — at the places where the interstitials have been formed. This explains the above three points as well as many properties of F center production and F^2/M equilibrium under x irradiation. It implies that the above reported x-ray destruction rate of F-aggregate centers has a direct correlation to the rate of formation and mobility of interstitials.

[1] F. Lüty and K. Seifriz, see Abstract No. 124.

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126 Vibrational Absorption and Radiation Damage of OH^- Ions in Alkali Halides

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High concentrations of OH^- ions (up to 10^{-2}) built into alkali halides allow a detailed analysis of their vibrational absorption, the fine structure of which gives informations about the lattice surrounding and coupling of the OH^- ion:

1. When built into the lattice together with divalent cations in some molecular complex,[1] the shape of the OH^- vibrational absorption is independent of temperature, revealing that its broadening is not produced by coupling to the lattice.

2. Substitutional OH^- ions have a main absorption band, the position of which is slightly influenced by the lattice (eg. LiF 2.68 μ, KBr 2.77 μ). An accurate analysis reveals substructure in the main band and several side band components, which can be due to coupling of the OH^- stretching vibration either to phonons or to librational or rotational modes of the OH^- molecule. Towards low temperatures the main band sharpens, looses oscillator strength and a good part of the side band structure freezes out. In several alkali halides (as KCl and KBr) a prominent side band is observed at about 0.04eV higher energy than the main OH^- band, in a

fixed relation to the main band independent of the OH⁻ concentration. This second band splits into several components at low temperatures without losing oscillator strength. It is tentatively assumed that this band is due to a combined excitation of the OH⁻ stretching vibration and the localized ("U-center type") vibration of the whole OH⁻ molecule against the lattice.

3. Long x irradiation transforms the OH⁻ vibrational spectrum into an absorption of completely different spectral distribution, structure and temperature behavior. This demonstrates that by radiation damage even a very high amount of OH⁻ ions (10^{-2} in the crystal) can be brought from their normal substitutional places into some other lattice configuration. Thermal annealing restores the situation to the original configuration.

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* Work done as guest under O.N.R.-Contract 3534 (00).

[1] B. Fritz, F. Lüty, and J. Anger, Z. Physik **174**, 240 (1963).

127 Localized Exciton Absorption of F-Aggregate Centers in Potassium Chloride

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The change in the localized exciton absorption (β and α band) was measured, when F centers in additively colored KCl, KCl:Na, and KCl:Li were optically converted into different types of F-aggregate centers. By control of the electronic spectra in the visible and the exciton spectra in the vacuum ultraviolet, the superposed spectra could be separated and the pure localized exciton absorption of M, F_A(Na), F_A(Li), and ionized F_A(Na) centers were obtained. In spite of the lower symmetry of these centers and their multiple electronic absorption they all give rise to only *one* localized exciton band with the following peak position at 5°K (in eV):

β	β_M	β_A(Na)	β_A(Li)	α	α_A(Na)
7.37	7.50	7.36	7.47	6.98	7.05

Whereas the β_A absorptions have roughly the same oscillator strength as the β band, the β_M absorption is lower by a factor 0.7. This can be understood both within the "excitation-" and the "charge-transfer model" for the exciton absorption, because the number of anions directly neighboring the imperfection (which deliver the electron for the perturbed excitation process) should determine the oscillator strength. This number reduces from $2 \times 12 = 24$ for two isolated F centers to 18, when two F centers aggregate to form one M center. It was qualitatively observed that further M → R aggregation continues to reduce the β-type absorption.

The α and α_A absorption, developed and separated out of optical F → F′

and $F_A \rightarrow F'_A$ conversion, has only a small accompanying absorption on the high energy side of the α or α_A band; this demonstrates that the γ band, found with irradiation induced α centers,[1] is not connected with the pure anion vacancy.[2]

[1] C. C. Klick and D. Patterson, Phys. Rev. 130, 2169 (1963).
[2] F. Lüty and W. Zizelmann, Sol. State Comm. 2, 179 (1964).

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128 Effect of Hydrostatic Pressure on Absorption and Emission of F Centers in Alkali Halides*

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Absorption measurements on the F and L bands and F-center emission measurements have been made in five alkali halides at 100°K under pressures up to 5 kbar. The pressure-induced blue shifts of the F-absorption bands are somewhat larger than those of Jacobs,[1] but the presence of F-aggregate centers tends to improve the agreement. The blue shifts of the F-emission bands are about 4/3 those of the absorption bands, except for CsBr which exhibits very little shift. In KCl and NaCl the emission band narrows under pressure while in KBr it splits, the splitting disappearing at higher pressures. Excitation spectra indicate the new emission component is the K′ band found by Maisch and Drickamer[2] at higher pressures. KI exhibits a broadening under pressure with no resolved structure, while CsBr changes very little. Fowler's[3] model of the excited F center qualitatively explains the blue shift in emission, while simple one configuration coordinate models[4] do not. The strong apparent K′ emission when the K′ absorption is weak implies that the oscillator strength for emission from this transition is not reduced as much by lattice relaxation as is that of the F band transition. Quantitative measurements of the absorption and emission strengths and lifetimes are in progress.

* This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.
[1] I. S. Jacobs, Phys. Rev. 93, 993 (1954).
[2] W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).
[3] W. B. Fowler, Phys. Rev. 135, A1725 (1964).
[4] P. B. Alers and R. L. Dolecek, J. Chem. Phys. 38, 1046 (1963).

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129 Elementary Treatment of the Modification of Lattice Vibrations by Imperfections

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A simple method for discussing the scattering of phonons by a point imperfection has already been given by the authors.[1] Similar methods can be applied to scattering by more complicated centers and also to determining the nature of the modified modes in the vicinity of such centers. These modifications are of importance in accounting for impurity activated infra-red absorption and in calculating the vibrational structure of visible and ultraviolet absorption bands. Localized modes may also be of importance and these are obtained automatically from the calculations. The essential idea of the method for obtaining the modified modes is to treat the imperfection as a number of extra masses and springs attached to a perfect lattice and to set up equations asserting that the motion of the extra masses and springs should require forces of which the negatives will produce the same motion of the corresponding points in the perfect lattice: the method is therefore essentially a Green function treatment expressed in more concrete physical terms than is usual. One requires the responses of the perfect lattice to various systems of applied forces and these responses are obtained by machine computations starting from a knowledge of the eigenfrequencies and eigenvectors of the vibrations of the perfect lattice. The difficulties of dealing with the response to a force with frequency in the continuum of lattice mode frequencies are avoided by supposing that a small but finite damping is applied to all the atoms of the lattice. The details of the procedure have been set up and tested in simple cases. There appear to be no insuperable difficulties in treating centers of low symmetry such as are responsible for the zero phonon lines and attendant vibrational structure in alkali halides.

[1] C. W. McCombie and J. Slater, Proc. Phys. Soc. (London) 84, 499 (1964).

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130 The Emission Spectra and Decay Time of Luminescence in Unactivated Cesium Iodide*

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The x-ray emission spectrum of nominally pure CsI is reported to consist of a band between 300 mμ-330 mμ and one between 400 mμ and 470mμ. Our measurements on single crystals grown from a melt exhibit emission bands centered at 300 mμ and 420 mμ at room temperature, whereas below 150°K an additional band was observed at 335 mμ. Below 150°K the amplitude of both the 335 mμ and 300 mμ bands increases rapidly. Decay time measurements have been made from room temperature to liquid nitrogen temperature using a Po^{210} alpha source. The decay times of both bands increase as the temperature is lowered, and at 100°K the 300 mμ and 335 mμ bands have decay times of about 150 nsec and 700 nsec, respectively. The 335 mμ emission has been tentatively associated with electron recombination at a V_K center, but the 300 mμ emission has not been identified. The intensity and decay time (≈ 15 μsec) of the 420 mμ band appears nearly temperature independent.

Although no thallium absorption bands were observed, the emission data indicated the presence of several parts per billion of thallium. The fluorescence emission reached maximum intensities when stimulated with light close to 245, 277, and 299 mμ, the thallium absorption bands in CsI. Spectral analysis showed the 550 mμ emission band of thallium. Stimulation with 277 and 299 mμ radiation at 77°K resulted in thermoluminescence in the 420 mμ band only, whereas stimulation with radiation of 245 mμ or less resulted in thermoluminescence in both the thallium band and the 420 mμ band. The experimental evidence suggests that the 420 mμ emission is associated with a defect structure in the vicinity of the thallium impurity and is indirectly due to the presence of thallium.

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131 ENDOR of the V_K Center in Calcium Fluoride*

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The V_K center has been observed by Hayes and Twidell[1] in CaF_2, which has an F-F spacing nearly the same as LiF but along ⟨100⟩ instead of ⟨110⟩. We have studied the ENDOR of the V_K center in CaF_2 and have identified neighboring nuclei from the angular dependence of the lines. The observed hyperfine constants give additional information on the F_2^- molecule that was studied in LiF by Gazzinelli and Mieher.[2]

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† Alfred P. Sloan Foundation Fellow.

[1] W. Hayes and J. W. Twidell, Proc. Phys. Soc. (London) 79, 1295 (1962).

[2] R. Gazzinelli and R. Mieher, Phys. Rev. Letters 12, 644 (1964).

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132 Elementary Exitations and the Interaction of Polariton Waves in the Exciton Absorption Region of Molecular Crystals

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The excitation spectrum of single and triple excitons in molecular crystals has been investigated by means of the Green's function method. Taking into account retardation, the effect of the interaction of polariton waves in the absorption region of the crystal has been studied. Expressions are developed for the energy of excitation, energy shift and width of the absorption band. An attempt has also been made to take account of the presence of impurities in the exciton absorption spectrum.

133 Validity of Configuration Coordinate Diagrams in Interpreting Optical Data

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In order to summarize criteria for the valid utilization of configuration coordinate diagrams and to review the justifiable methods by which they may be treated in interpreting optical data, we re-examine the physical basis upon which the diagrams are constructed. The conclusions reached in this work are drawn from a consideration of the semi-invariants of a coupled electron-lattice system, and the answers regarding validity of the c.c diagrams depend upon the questions one asks concerning the experimental results. A first conclusion is that a proper quantum treatment of absorption (or emission) lineshape must come to grips with so many important factors and difficulties that interpretations of real systems based upon the usual quantum treatments of the c.c diagram cannot be justified except under extraordinary special circumstances. When one is concerned, however, with optical bands which are broad in relation to the Debye energy, a semi-classical approach is valid and, within the semi-classical framework, the major factors embarrassing the quantum treatment are overcome by a natural generalization of the Franck-Condon approximation. The usual definite and long-recognized limitations of this approach, and consequently of the interpretation derived from it, still remain, but it would appear that limited information gained from an approach which is physically justifiable may well be preferable to that based upon exact treatments of a model system which is obviously incorrect. The most important limitations of the semi-classical treatment are: the transition energy of the semi-classical lineshape must be taken as the difference between the adiabatic interaction energy for the excited electronic states and that for the lower electronic level, a procedure which does not produce certain curvature terms arising from other semi-classical treatments where the requirement of conservation of both "lattice-only" kinetic and potential energies is not satisfied; quadratic coupling terms, which reflect vibrational frequency changes, are justified in so far as they are related to general features of the optical behavior, e.g., line-breadth changes and temperature dependence or Stokes shifts, but they may not be employed in interpreting certain detailed features of the semi-classical lineshape, e.g., the zero temperature skewness, because quadratic couplings are easily shown to be "always" weak and therefore to give some qualitatively incorrect semiclassical results; finally, the use of only one or a few configuration coordinates as determined from symmetry considerations requires that the interpretations refer to appropriately weighted average interactions. In summary, although interpretations of the detailed features of lineshapes obtained from the c.c diagrams either through a semi-classical or, except in rare cases, a straightforward quantum treatment have little basis for validity, the determination of important interaction parameters of the electron-lattice system through a comparison of the semi-classical treatment of the c.c. diagrams with gross features of the data for broad optical bands does appear adequately justified provided, of course, that effects such as failure of the Condon approximation and anharmonicity are properly taken into account when they are, in fact, important.

134 Color Centers in Magnesium Doped Lithium Fluoride

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Optical absorption and electron spin resonance studies have been made on vacuum grown LiF doped with 0.1% by weight magnesium. Crystals which are rapidly quenched from 600°C and then x irradiated at room temperature show, in addition to F absorption, a strong absorption band at 4.0 eV and a weaker one at 5.5 eV. Bleaching *either* the F band or the 4.0 eV band leads to the growth of the band at 5.5 eV. The rate of conversion at 300°K is slow but increases at higher temperatures. By prolonged bleaching we can obtain essentially a pure 5.5 eV band which can be fitted quite well with a single Gaussian with full-width at half maximum, $W_{1/2}$, of 1.0 eV. The stability of this center is indicated by the fact that it can be produced by electron irradiation at 350°C whereas the 4.0 eV center thermally bleaches at about 135°C. No structure is resolved at 77°K but the peak shifts to 5.7 eV and $W_{1/2}$ reduces to 0.8 eV. At 77°K the band at 4.0 eV shows partially resolved structure indicating that it consists of overlapping bands. In unquenched, doped crystals the 4.0 eV band is not observable and the magnitude of the 5.5 eV band obtainable is much smaller. The absence of either of these centers in quenched crystals of undoped LiF suggests that they are associated in some way with the magnesium impurity.

The evidence so far obtained is consistent with the new centers being Z-type in nature. In common with other centers in LiF, they are much more stable than their counterparts in other alkali halides. Electron spin resonance studies of these centers are now in progress.

135 Electron Spin Resonance Spectrum of S_2^- in Potassium Bromide

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It has been suggested[1] that the luminescent centers formed in certain alkali-halides upon exposure to sulfur vapor are S_2^- molecule-ions. Electron-spin resonance spectra of this species have now been detected in a KBr crystal at 4.2°K. A Varian V-4502-14 spectrometer was used, the magnetic field being measured with a Varian F-8A proton-fluxmeter and associated frequency counters. The liquid helium dewar vessel was similar to that described by Hornig and Hyde.[2]

As expected, by analogy with the well-known[3, 4, 5] fluorescent center O_2^-, the S_2^- radical-ions were found to lie along the face-diagonals of the crystals. The resonances of S_2^- were less easily saturated than those of O_2^-, and could be observed at 4.2°K but not at 77°K.

The position of the S_2^- resonances could be described by the following equation

$$h\nu = (g_{\|}^2 \cos^2\Theta + g_{\perp}^2 \sin^2\Theta)^{1/2} \beta H_o$$

where Θ is the angle between the magnetic field H_o and the inter-atomic axis, i.e. ⟨110⟩, and

$$g_{\|} = 3.5010 \pm 0.0002$$
$$g_{\perp} = 1.05 \pm 0.05$$

The very large error in $g_{\perp}$ is due to the highly anisotropic line width of the S_2^- resonances. For example, at $\Theta = 0°$, the maximum slope width was 3.5 gauss, for $\Theta = 45°$, 7 gauss; $\Theta = 60°$, 14 gauss; $\Theta = 75°$, ~50 gauss. The resonances were quite undetectable for $\Theta = 90°$, thus preventing a direct determination of $g_{\perp}$.

The values of $g_{\|}$ and $g_{\perp}$ depend[3] on the relative magnitudes of λ, a spin-orbit interaction constant, and Δ, the crystal-field splitting of the π_g molecular orbitals. Assuming axial symmetry, and neglecting terms in λ/E, where E is the excitation energy for the spin-orbit interaction, it appears that

$$g_{\|} = g_e + 2\lambda(\lambda^2 + \Delta^2)^{-1/2}$$
$$g_{\perp} = g_e\Delta(\lambda^2 + \Delta^2)^{-1/2}$$

where g_e is the free-spin g-factor, 2.0023.

If $\Delta >> \lambda$ the orbital angular momentum is essentially quenched, and both $g_{\|}$ and $g_{\perp}$ approach the free-spin g-factor. However, if $\lambda >> \Delta$, $g_{\|}$ approaches 4, and $g_{\perp}$ approaches zero, and for $\Delta = \lambda$, $g_{\|} \simeq 3.4$ and $g_{\perp} \simeq 1.4$.

The present results indicate that for S_2^- in KBr λ/Δ is approximately 1.1.

The author gratefully thanks Drs. J. H. Schulman and R. D. Kirk for supplying the crystal used in these experiments, and also acknowledges stimulating discussions with Dr. J. Rolfe.

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136 Thermally Excited Reorientation and Migration of V_K Centers in Potassium Iodide*

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The thermally excited reorientation of V_K centers has been studied in KI in a series of isothermal annealing experiments near 80°K. Doped crystals of KI were irradiated at 78°K and prominent V_K absorption bands were observed at 404 and 800 mμ. Bleaching with linearly polarized light at 404 mμ induced anisotropic V_K absorption. The crystal was then quickly warmed to a fixed temperature and the anisotropy was measured as a function of time. In all cases it was found the anisotropy $A(t)$ was accurately described by $A(t) = A(o)\ \exp(-Kt)$, where K is a rate constant characteristic of the temperature. Two series of experiments were performed. In Series I the electric vector of the orienting light was parallel to a $<110>$ direction, and in Series II the electric vector was parallel to a $<100>$ direction. In both series it was found that K was described by $K = s\ \exp(-E/kT)$. Denoting Series I and II experiments by the subscripts 110 and 100, we find that $E_{110} = E_{100} = 0.273$ eV, but at any temperature $K_{110} = 2/3\ K_{100}$. The difference between K_{110} and K_{100} is attributed to a preferential thermal reorientation of V_K centers. Analysis of the reorientation kinetics shows that $K_{110}/K_{100} = 2/3 + (1/3)(P_{90}/P_{60})$, where P_{90} is the probability per second that a V_K center reorients through 90°, similarly for P_{60}. Comparison with experiment shows that $P_{90} << P_{60}$ from which we conclude that reorientation occurs almost entirely through one-step jumps in which the V_K axis changes direction by 60°.

The migration of V_K centers through the lattice is being studied at higher temperature. V_K absorption decays according to second-order kinetics at small t. Analysis of the data will permit a determination of the activation energy for migration, and this will provide an estimate of P_0 compared to P_{60}, where P_0 is the frequency of reorientation through 0° (i.e., a translational jump along $<110>$).

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137 Hardening of Potassium Chloride by V_K Centers

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The radiation hardening of pure alkali halides has been attributed to interstitial-type halide defects resulting from the F center formation process. This process is suppressed in silver doped KCl which is irradiated at 77°K. The dominant photochemical reaction becomes

$$\begin{array}{lcl} Cl^- & \xrightarrow{\text{X-ray photon}} & Cl^\circ + e \\ Cl^\circ + Cl^- & \longrightarrow & Cl_2^- \, (V_K) \\ Ag^+ + e & \longrightarrow & Ag^\circ \end{array}$$

Of the two defects which result (Cl_2^- and Ag°), only Cl_2^- is expected to cause significant hardening because it has tetragonal symmetry.

In the present experiments KCl crystals doped with ~.05% AgCl were x irradiated (70kV) at 77°K. Optical absorption and compression tests were made. The flow stress was increased about two order of magnitude by irradiations of two hours duration. Most of the radiation hardening disappeared at about 200°K during pulse annealing, which corresponds well with the disappearance of Cl_2^- centers from the optical absorption spectrum. The Ag° absorption was only slightly diminished by this annealing process thus confirming the expectation that Cl_2^-, and not Ag°, is an effective hardening agent. Furthermore, the fact that Ag° does not cause significant hardening while Cl_2^- does, suggests that the important hardening interactions between dislocations and point defects are elastic rather than electrical.

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138 Exciton Absorption in Mixed Alkali Halides

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The effects of foreign alkali metal ions on the exciton absorption in some alkali chlorides and alkali bromides have been investigated. Mixed system KCl–RbCl, NaCl–KCl, KBr–RbBr, and NaBr–KBr were chosen. These are characterized as containing two kinds of alkali metal components with common halide ions. In the mixture of potassium- and rubidium-halide, positions of the exciton peaks shift fairly linearly with the change in relative concentration. In the mixture of sodium- and potassium-halide, the long-wavelength shift of the peaks is remarkable. It is of interest to note that the exchange of the alkali, rather than the halogen, ions gives rise to only the shift and relatively slight broadening of absorptions bands. This should be contrasted with Mahr's[1] observation for the KCl–KBr mixture in which both Cl^- and Br^- absorption bands can be identified in the absorption spectrum. Mahr's result seems to support the predictions of a simple semiclassical electron-transfer model for the excitons in the alkali halides.

However, since there was no indication of two absorption bands which might be related to the presence of two alkali ions in the mixture treated in the present study, application of the simple electron-transfer model seems hopeless. On the other hand, Taglauer and Waidelich[2] also confirmed that there is no indication of two bands in the mixed system AgCl–AgBr which might be related to the presence of Cl^- and Br^- ions in the mixture. This means that the simple electron-transfer model encounters difficulties in explaining even the case of exchanging halogen ions in the silver halides as well as the case of exchanging alkali ions in the alkali halides. From these facts it is suggested that the excitation model will be more fruitful in describing the excitons in the alkali and silver halides.

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139 Low-Temperature Photoconductivity of Potassium Chloride with F Centers

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Extensive measurements were carried out on the primary photoconductivity of additively colored KCl as a function of applied electric field and excitation wavelength, mainly in the range of temperature between 4.2°K and 80°K. The main conclusions can be summarized as follows.

(a) The quantum yield of producing electrons by excitation into the L_1 and L_2 band is nearly unity in the temperature range from 170°K down to 2°K.[1] In the high energy side of the K band, there exists a band in the photoconductivity spectrum, centered at 3.2 eV whose quantum efficiency is also nearly unity even at the lowest temperature.

(b) At temperatures below 35°K, the hot electron effects are the predominant factor in the electric field dependence of photoconductivity in the L_1 band. The critical field strength for onset of hot electron effects decreases with lowering the temperature and also reducing the concentration of F centers. For F center density of 2.5×10^{15} cm^{-3}, the critical electric field is about 1×10^2 volt/cm at 4.2°K.

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140 Emission and Associated Excitation and Absorption Spectra for X Irradiated Lithium Fluoride

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We are concerned here with three emission bands at ~ 670mμ, 910mμ and 1120mμ, the 670mμ band apparently being a composite band made up of at least two bands at approximately 650mμ and 700mμ. While this 670 mμ band can be produced by excitation in R_1 and also probably the F band, the efficiency is considerably higher for excitation in the M band region. Detailed measurements, however, indicate that the excitation band for this emission has a maximum at 445mμ and is separate from the M band at 441.2mμ.[1] Similarly the 910mμ emission can be produced by excitation in the R_1 band and at 445mμ and 650mμ but the efficiency is by far the highest for the latter wavelength. The 1120mμ emission can be excited by excitation at 445mμ and 650mμ, but is more efficiently produced by excitation in the vicinity of 880mμ. Bands have been found in absorption at 445mμ and 650mμ which agree with the appropriate excitation bands,[1] and an absorption band at 1000mμ seems to be associated with the 1120mμ emission. All wavelengths are for liquid nitrogen temperature. Measurements as a function of temperature and irradiation conditions suggest that each emission band and its associated (maximum efficiency) excitation band is due to a separate lattice defect. The simultaneous emission of two or three bands due to a single excitation wavelength can then be due to the overlap of emission and absorption bands. By a cascade process then all three emission bands can be produced. From the temperature dependence of the half widths or the resolved phonon structure, a vibrational energy of 0.03 eV can be deduced for the 445mμ and 650mμ excitation bands, absorption bands at 800mμ and 1000mμ, and the pure M band. This same energy is reported by others for the R_2 band and suggests the possibility that these defects are strongly coupled to the lattice.

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141 Effects of Radiation Damage on Exciton Spectra at Low Temperatures

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The effects of irradiations in a reactor on the exciton spectrum of Cu_2O have been studied in absorption and reflection, at low temperatures.

The results are compared with those of gamma ray irradiations, electric fields, impurities and thermal quenching. It is shown that the modification observed in the exciton spectrum are produced by the deformation potentials resulting from large defects created by fast neutrons in the Cu_2O lattice.

A model is presented in which the dislocation loop is considered as the large defect involved. This model allows us to deduce from measurements of the exciton spectrum both the number and the dimensions of the defects contained in the crystal.

Some preliminary results on similar studies in copper halides are also presented.

142 Transition Rate Effects Observed in the Magnetic Resonance of F Centers

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At 4°K a portion of the magnetic resonance spectrum of F centers in KCl may be saturated. The Gaussian line may be described as having a "hole burned" in it in analogy to the experiments on a nuclear resonance broadened by an inhomogenous magnetic field. The saturation factor as a function of field may be described by a shape, width, and depth. The experimental procedure consists of three steps: relaxation, saturation and observation. The observation process avoids saturation by using very low power levels. Saturation periods of the order of a minute establish a steady state condition at all power levels. These experimental results for the width, shape and depth could not adequately be described by using a spin packet model. Experiments were also performed by applying saturation pulses varying in time from seconds to milliseconds. The results showed that the width of the saturation increases with pulse time and power level. The results depend to some extent on an effective g value which is determined by the ratio of the frequency to field during saturation. There is no growth in width in the absence of external interaction. Throughout the course of these experiments, partially resolved structure within the saturated region of the resonance was observed. The position of the subsidiary "holes" were found to be independent of the magnetic field orientation. The spacing of these subsidiary "holes" from the principal saturation correspond to frequency differences ranging from 2 to 33 mcps. In order to explain these results an improved theory of the energy levels and state functions for the spin Hamiltonian is required. The Zeeman and contact hyperfine terms can be solved generally, including several shells of nuclei. Several transitions with different probabilities may be identified. The results of observation may then be described in terms of the kinetics of the saturation process.

143 Interaction Between Dislocations and O_2^- Centers

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Measurements of flow stress vs. temperature were made on zone-refined Harshaw and O_2^- -doped KCl crystals between 4.2°K and 300°K. The principal aim of this study is to see if the interaction between O_2^- -center and moving dislocation becomes appreciable in a certain temperature range.

A substantial increase in flow stress in O_2^--doped KCl compared with that of zone refined KCl was observed below 35°K. The effect of hydroxyl ions on the temperature dependence of the flow stress was also examined, since O_2^- -doped crystals contain a considerable concentration of hydroxyl ions. From these measurements and the theory of Fleischer[1] the following quantities can be calculated: the tetragonality of lattice distortion around O_2^- center, $\Delta\epsilon$, and the concentration of O_2^- centers. The value of $\Delta\epsilon$ is compared with the results obtained by ESR measurements.[2] The mechanisms of dislocation -O_2^- interaction are discussed.

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144 The Excited State of the F Center in Potassium Iodide

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The spectroscopy on the excited state of the F center (here called F*) in KI using a pulsed ruby laser as an excitation source yielded the absorption spectrum of the F* center as reported earlier.[1] Additional data will be presented to support further a kinetic model which contains an additional term beyond those in the usual models due to the overlap between the strong absorption of the F* and the ordinary fluorescence of the F*. It is planned to extend the absorption data, which have been heretofore limited to wavelengths less than 5 μ, further into the near infrared. Such absorption data can then be compared with predictions based on the kinetic model.

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145 EPR and Optical Absorption of Br_2^- and Cl_2^- in the Ammonium Halides

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When single crystals of NH_4Br and NH_4Cl are irradiated with x rays at low temperature, one of the products is the halogen molecule-ion oriented along the ⟨100⟩ directions. Känzig and coworkers[1] have reported the electron paramagnetic resonance (EPR) absorption of Cl_2^- in NH_4Cl. We have observed the EPR spectrum of Br_2^- in irradiated NH_4Br, and identified optical transitions associated with the halogen molecule-ion (V_K center) in both ammonium halides.

The Br_2^- portion of the EPR spectrum of NH_4Br irradiated at low temperature can be adequately fitted to an axial Spin Hamiltonian with the principal symmetry axis aligned along any of the three ⟨100⟩. The resulting values for the g-tensor and hyperfine tensor are very nearly the same as those obtained in KBr.[2] However, the halogen molecule-ion exists in a site of tetragonal symmetry in the ammonium halides versus orthorhombic symmetry in the alkali halides.

Optical absorptions belonging to the transitions $^2\Sigma_u \rightarrow {}^2\Sigma_g$ and $^2\Sigma_u \rightarrow {}^2\Pi_g$ have been observed at 800 mμ and approximately 380 mμ, respectively. The band at 380 mμ comprises less than one fifth of the intense radiation-induced band previously observed by Rüchardt,[3] and which was suggested by Känzig[1] as being partially due to the V_K center. Dichroism has been induced in the 800 mμ band by polarized bleaching which is consistent only with an electric dipole lying along the ⟨100⟩. A dichroism of the 800 mμ band can be stimulated by polarized bleaching into the 380 mμ band.

EPR and optical measurements made concurrently on an NH_4Br crystal in a combination optical-EPR Dewar after successive applications of bleaching light in a ⟨100⟩ direction have shown a correspondence in the induced dichroism. The magnitudes of the EPR and optical absorption do not decrease in the same ratio, probably largely due to the effects of saturation of the magnetic resonance signal.

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146 Low-Temperature Fluorescence and Absorption of OH^- and OD^- in Potassium Halide Crystals

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The optical properties of OH^- and OD^- in KCl and KBr have been measured at low temperatures. A new fluorescent emission has been found in KBr and KI and related to the OH^- center by excitation measurements, by association of its three peaks with vibrational energy levels of the OH^- molecule, and by observation in KBr of the predicted isotopic shifts of the peaks. In KCl:OH, a very weak fluorescence was observed at 77°K which might have been due to OH^-; it was not observed at 5°K. No fluorescence was observed in any of the crystals at room temperature.

A pronounced asymmetry on the high energy side of the experimental absorption curves has been ascribed to additional unresolved bands. This was baseu upon the observation of a larger isotopic peak shift than predicted, the appearance of a broader absorption curve in OH^- than in OD^-, and a graphical resolution of the measured curves, making some simple assumptions, into reasonable bands. These component bands were attributed to transitions to different molecular vibrational levels in the electronic excited state. A generalized configuration coordinate diagram incorporating the internal vibrational levels of the molecule is proposed to account for the absorption and emission of the OH^- center.

The shift of the apparent absorption peak to lower energy with decreasing temperature below 100°K, investigated to 20°K by Fisher[1] in KCl:OH and KCl:OD, has also been observed in KBr:OH and KBr:OD. The measurements have been extended down to 6.3°K with no further shift being observed. The anomalous peak shifts have tentatively been interpreted in terms of hindered rotation of the OH or OD.

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147 Evidence for Frenkel Defect Formation in Lithium Fluoride X Irradiated at Room Temperature

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In discussion of the different possible mechanisms for the defect formation in alkali halide crystals, there is an important question whether Schottky or Frenkel defects are created. Information about this can be obtained from combined studies of lattice parameter change and macroscopic density change during the defect formation by x-irradiation.

We have irradiated LiF single crystals homogeneously by x rays from a W target (150 kV, 12 mA) filtered through 2 mm glass. The lattice parameter change was determined from the exact position of a Bragg maximum. For the density measurements we have chosen a hydrostatic flotation method, using a temperature gradient in a liquid. The F-center concentration after irradiation was estimated by a curve fitting method because it was not always possible to observe directly the large absorption constants at the band maximum.

If vacancies (concentration: c_v) and interstitials (c_i) are created in a crystal the following relation between relative density and lattice parameter change is expected: $-\Delta\rho/\rho = 3\Delta a/a + c_v - c_i$. If only Schottky defects are created: $c_i = O$ and $c_v = -\Delta\rho/\rho - 3\Delta a/a$. If only Frenkel pairs are created: $c_v = c_i$ and $-\Delta\rho/\rho = 3\Delta a/a$. Our measurements show that, after an initial deviation, at prolonged irradiations there is a direct equivalence between $-\Delta\rho/\rho$ and $3\Delta a/a$ in LiF after X irradiation at room temperature. That means that Frenkel defects are formed during irradiation. We now are extending these investigations to low temperatures.

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148 Ionized F-Aggregate Centers in Sodium Chloride*

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Two new color center bands have been observed in relatively heavily colored NaCl which have been illuminated with white light or light of selected wavelengths at He temperature. These peak at 1.20μ and 1.47μ

with strong 0-phonon lines at 1.3065μ and 1.5491μ. The 1.2μ band is produced most efficiently by illumination in the M region of 6500–7400 Å, while the 1.47μ band is generally produced by illumination anywhere in the range from 4000–7000 Å. This is consistent with the ionization of R centers on the basis of Silsbee's recent results in KCl that there are several R center transitions in the region between F and N bands.[1] Growth rates and maximum intensity depend upon light intensity as well as wavelength, with several minutes generally required to approach an asymptotic value. When the exciting light is turned off, up to 50% of the band intensity may decay within one second, but the remainder decays over a period of hours. We have also observed the splitting of the 0-phonon lines with uniaxial stress along [100], [110], and [111] directions. The 1.5491μ line splits into 2, 3, and 2 components under the above stresses. This is consistent with a rhombic center with two-fold axes along [001], [110], and [1$\bar{1}$0] directions (M center). Splitting of the 1.3065μ line is much smaller for a given stress, and the results are not so well delineated. We see 2, 2, and 2 or 3 components with stress oriented as above. This is not consistent with any possible center in a cubic crystal but could be associated with a rhombic or monoclinic center if we have failed to resolve all of the components. As a corollary to these measurements we also observed the splitting of the R_2 zero-phonon line, with results completely consistent with the trigonal symmetry of the F_3 model. The most probable explanation for the disagreement between the stress and growth measurements is that the application of stress can lift electronic as well as orientational degeneracies, giving rise to more components of the 0-phonon lines. In any case, it seems reasonably certain that these are ionized states of the R and/or M centers, primarily on the basis of the growth characteristics and stability. Any excited state with the observed lifetime should continue to grow with excitation until all of the ground state is transformed, whereas the ionized center would reach an equilibrium with the free electrons dependent on the rates of ionization and recombination.

* This work was supported by the United States Atomic Energy Commission.

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149 Color Centers in Calcium Fluorophosphate

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Synthetic crystals of $Ca_5(PO_4)_3F$ can be grown from the melt[1] or from a saturated solution of CaF_2. These crystals have the apatite structure which is characterized by isolated linear chains of F^- ions parallel to the *c* axis.

Both the melt-grown and the solution-grown crystals possess the same color center which may be produced at room temperature by x rays or by

1850Å radiation. The optical absorption band is dichroic and has been correlated with a specific spin resonance spectrum. An analysis of the F^{19} and P^{31} ENDOR spectra conclusively locates this center at an F^- site. In many respects the center resembles the F center of the alkali halides, and we conclude that the center consists of an electron trapped at an isolated F^--ion vacancy.[2] An LCAO calculation of the g-shift supports this conclusion.

A second simple defect which has been observed in resonance but not optically in all these crystals is an effective hole trap. The model given for this center is an $O^=$ ion substituted at an F^- ion site.[3] Upon trapping a hole the center becomes paramagnetic. ENDOR measurements[2, 3] have confirmed the location of this center. Irradiation at 77°K has revealed three distinctly different but closely related spectra[2] which have been localized by ENDOR.

In addition to these defects common to both melt-grown and flux-grown crystals, several other electron-excess and hole-excess centers have been observed. The melt-grown crystals are known to be deficient in fluorine, and it is reasonable to expect a relatively high concentration of F^--ion vacancies partially filled with $O^=$ ions. Two centers are seen both optically and in spin resonance which are consistent with the model of the association of two vacancies and an $O^=$ ion in two different configurations.[2]

The flux-grown crystals contain additional defects capable of producing one dichroic color center and several resonance centers not seen in the melt-grown crystals. None of these resonance centers possess axial symmetry about the F^- chain. Preliminary ENDOR measurements on the hole-excess center suggest the presence of $O^=$ at a F^- site associated with a Ca^{++} site defect.

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150 F Center Production by a Low Energy Mechanism

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A model for F center production in alkali halides has been studied which is dependent on the radiationless decay, to the ground state of the crystal, of an exciton. In this model a replacement sequence in a [110] line of halide ions is responsible for the separation of the ion from the vacancy.

It has been found that the probability of the radiationless transition at low temperatures is of the right order to explain the observation of both exciton luminescence and F center production in KCl and KBr at 4°K. In KI, on the other hand, the low temperature transition probability is calculated to be 10^{-8}, in agreement with the low F center production rate in KI at 4°K. The model is successful in predicting a relatively temperature independent coloration rate in KCl and KBr[1] and gives a temperature dependent rate in KI which is in fairly good agreement with experiment.[2]

Replacement sequence threshold energies have been calculated using a linear many-body model. They have been found to be sufficiently low to allow F center production by this mechanism except in certain materials, such as NaI, where F center production is observed experimentally to be very difficult. The effect of the Coulomb interactions on the replacement sequences is to cause the production of the vacancy at a distance of up to three lattice spacings from the excitation.

The model is easily modified to explain F center production by ultraviolet irradiation.[3] It also explains the impurity sensitivity of F center production in alkali halides.[4]

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151 Defect Production in Ionic Crystals by Low-Energy Radiation*

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The question of a threshold for radiation damage to alkali halide crystals by ionizing radiation has not been resolved. The possibility of an exciton mechanism for producing color centers has been discussed by Seitz and others, but the problem is complicated by possible photochemical reactions of impurities in the crystals. There is evidence that impurities such as OH^- account for some coloration of KBr and KI under ultraviolet light, and a low-energy photochemical transformation of $O^=$ to OH^- may cause the coloration of LiH crystals at room temperature. However, under intense ultraviolet light at 80°K, KI crystals can be colored to much greater densities (10^{18} to $10^{19} cm^{-3}$) of α plus F centers than would be expected from OH^--type impurities in the crystal unless the impurity species is reformed as in a catalytic process. Ultraviolet light also enhanced the coloration of KI simultaneously exposed to x rays compared to the rates found when each radiation was used separately. It is proposed that radiation damage occurs by a mechanism comparable to that given by Ritz for x rays.[1] However, since a high ultraviolet flux is required for intense coloration and an ultraviolet photon lacks sufficient energy to create two adjacent ionizations, the radiation-damage intermediate may be produced by a stepwise mechanism. This could occur through the secondary ionization of a self-trapped I_2^- molecule ion, which is a comparatively stable primary ionization product at 80°K. This mechanism may be important to the understanding of high flux irradiations of many alkali halides at 80°K using either soft x rays or β rays.[2]

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152 F-Aggregate Centers in Alkali Halide Crystals

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Optical studies have given considerable insight into the nature of centers known as the F aggregates. The formation, conversion, and destruction of these centers has been invesigated in additively colored specimens and specimens exposed to ionizing radiation, over a wide range of temperature, and in several different alkali halides. Both polarized light and unpolarized light have been advantageously used in absorption and emission measurements. The existence of higher excited states has been established, zero phonon transitions have been observed, and metastable multiplet states (e.g. the M-center triplet) have been identified. Models of at least two of the F-aggregate centers have been reasonably well established. The results of optical studies and other corroborative evidence indicates that the M center consist of a pair of associated F centers, and the R center consists of three neighboring F centers in an equilateral triangular configuration. Models of the N_1 and N_2 centers, as well as models of centers associated with other long wavelength bands are yet to be established on an equally secure foundation. Our understanding of the mechanism of formation of F-aggregate centers is likewise incomplete and is deserving of further attention. The models of various charged varieties of the F-aggregate centers have also been identified; these centers consist of either the normal F-aggregate center with an additional electron (M′, R′ centers) or the normal aggregate center lacking an electron (F_2^+, F_3^+ centers). A review of our current knowledge of the F-aggregate centers and their charged varieties will be given, and suggestions as to possible areas of further investigation will be made.

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153 Ionized M Centers in Alkali Halide Crystals

HERBERT RABIN and IRWIN SCHNEIDER, U.S. Naval Research Laboratory, Washington, D.C.

New absorption bands, attributed to optical transitions of ionized F-aggregate centers, are produced as follows. F-aggregate centers are first introduced into a crystal at room temperature by bleaching at the wavelength of the F band. The crystal is cooled to liquid helium temperature (LHeT) and exposed to x rays to introduce trapped-hole centers, namely V_K and H centers. Subsequent optical excitation into the spectral overlap region of the V_K and H bands at LHeT results in a decrease of both F-aggregate center and V_K-H absorption, and the production of new bands in the near infrared.

In KCl and KBr containing M centers, new bands appear at 1.40 μ and 1.49 μ, respectively. In KCl the ratio of the change in peak height of the M band to the 1.40 μ band is 3.7, and the corresponding ratio in KBr is 3.2. These ratios have the same magnitude for both the destruction of the M band with V_K-H light and the restoration of the M band with subsequent F-light exposure. It is also observed that when optical dichroism is induced in the parent M bands, the same dichroism is present in the new bands. These observations support the identification of the new bands with the F_2^+ center.

It is furthermore observed that weak F_2^+ bands can occur by *direct* x ray exposure at LHeT of either a virgin crystal or a crystal containing M centers. The production of F_2^+ centers in a virgin crystal might occur as the result of an intrinsic ionic process, while in the latter case x rays may act directly to ionize the M center.

154 Thermal Conductivity of Potassium Chloride with U Centers*

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Low temperature thermal conductivity measurements have been made in an attempt to observe phonon resonant scattering states induced by U-center impurities. The most complete measurements have been done on KCl. For KCl with H^- impurities the data divide into two regions. Above the conductivity maximum a resonance dip, usually associated with pseudo-localized modes, is observed. A computer analysis of the data, based on Krumhansl's model,[1] shows that the peak in the phonon scattering cross-section occurs at a frequency of about 1.3×10^{13} rad/sec. (70 cm^{-1}) ± 15%. Below the conductivity maximum a second resonance dip appears at about 0.4°K, but this cannot be attributed to the H^- ion since it seems to be dependent on the details of crystal preparation. KCl has also been studied with D^- impurities, but at the early date of this abstract the computer analysis has not been completed.

* Work supported by the Advanced Research Projects Agency.

[1] J. A. Krumhansl, International Conference on Lattice Defects, Copenhagen (1963), in print.

155 Photoelastic Measurements of Volume Expansion in Potassium Bromide and Potassium Chloride by U → α and U → F Conversion*

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Volume expansion effects have, for the first time, been observed in connection with the optical transformation of point defects in a system where the microscopic structure of all the reaction products are known and are under quantitative control. U centers in KBr and KCl were converted by UV irradiation at low temperature into vacancies and interstitial H^- ions. The change in crystal volume due to this transformation and the characteristic temperature structure of its thermal annealing were measured with a sensitive automatic photoelasticimeter. A definite correlation between $\Delta V/V$ and the number of H^- Frenkel pairs was obtained. Similarly, ultraviolet light or x irradiation at room temperature and its annealing produces a reversible volume change correlated to the number of U → F transformations. As lattice parameter measurements for KBr:KH are available, it is possible to assign specific volume expansions, compared to the unperturbed crystal, to the vacancy-H^- interstitial pair as well as to the F center-interstitial hydrogen molecule pair. Since the latter are neutral defects, Eshelby's elastic theory can be applied and, neglecting effects from the small interstitial H_2 molecule, the microscopic deformation around the F center can be obtained. The results on the H^- Frenkel pair cannot be interpreted in this way because ionic polarization around the charged imperfections strongly influences the elastic problem.

* Work done under ONR Contract Nonr-3534.

156 Vacancy Production Efficiencies in Potassium Bromide

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The growth of the prominent absorption bands produced by low energy x-ray and 2.0-MeV electron irradiation has been studied in KBr at temperatures between 5 and 9 degrees Kelvin. The growth curves (α, F, "H", 2300Å band and total vacancies) are not linear when plotted as a function of absorbed dose. The alpha band begins to grow linearly and then continues at a decreasing rate. The F band grows fairly rapidly at first, slows down and then seems to rise at an increased rate. The composite "H" band generally follows the F band, although the F/"H" ratio seems to decrease as the irradiation progresses. The band at 2300Å, which has been attributed to the interstitial halide ion, is directly proportional to the alpha band at all points on the growth curve. The total vacancy production (F plus alpha centers) is a smooth but non-linear function of absorbed dose.

The α/F ratio is not constant as the irradiation progresses. The ratio is initially 4:1 and reaches a maximum 9:1 at an F-center concentration of 5×10^{16} F centers/cm^3. Continued irradiation causes the α/F ratio to drop to about 4:1 at 3×10^{17} F centers/cm^3. This variation in the α/F ratio is the same for all types or "qualities" of radiation when plotted as a function of the F-center concentration. The intensity dependence of vacancy production was investigated by varying the beam current by a factor of 120 for the 2.0 MeV electron irradiations. More energy is required to produce a vacancy at higher intensities, but the α/F ratio is unaffected.

Deductions regarding vacancy production mechanisms at low temperature were made earlier[1] on the basis of F-center production efficiencies. The variation of total vacancy production efficiency in KBr with radiation "quality" reported here parallels the F-center efficiencies reported earlier. One is led to the same conclusion reached previously; i.e., the low temperature coloration process is dominated by mechanisms involving the single ionization of two adjacent halide ions.[2, 3]

[1] V. H. Ritz, Phys. Rev. **133**, A1452 (1964).
[2] F. E. Williams, Phys. Rev. **126**, 70 (1962).
[3] C. C. Klick, Phys. Rev. **120**, 760 (1960).

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157 Concentration Dependence of the α/F Ratio in Potassium Bromide Irradiated at 5°K

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The shape of the growth curves of the alpha and F bands in KBr irradiated at 5°K and the variation in the α/F ratio which were reported in a previous abstract[1] may be explained in terms of the influence of the intense recombination luminescence associated with the irradiation.[2] The fraction of halide ion vacancies which contain electrons depends largely upon the kinetic balance between two competing processes: One, α-center formation through bleaching of F centers by absorption of recombination luminescence; the other, F-center formation through electron trapping by α centers. The measured bleach rate increases uniformly from zero and approaches saturation at an F-center concentration of roughly 5×10^{16} cm^{-3}; this concentration is high enough to absorb most of the luminescence within the range of spectral overlap. Initially, since the bleaching rate is zero, the net growth rate is a measure of the effective trapping rate. The latter will increase with irradiation as more α centers are created. If one assumes that the trapping rate varies less rapidly with concentration than the bleaching rate, the F-center growth rate will first decrease, pass a minimum as the bleaching saturates, and then tend to increase until other processes cause the Frenkel defect creation rate to saturate. This accounts satisfactorily for the observed growth curves and for the α/F ratio variation.

[1] V. H. Ritz, see Abstract No. 156.
[2] M. N. Kabler, see Abstract No. 100.

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158 The Spatial Distribution of Color Centers in Diffusion-Colored, X-Ray-Colored and Electrolytically-Colored Crystals

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The time, temperature, dose and electric charge dependences of the micro-spatial distributions of color centers have been studied in KCl by microscopy with monochromatic illumination in the visible and ultra-violet. Significant correlations are found with the dislocation patterns for recently-deformed crystals. The influence of excess electronic conduction along and in the close neighborhood of edge dislocations in sufficiently pure crystals will be discussed.

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159 Anionic Impurities in Alkali Halide Crystals

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The purpose of this paper is to review as much as possible all of the work on anionic impurities that has been done since the Stuttgart conference in 1962. Because of time limitations we will restrict the review to these impurities stable in the melt. Thus transient species produced by irradiation into an absorption band, or by the action of ionizing radiation, will not be considered. Two classification methods will be used; by solid solubility of the impurity in the host crystal, and by the methods used to detect the presence of the impurity.

The first classification leads to a fairly sharp separation between high and low solubility impurities. High solubility impurities, such as O_2^-, X^- (halogen) and HS^-, have the property that the co-ordination number of the anion in the normal crystal form of the impurity itself is six, the same as the co-ordination number of the ions in the sodium chloride structure. As far as is known, all divalent anions, such as $CO_3^{=}$, $O^{=}$, have a very low solubility in alkali halide crystals.

Nearly all anionic impurities can be detected by optical methods. Absorption bands can be measured over a very wide wavelength range. Examples are the ultraviolet electronic absorption band of iodide ions in bromide and chloride crystals; the infrared vibrational absorption band of hydrosulfide ions; and the far infrared absorption bands induced by nitrite ions in the phonon gap of KI. Luminescence is the most sensitive method of detecting the impurities O_2^- and S_2^-.

Finally, divalent anionic impurities will affect the ionic conductivity of the host crystal. A comparison between experimental results and theoretical predictions will be made for such systems.

160 Strain Effects on Aggregate Color Centers in Alkali Halides

M. N. RUDDEN and **E. E. SCHNEIDER**, Department of Physics, University of Newcastle upon Tyne, England

The absorptions in the F-band region of oriented M and R centers formed in alkali halides by 50 kV X irradiation and subsequent polarized bleaching under externally applied stress have been investigated. The digitized data from a double beam spectrophotometer (maximum resolution 5Å) was processed with an electronic computer. The dichroic curves of individual M_F and R_F absorptions (at 12 and 80°K), i.e. the difference between absorptions observed with light polarized in appropriate perpendicular directions, were obtained automatically.

In the strictly elastic region, shear stress applied parallel to the direction of polarization of the bleaching light enhances the degree of orientation and the rate of production of aggregate centers but does not affect the shape or position of the absorption bands. The most interesting result of strain orientation is the increased resolution of the absorption of aggregate centers in the F-band region. This has now been found to occur only beyond the elastic limit as a consequency of plastic deformation. Apart from the remarkable sharpening, the dichroic spectra of the M_F and R_F bands produced under such conditions show characteristic shifts and satellite components which can be explained by assuming that aggregate centers are preferentially formed at defects, where they are subjected to strong crystalline fields of low symmetry. For the particular case of the M_F absorption arising from the two transition moments, $\langle 1\bar{1}0 \rangle$ and $\langle 100 \rangle$ normal to the molecular axis $\langle 110 \rangle$, the effect of stress fields are considered which are appropriate to locating of the M center in close proximity and with its axis parallel to an edge dislocation.

Preliminary observations have been made on the shape of individual dichroic absorption lines as a function of temperature. The very small width, < 10 Å, of some of the lines in deformed crystals, must be related to a restriction in the participating lattice modes caused by the local distortions of the lattice.

161 On the Configuration of the Radiation Induced Defects and the Kinetics of the Colloid Formation in Sodium Chloride*

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The kinetics of formation and the behavior of two optical absorption bands, namely the C_1 (at about 560 mμ) and the C_2 (at about 670 mμ), are investigated in γ-irradiated sodium chloride by employing the methods of optical and/or thermal bleaching and also subsequent x-irradiation of the bleached crystals. From these investigations the following points emerge:

1. The C_1 and the C_2 bands are not observed in as-irradiated crystals. The C_2 band appeared on optical bleaching (either by prolonged F light or white light bleach) and the C_1 band appeared on thermal bleaching (at any temperature in the range 160-200°C).[1] Also, crystals containing C_2 centers when thermally bleached showed the evolution of the C_1 band.

2. Both the C_1 and C_2 bands are resistant to bleaching with monochromatic light of wavelength corresponding to their respective peak positions. Also they are relatively insensitive to the changes in the temperature of the crystal (RT to LNT). It is observed that the C_1 band is influenced by concentrated white light, as well as ultraviolet light, the result in each case being the shift of the peak towards longer wavelengths and the increase in the half-width of the absorption band with the area under the band remaining constant. During this process the initial violet color of the crystal changed to blue.[2] But this blue crystal when thermally bleached became violet again and the peak shifted towards the shorter wavelength. These studies indicate a similarity between the entities responsible for the C_1 and the C_2 bands. The C_1 band has the characteristic properties of a colloid band. In regard to this band, despite the similarities (as far as the insensitivity to temperature change and resistance to monochromatic light bleach) there are some differences (as regards the thermal stability, half-width, etc.) between irradiated and additively[3] colored crystals.

3. The evolution of these absorption bands is observed only in heavily irradiated crystals, that is crystals irradiated well into the second stage, thus indicating that the presence of the lattice damage created by radiation is essential for the evolution of these bands.

4. We found enhanced colorability and evidence or perturbed F centers (F centers created by the trapping of electrons at anion vacancies situated in the neighborhood of lattice perturbations like edge dislocations) in γ-irradiated crystals which are thermally bleached at moderate temperatures ($\leq 200°C$) and subsequently x irradiated. These studies indicate that decoloration of an irradiated crystal at moderate temperatures does not mean the annealing of the lattice damage, and that the excess anion vacancies created by the radiation have different environment. Also the damage is annealed completely at higher temperatures ($\simeq 350°C$) and the crystal returned to its virgin state. However, significant difference between hard and soft x-ray irradiation is observed in regard to the observation of the perturbed F band.[4]

These results are discussed in the light of the defect generation and color center formation by radiation damage.

* Supported in part by a grant from the National Science Foundation and by the Air Force [Contract AF19(628)-4029].

[1] P. V. Sastry and K. A. McCarthy, Phys. Rev. Letters 12, 690 (1964).
[2] K. Przibram, *Irradiation Colors and Luminescence* (Pergamon Press, New York, 1956), p. 145.
[3] See F. Seitz, Rev. Mod. Phys. 26, 36 (1954); J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon Press, New York, 1962) p. 256.
[4] P. V. Sastry and K. A. McCarthy, submitted for publication in Phys. Stat. Solidi.

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162 Thermoluminescence in Quartz*

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In a recent communication[1] Lietz and Matheja report on a study of the trapping levels responsible for the thermoluminescent emission in quartz. These authors assert that "the glow curves do not always show defined, single-valued temperature maxima" and furthermore that "the interpretation of the general glow-curves (light vs. temperature) is difficult, since the exponential emptying of the trapping levels with increasing temperature does not hold."

We have recently been concerned with some of the optical properties of quartz and in particular with the thermoluminescent emission. From the thermal bleaching behavior of the various color centers as well as the width and shape of the glow peaks it seems that they are rather complex and consist of several components. The relative intensities of the components (and therefore the *apparent* glow maxima) seem to depend on several factors, e.g. irradiation temperature, dosage, etc. In this case the best method for analyzing the glow-curves is the "initial rise"[2] method. In our experiments we recorded a sequence of initial rise curves and plotted the thermal activation energies vs. temperature. In the germanium-doped crystals, for example, thermal activation energies varying from 0.8 to 1.9 eV in the temperature range 100°K-600°K were found. In the case of rose quartz the corresponding values are 10% higher. The conclusion that the emptying of the trapping levels is non-exponential seems not to be justified.

Of further interest are the previously reported[3] thermal bleaching curves of various color centers and their correlation to the different glowpeaks.

It seems that in quartz, just as in the case of alkali-halides, a careful examination of the thermoluminescent glow curves furnishes one with a considerable amount of useful information concerning the electronic processes in these crystals.

* Work supported by U.S. Army Research Office (Durham) and National Aeronautics and Space Administration.

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[1] J. Lietz and J. Matheja, Naturwissenschaften 51, 504 (1964).
[2] See for example *Luminescence of Crystals*, D. Curie (Translated by G. F. S. Garlick), (Methuen and Co., 1963).
[3] F. Feigl, M. Schlesinger, and J. H. Anderson, Bull. Am. Phys. Soc. 9, 635 (1964).

163 Moment Analysis of the K Band in Alkali Halides*

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Three simple models of the K band are tested by calculating the changes in zeroth and first moments of the band to be expected upon warming from 0°K to 300°K, and by calculating the changes in the same two moments caused by applied uniaxial stresses. The models tested are:

1. s-state model. In this model the K band is presumed to be due to transitions from the s-like ground state to an s-like excited state. The transitions are made partially allowed by admixture of some F-band p-like state into the s-like excited state by odd parity lattice vibrations.
2. d-state model.[1] In this model the K-band state is d-like and the transitions are, as above, made partially allowed by odd parity lattice vibrations.
3. p-state model and many-p-state model. In this model the K band is presumed to be due to transitions to a p-like state or, as proposed by Mott and Gurney,[2] a series of p-like states approaching the series limit at the conduction band edge.

Both the s-state model and the d-state model predict a strong temperature-dependence of the zeroth moment or area of the K band. The minimum area increase is estimated to be a factor of 1.5 upon warming from 0°K to 80°K, and nearly a factor of 3 upon warming from 0°K to 300°K for RbCl. Such changes are not observed.[3] The s-state model also disagrees with the measured first moment change due to applied uniaxial stresses.

The p-state and many-p-state models are both consistent with the observed temperature-independence of the high energy side of the K band. An approximate calculation shows that in the case of these models, the K band increases in area by 39% and shifts .06 eV to the red upon warming from 0°K to 300°K. Such a change leaves the high-energy side of the K band nearly unchanged. The p-state and many-p-state models are also consistent with the observed changes in zeroth and first moments due to applied uniaxial stresses, although this measurement does not severely test these models.

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* Supported in part by a grant from the National Science Foundation.

[1] R. F. Wood, Phys. Rev. Letters 11, 202 (1963).

[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals,* (Dover Publications, Inc., New York, 1964) 2nd ed., p. 114.

[3] F. Lüty, Zeit. Physik 160, 1 (1960).

164 The Effect of Applied Uniaxial Stresses on the Optical Absorption of F Centers in Alkali Halides*

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The optical absorption of F centers in alkali halides subjected to uniaxial compression depends on the polarization of the light. Measurements are made of the polarization-dependence of the absorption by rotating the plane of polarization of light passing through the sample at a fixed frequency. A small ac component appears in the intensity of transmitted light, the magnitude of which is a measure of the difference in absorption for light polarized parallel and perpendicular to the applied stress. The differences in the first and third moments of the F band for light polarized parallel and perpendicular to the applied stress are evaluated using the measured data.

The changes in first moment for stresses applied in ⟨100⟩ and ⟨110⟩ directions can be related to the coupling of the F-center excited state to lattice distortions of tetragonal (Γ_3) and trigonal (Γ_5) symmetries, respectively. The changes in third moment for the same applied stresses can be used to obtain the contribution to the second moment of the band of dynamic lattice distortions of tetragonal and trigonal symmetries. The contribution to the second moment due to breathing (Γ_1) modes can be obtained if in addition the total second moment of the band is measured.

The first moment changes indicate that for the static case, the coupling to a breathing distortion is two to three times larger than the coupling to tetragonal and trigonal distortions. The relative magnitudes vary considerably, however, upon changing from one alkali halide to another. All three coupling coefficients have the same sign, indicating that there is a net repulsive interaction between the F-center electron and both positive and negative ions. The third moment changes indicate that, for the alkali halides studied, the second moment is typically 70% due to breathing modes, 15% due to tetragonal, and 15% due to trigonal modes at 80°K.

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165 Luminescence of Ionized F-Aggregate Centers in Potassium Chloride and Potassium Bromide

IRWIN SCHNEIDER and MILTON N. KABLER, U.S. Naval Research Laboratory, Washington, D.C.

Infrared luminescence resulting from optical excitation into absorption bands associated with ionized F-aggregate centers has been observed in KCl and KBr at LHeT. The ionized F-aggregate centers were produced by cooling additively colored crystals containing F-aggregate centers to LHeT, irradiating with x rays, and then bleaching in the spectral region of the self-trapped hole absorption.[1] Excitation into the F_2^+ absorption band (peak 1.40μ in KCl, 1.49μ in KBr) gives an emission band at 1.65μ in KCl and 1.80μ in KBr. For F_3^+ excitation (peak 0.96μ in KCl, 1.02μ in KBr), the emission band occurs at 1.08μ in KCl and 1.18μ in KBr. The polarization properties of the emission from F_2^+ and F_3^+ centers have been determined, and are consistent with the models of these centers.

Often, additional ionized F-aggregate absorption bands are present which partially overlap the F_2^+ absorption and which are characterized by zero-phonon lines at 1.414μ in KCl and 1.547μ in KBr. These bands give emission at approximately 1.47μ and 1.61μ, respectively. Finally, absorption bands are observed (peak 1.67μ in KCl, 1.80μ in KBr) which give rise to emission bands at 1.79μ and 1.94μ. These bands, as well as the F_2^+ overlap transitions, are greatly enhanced in crystals which were annealed at 85°C following F-aggregate center formation at room temperature.

For all the centers investigated, the Stokes shifts and band widths are such as to suggest the occurrence of zero-phonon transitions. Sharp absorption lines at the proper wavelengths do appear in all cases, though their origin has not been uniquely determined.

[1] I. Schneider and Herbert Rabin, Phys. Rev. Letters 13, 690 (1964).

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Ionized R Center and Other Ionized F-Aggregate Centers in Alkali Halide Crystals

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The technique of ionizing F-aggregate centers by means of x ray and V_K-H light exposures at LHeT has been applied to additively colored crystals containing R, as well as other F-aggregate centers in both KCl and KBr. The R band transforms in one-to-one correspondence to a new near infrared band attributed to the F_3^+ center. In KCl this new band at 0.96μ closely overlaps the spectral position of the N_1 band. In KBr, the F_3^+ transition lies at 1.02μ and is clearly resolved from the N_1 band which peaks at 1.07μ. ⟨110⟩ dichroism is present in these new bands when produced from R bands having ⟨110⟩ dichroism. There is evidence to indicate that the F_3^+ band is also produced at room temperature as a result of either x-ray exposure of a virgin crystal or bleaching with F light of an additively colored crystal.

For crystals containing relatively large R and N bands, the LHeT ionization process also results in additional bands. First, a new absorption band forms overlapping the F_2^+ transition. This is evident by the shift in peak position of the F_2^+ band to shorter wavelengths with a superimposed zero phonon-type line (1.414μ in KCl and 1.547μ in KBr). The origin of these overlapping transitions is unknown. Second, a new band forms at 1.67μ in KCl and 1.80μ in KBr. These bands, as well as the F_2^+-overlap transitions, are greatly enhanced in crystals which have been annealed at 85°C following the production of F aggregates at RT. The 1.67μ band in KCl (and the 1.80μ band in KBr) is probably associated with an ionization product of the N_1 band. No transition has been identified with an ionization product of the N_2 center.

167 Electron Spin Resonance Study of the V_K, V_F and V_A Type Cl_2^- Centers*

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Irradiation of RbCl, KCl, NaCl, and LiCl with x rays at 77°K produces the "self trapped hole" or V_K type centers, which are ⟨110⟩ oriented Cl_2^- molecule ions not associated with any kind of lattice defect.[1-3] Other types of Cl_2^- centers can be produced in these crystals by suitable doping. When Pb^{++} is incorporated in NaCl and KCl a "Bent Bond" or V_F type [4] Cl_2^- can be formed after thermally destroying the V_K type Cl_2^- centers. The molecular axis of these Cl_2^- centers, though still oriented along [110] are bent in the (001) plane, the bending angle being about 1.5° in KCl and 3.5° in NaCl. The defect responsible for this bending is probably an adjoining positive ion vacancy. V_A type[5] Cl_2^- centers can be formed in crystals doped with lighter alkali ions. For example in KCl doped with NaCl, V_A Cl_2^- in which one of the two adjoining K^+ is replaced by a Na^+ ion can be created after thermal destruction of the V_K type Cl_2^- center. Similarly, Li^+ associated Cl_2^- centers have been produced in Li^+ doped KCl and NaCl crystals. There is only a slight indication of bending of the molecular axis of these V_A centers, and in the three cases an upper limit of the bending angle is $\sim$0.2°. The electron spin resonance spectra of these Cl_2^- centers have been carefully and quantitatively analyzed. From this analysis it is strongly inferred that the hyperfine compounds all have a positive sign. It follows that for the Cl_2^- molecule ion $<r^{-3}> = 27.7 \times 10^{24}$ cm^{-3} and its value varies about 1% throughout the series. The value of $|\Psi(0)|^2$ at each Cl nucleus varies more, and its two extremes are 4.91×10^{24} cm^{-3} for the V_F type centers to 4.01×10^{24} cm^{-3} for the V_K center in LiCl. Finally, the experimental g components contain interesting information about the influence of the crystalline environment on the Cl_2^- molecule ions.

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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[5] I. Bass and R. Mieher, Bull. Am. Phys. Soc. 9, 643 (1964).

168 Electron Spin Resonance Study of the $ClBr^-$ and Br_2^- Centers

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X irradiation at 77°K and subsequent thermal destruction of the Cl_2^- molecule ions in Br^- doped RbCl, KCl, NaCl, and LiCl produces ⟨110⟩ oriented $ClBr^-$ molecule ions[1, 2] not associated with any lattice defect. When the crystals contain also Pb^{++} ions a further thermal treatment produces $ClBr^-$ molecule ions whose molecular axis make an angle ϵ with the [110] direction in the (001) plane.[1] The value of ϵ increases going from NaCl to RbCl. These centers are $ClBr^-$ molecule ions probably associated with a positive ion vacancy. In a Br^- doped KCl crystal containing also Na^+ ions a $\langle 110\rangle$ oriented $ClBr^-$ has been found in which one of the two adjoining K^+ ions is replaced with a Na^+ ion. After a similar thermal treatment and at higher Br^- concentrations ($\sim$1% and up), two types of Br_2^- molecule ions are readily observed in the Pb^{++} doped alkali chlorides. The first type has a straight molecular axis in the $\langle 110\rangle$ direction, while the other has a bent molecular axis. The bending angle δ increases going from KCl to LiCl. These two types of Br_2^- centers have also been found in Pb^{++} doped KBr and NaBr. Finally in a Na^+ containing KBr crystal a V_A type[3] Br_2^- was observed with $\delta \cong 0°$. Quantitative analysis of the electron spin resonance spectra indicate that very probably the components of the Cl and Br hyperfine tensors in Br_2^-, $ClBr^-$, and Cl_2^- have a positive sign. From it one calculates that $<r^{-3}>$ with respect to the Br nucleus is 45.2×10^{24} cm^{-3} for $ClBr^-$ and 47.6×10^{24} cm^{-3} in Br_2^-, while $<r^{-3}>$ with respect to the Cl nucleus is 26.8×10^{24} cm^{-3} in $ClBr^-$ and 27.7×10^{24} cm^{-3} in Cl_2^-. These $<r^{-3}>$ values do not change very much for each molecule throughout the series. The density on the nucleus $|\Psi(0)|^2$ varies more. Taking average values, one sees that on the Cl nucleus it decreases from 4.3×10^{24} cm^{-3} to 3.0×10^{24} cm^{-3} going from Cl_2^- to $ClBr^-$. On the other hand, $|\Psi(0)|^2$ on the Br nucleus increases from 6.9×10^{24} cm^{-3} to 8.8×10^{24} cm^{-3} going from Br_2^- to $ClBr^-$.

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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169 Electron Spin Resonance of Sulfur and Selenium Radicals in Alkali Halides

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Three classes of paramagnetic radical molecules have been detected in alkali halides: S_3^- and Se_3^-, SO_2^- and SeO_2^-, S_4^- and Se_4^-. The S_3^- and Se_3^- radicals are bent molecule ions having C_{2v} symmetry. They occupy a lattice void formed by one metal and two halide vacancies.[1] The C_2 axis of the radical is oriented along a face diagonal axis of the crystal. For Se_3^-, strong hyperfine interaction of the unpaired electron with the central Se^{77} nucleus was observed as well as a weaker interaction with the outer two equivalent Se^{77} nuclei. The unpaired electron is localized in a π-type molecular orbital formed by atomic p-orbitals pointing normal to the plane of the molecule. The S_3^- and Se_3^- radicals are stable at room temperature. No change in the ESR spectrum of the S_3^- radical in KCl was observed when the crystal was heated to 300°C. Numerical values of the g-tensor are given in the table.

The electronic structure of the SO_2^- and SeO_2^- radicals is analogous to that of S_3^- and Se_3^-. However, these radicals *probably* occupy only one halide vacancy site, see the table. In contrast to the S_3^- and Se_3^- radicals, internal rotation was observed for SO_2^- and SeO_2^-, resulting in isotropic ESR spectra at elevated temperatures.

KCl crystals containing S_8^- or Se_3^- radicals were irradiated with x rays at room temperature. After this treatment, the ESR spectrum of the S_3^- and Se_3^- radicals had entirely disappeared. Instead, a new paramagnetic center was observed having axial symmetry with respect to the cubic crystal axis. Hyperfine interaction with four equivalent Se^{77} nuclei was detected. The g-tensor components are given in the table. We *tentatively* assign this type of paramagnetic center to planar S_4^- and Se_4^- radical ions having their unpaired electron localized again in a π-type molecular orbital.

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[1] This model has been further confirmed by ENDOR studies performed by Drs. Suwalski and Seidel in Stuttgart.

Components of the g-Tensor of S_3^-, Se_3^-, SO_2^-, SeO_2^-, "S_4^-" and "Se_4^-"

Crystal	Center	Temperature (°K)	g_x	g_y	g_z	$g_{rotating}$
NaCl	S_3^-	300	2.0465	2.0308	2.0014	
KCl	S_3^-	300	2.0499	2.0319	2.0026	
NaBr	S_3^-	300	2.0500	2.0348	2.0003	
KBr	S_3^-	300	2.0508	2.0327	2.0004	
KCl	Se_3^-	77	2.2205	2.1545	1.9885	
KCl	SO_2^-	77	2.0110	2.0071	2.0025	
		300				2.0067
		400				2.0068
KBr	SO_2^-	77				2.0075
		300				2.0070
KCl	SeO_2^-	77	2.0367	2.0155	1.9989	
		300				2.0165
		400				2.0165
KBr	SeO_2^-	77	2.0368	2.0181	2.0001	
		300				2.0168
		400				2.0171
KI	SeO_2^-	77	2.0365	2.0182	2.0000	
		300				2.0169

			$g_{\parallel}$		$g_{\perp}$	
KCl	S_4^-	300	2.0033		2.0338	
KCl	Se_4^-	300	2.0005		2.1800	

170 Color Centers in Inorganic Glasses

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Charge trapping by ions, added to inorganic glasses, has been used to classify empirically radiation-produced optical absorption and magnetic resonance spectra as being due to trapped holes or trapped electrons.[1]

Addition of a variety of multivalent ions, such as cerium, iron, europium, and others inhibits the formation of intrinsic centers by capturing holes and electrons, respectively. For example, Ce^{3+} captures holes and Ce^{4+} captures electrons. To first order, the formation of intrinsic color centers decreases exponentially with increasing concentration of the ion. We have applied this technique to classify some of the radiation-produced centers in binary silicate, phosphate, and borate glasses. The two absorption bands in the visible in both the silicate and phosphate glasses are due to trapped holes, while in high alkali borate glasses the band in the visible is due to trapped electrons. In all three glasses there is an EPR absorption spectrum near $g = 2.010$ which is caused by trapped holes.

In order to see if the same hole trap gives rise to the optical and EPR spectra in the silicate and phosphate glasses the dependence of the spectra on such variables as the dosage of the ionizing radiation, composition ratio of the glass, and bleaching temperature was studied. These experiments indicate that the same type of intrinsic hole trap causes both of these spectra. The characteristics of the spectra are in qualitative agreement with a model of the hole trap in which the hole is trapped on the oxygens of a single network tetrahedron.

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171 Electron Spin Resonance of Electron Excess Centers in Alkali Halides

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The following topics will be discussed:

Characteristic spin resonance behavior of electron excess centers:[1] g-shifts. Hyperfine structure. Inhomogeneous broadening of ESR lines. Importance of ENDOR. Spin-lattice relaxation, dependence on temperature and field, physical interpretation.[2] Spin-spin relaxation.[3] Experimental problems.

Advances about F centers. Detection of spin resonance and relaxation by optical methods. ESR of F centers in CaF_2 and BaF_2.[4] ENDOR measurements on Z_1 centers.[5]

ESR of the R-center ground state.[6] Consequences of orbital degeneracy.

Paramagnetic resonance of metastable multiplet states of F-aggregate centers: M center triplet state[7] and R center quartet state.[8] Methods of optical excitation, lifetimes. ESR spectra, fine structure, electron spin-spin interaction. ENDOR measurements. Electronic wavefunction of the F aggregate multiplet states, overlap integrals, influence of the lattice ions. Problems about excitation and decay. Optical spin polarization of M-like centers in CaO.[9]

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172 Zero and One-Phonon Lines in Magnesium Oxide Color Centers

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Sharp spectral lines associated with trapped carrier transitions in defect lattices or impurity centers in ionic crystals have received much attention. The narrowest one is usually the zero-phonon line. The structure next to it is associated with the creation of one or more phonons. Additional lines appear at elevated temperatures where the phonon-assisted process also becomes probable. Such structure appearing in the absorption spectrum of color centers induced by neutron-irradiation of MgO[1] has been interpreted in terms of the optical analog of the Mössbauer effect[2] and one or a few phonon transitions.[3] Subsequent measurements of the shift of the zero-phonon line at 27,630 cm^{-1} induced by uniaxial stress has shown a linear shift-stress dependence without any line splitting.[4] Absorption spectroscopic measurements of an infrared color center with a zero-phonon line at 9,572 cm^{-1} and its associated one phonon spectrum have also shown the vibrational spectrum of the MgO lattice.[5] When uniaxial stress is applied in the ⟨010⟩ direction, this line splits into two components of unequal absorption. The ratio of both absorption peaks depends upon the polarization of the sample beam. The stress-shift relation of the main peak, as measured with the unpolarized light, is linear with a slope of 5.6×10^{-3} cm^{-1} bar^{-1} at 80°K. Upon consecutive applications of the stress, the slope decreases. The perturbation potential analysis of the absorption spectroscopic data yields peaks in the phonon density of states curve[6] which agree with Raman's Reststrahlen measurements.[7] The results of our theoretical analysis agree with suggestions made by Wertz.[8]

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173 The Use of Flow Stress Measurements for Investigation of Radiation Produced Interstitials in Potassium Chloride*

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Recent evidence stemming from observations of the x-ray lattice expansion, thermal conductivity, and flow stress of room temperature irradiated KCl crystals has indicated that interstitial halide is produced simultaneously with F centers. Previous x-ray lattice expansion measurements[1, 2] have suggested that interstitials are produced in the late stage but not in the early stage coloration. By combining flow stress and optical measurements we have been able to confirm this for KCl. In fact, we found that when a sample is so heavily doped with Ca or Pb impurity that late stage coloration is totally suppressed there is very little increase in the hardening. Recently we have studied the effect of irradiation temperature on F-center and interstitial defects by a similar method of combining flow stress and optical techniques. It is found that interstitials are produced during irradiation at liquid nitrogen and dry ice temperature, as well as at room temperature. The majority of the defects remain stable upon warming to room temperature; however, we find that the stability against optical bleaching at room temperature of both the F centers and the interstitials is less for irradiations performed below room temperature. This may result from the production of different sized clusters of interstitials during irradiation at the various temperatures.

* Research sponsored by the U.S. Atomic Energy Commission under contract with Union Carbide Corporation.

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174 Far-Infrared Impurity States in Alkali Halide Lattices*

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With an incoherent source and optical techniques, the far-infrared (100 cm^{-1} to 10 cm^{-1}) transmission of alkali halide crystals doped with small concentrations of impurity ions has been studied at low temperatures. For almost any choice of host lattice and dopant, impurity-induced absorption is observed in this low frequency region. Broad absorption bands usually appear at frequencies less than the T.O. mode phonon branch of the host lattice; however, for some dopant-lattice combinations, sharp absorption lines have been observed. If the impurity mass is much larger than the host lattice mass or if the impurity is weakly bound in the lattice, a sharp low frequency absorption line appears in the acoustic phonon continuum. Also, when a frequency gap exists between the optic and acoustic bands of the host crystal, a sharp absorption line is usually found at gap frequencies. Finally, when a molecular impurity rather than a monatomic impurity is used as a dopant, more than one sharp absorption line is observed at gap frequencies. For each of these three cases, a sharp absorption line can be identified with the vibrational transition of an infrared-active lattice mode which is localized spatially around the substitutional impurity site. Weak subsidiary absorption bands, which are found in all cases, cannot be directly identified with the one phonon density of modes of the host lattice. We are presently measuring the temperature dependent properties, strain dependent properties and isotope shifts of some of the localized lattice modes.

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175 A Calculation of Excited States of the F Center

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An extension of the static method outlined earlier[1] is used to calculate the wave functions and energies of the excited states of the F center. Improved initial conditions for both the absorption and emission transitions are obtained by the application of a first-order Mott and Littleton (M-L) calculation to determine the displacement and induced dipoles on the ions adjacent to the center before the transition takes place. Before applying the method to the calculation of higher excited states, parameters for the principal absorption process — from ground state (1s) to first excited state (2p (1s)) when the surrounding ions are in a ground state configuration — and the related emission process were determined and gave the following results:

Material	Transition energies (eV)		Radius (Å) of $\psi^2 r^2$ max. in equilibrium	
	Absorption	Emission	Ground State	First Excited State
KCl	2.20	1.33	1.52	6.68
KBr	2.06	1.32	1.58	7.08

The higher excited states usually designated L_1, L_2, L_3 appear to arise from hydrogen-like transitions in which electrons are excited from the ground (1s) state to 3p (1s) state, 4p (1s) states, etc. These higher states are below the conduction band but are raised during the relaxation process that follows the transition and the electrons are released. Photoconductivity is therefore expected to accompany these excitation processes.

Preliminary values of the theoretical excitation energies obtained are shown together with experimental values in the following table:

Material	Optical Dissociation Energy (eV)*	Transition Energies (eV)				
		Theoretical		Experimental		
		1s−3p (1s)	1s−4p (1s)	L_1	L_2	L_3
KCl	5.34	3.85	4.31	3.6	4.3	4.9
KBr	5.05	3.68	4.12	3.3	3.9	4.5

* Neglecting the "electron affinity" of the crystal.

The L_3 band probably corresponds to a higher excited state about 0.4 eV below the conduction band. The K band does not fit into this scheme and may correspond to a partially forbidden transition, e.g. 1s — 2s (1s). The investigation of these matters is continuing.

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176 A Second Order Mott and Littleton Calculation

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A method of calculating the energy to form a Schottky defect in an alkali-halide crystal is described. The procedure is an extension of the first-order procedure of Mott and Littleton[1] (M-L) in which the displacement z_1 and induced dipole m_1 of an ion in the first shell surrounding the vacant lattice point are determined exactly from the condition that the sum of the electrostatic and repulsive forces acting on these ions be zero. In the present case the displacement z_2 and induced dipole m_2 of a second shell ion (next nearest neighbor of the vacancy) are determined in a similar manner. Values for the two shells are made self-consistent by an iterative process. The properties of the ions in the third and subsequent shells are determined on the assumption that these ions are acted upon by the average (continuum) electrostatic forces as in M-L and a Brauer[2] (elastic) term. Other modifications include the addition of Van der Waals forces and the use of the generalized Huggins-Mayer form for the repulsive energy.

The effect of the second order calculation is to decrease the displacement and induced dipoles for the first shell and increase those for the second shell. The net effect is to increase the Schottky energy relative to most theoretical values in the literature and to bring them more in line with experimental values. Theoretical Schottky energies for KCl, KBr and NaCl are all about 2.20 eV. The change in the first and second shell dipoles is expected to be more important in establishing the initial conditions for static F-center calculations than in the Schottky energy calculation.

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177 Influence of External Perturbations on Optical Transitions in Electron Excess Color Centers†

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The theory of optical absorption line shapes usually assumes the ground and excited electronic states are orbital singlets. The recent experimental studies of the Faraday effect in F centers by Lüty, Mort, and Brown and on circular dichroism by Karlov, Margerie, Romestain, and Merle-d'Aubigné require consideration of orbital degeneracy since the spin-orbit "splitting" involves the removal of this degeneracy by the spin-orbit coupling. One is then confronted by two major theoretical difficulties: 1) the failure of the adiabatic condition which is usually invoked to separate the electronic motion from the lattice motion and, 2) the fact that the lattice coupling is typically as strong as or stronger than the spin-orbit coupling. That the adiabatic hypothesis is in difficulty can be easily seen by recognizing that its validity usually rests on the condition that electronic energy differences are large compared to lattice energy differences (i.e., the electronic motion is "fast" compared to that of the lattice). Such a situation is clearly violated when there is electronic degeneracy since there is zero energy difference between degenerate electronic states.

Henry, Schnatterly, and Slichter have shown that it is still possible to calculate the moments of the absorption line, and the change in moments resulting from applications of applied external perturbations. From such analyses one can determine spin-orbit coupling constants, and separate the contributions of the cubic and the non-cubic lattice vibrations to the width of the absorption line. Henry has carried out experiments on circular dichroism for both F and F_A centers, the latter demonstrating what happens when some of the electronic degeneracy is removed. Schnatterly has measured the effect of applied stresses on the circular dichroism of F centers to unravel the relative contributions of cubic and non-cubic lattice modes to the optical line-width. Moran has looked in detail at the manner in which lattice vibrations and spin-orbit couplings split excited states in the limit of rather large spin-orbit coupling and has thereby explained the anomalous structure on the F band of the cesium halides.

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178 Color Centers in Alkaline Earth Fluorides

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The color centers in alkaline earth fluorides are complicated by crystal structure (having coordination numbers 4 and 8), impurity of starting materials (O, OH, Y, rare earths), and subsequent contamination (by O_2, H_2O, CO_2). Although the concentration of impurities can be kept lower ($\sim 10^{-6}$) than in the alkali halides, they have a strong influence on spectral position and intensity of the color center absorption bands. Absorption spectra can be divided according to the coloration method, purity of the crystals, and coloration temperature. Of the three alkaline earth fluorides, CaF_2, SrF_2 and BaF_2, only the first one has been extensively studied.

Coloration of natural or synthetic CaF_2 crystals, by internal ionization (subtractive) or by vapor (additive, with subsequent slow cooling), produces four bands. The position of the bands varies by about 0.1 eV in various samples, and additional bands appear in some samples. This indicates that some impurities or defects may be involved. Doping enhances some of the bands more than others.

The color center spectra of SrF_2 and BaF_2 have a different structure from that of CaF_2 and there seems to be no reliable correlation between the three compounds. Only in crystals grown from purest synthetic materials doped with yttrium do similar bands appear in CaF_2, SrF_2 and BaF_2.

Contrary to internal ionization, coloration of CaF_2 crystals grown from natural materials by metal vapor can produce either four or two bands, depending on the degree of coloration and the subsequent heat treatment. CaF_2 crystals grown from purest synthetic material show neither four bands after x-ray irradiation nor two bands after vapor coloration. There might be a fundamental difference between the two coloration methods. Coloration at low temperatures (190°C) produces in all three crystals only two broad bands which are quite different from the bands obtained at 25°C, but interrelated for the three materials, showing a regular shift from CaF_2 to BaF_2. At 25°C the bands either transform into 25°C bands (in CaF_2), or disappear (in SrF_2, BaF_2).

Compared with alkali halides, the color centers of alkaline earth fluorides show the following main differences: impurities and defects play a greater role, there is no sharp difference in the stability between various bands as in F and V centers, temperature influence is smaller on band position but greater on coloration, and there is a strong difference between coloration by radiation and by vapor.

Various models have been suggested for the explanation of color center optical bands, but none is considered reliable at present.

179 Color Centers in Mixed Crystals of Rubidium Chloride-Rubidium Bromide and Potassium Bromide-Rubidium Bromide

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In continuation of our study of trapped charge carrier centers in KCl, RbCl, KBr, RbBr and in their solid solutions, the systems RbCl–RbBr and KBr–RbBr were investigated. Crystals of various compositions were irradiated with electrons, 3 MeV, 10^4 to 10^6 rads at temperatures 20°C, −80°C and −190°C. The influence of radiation dose, irradiation temperature and crystal composition on spectral position, half width and intensity of the electron and hole trapped centers were studied. A variety of bands (M, F, K, V_K, V_1 and V_2 and some others) were observed. In no case is the Mollwo relation valid. In solid solutions the shift of most bands does not go linearly with the composition but deviates toward lower energy. The half width of bands in solid solutions is always greater than in pure components. The concentration of trapped centers increases with irradiation, but at a decreasing rate. Most of the observed bands have been correlated to already-known models, but the correlation of some new ones (L_x, V_x) is still uncertain.

180 Pseudopotential Theory in the Hartree-Fock Approximation and its Application to Localized States in Solids†

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A pseudopotential formulation for the calculation of electronic wavefunctions and energy levels may be derived in the Hartree-Fock approximation.

In general, the resulting pseudopotential consists of the familiar Phillips-Kleinman pseudopotential plus an electron-electron interaction term that may be roughly regarded as a self-energy. In the case of large systems, in which the electronic states are not localized, it may be shown that the electron-electron interaction or self-energy term in the pseudopotential goes to zero, justifying the use of the Phillips-Kleinman form for band structure calculations. For localized states such as atoms, molecules or defect states in solids, the electron interaction terms correspond to a Coulomb repulsion between the localized state and electrons occupying core states. Depending on the degree of localization of the state, this repulsion may raise the energy of the localized state by up to several tenths of an electron volt. The structure of the "Hartree-Fock" pseudopotential has been investigated and several approximation schemes for applying it have been considered. In many systems of physical interest, particularly the case of an extra electron or hole in an otherwise closed shell system, it appears that the self-energy term may be incorporated in the other terms in the pseudopotential. The result is then of the Phillips-Kleinman form, but calculated with energies appropriate to the system with the extra electron or hole absent. This result suggests that calculations using this approximation may be useful in treating some color center problems.

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181 Influence of Impurity on Defect Production at 80°K*

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Trace impurities influence the rate of F-center production at 80°K to much greater degree than has usually been assumed. The F band grows three to four times as fast in KCl containing 20 ppm lead or 50 ppm calcium than it does in nominally pure material. As the lead concentration increases and exceeds 100 ppm, the enhancement of the F-center production saturates and actually begins to decrease again. This decrease appears to be compensated by a corresponding increase in the rate of production of α centers, which in nominally pure or lightly doped KCl are produced much more slowly than F centers. To determine whether electronic processes are responsible for these impurity effects, we compared the growth curves of the trapped hole (V_K) band with that of the F band in lead-doped samples. The optical absorption in the V_K band region quickly saturates as the irradiation progresses, the level of saturation increasing with lead content. There is no reflection of this saturation in the shape of the F-coloration curves. This absence of a relation between trapped holes and F-center production suggest that the impurity enhancement is not purely an electronic effect. We believe that the results can be accounted for as follows: At 80°K radiation causes vacancies and mobile interstitials to be formed. The interstitials tend to be trapped or stabilized by the impurities. On the basis of this idea, the saturation of the F growth enhancement occurs when enough impurity is present to stabilize all the interstitials formed.

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182 ENDOR Measurements on U_2 Centers in Potassium Chloride

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U_2 centers in alkali halides are hydrogen atoms on interstitial sites, as has been shown by ESR measurements.[1, 2] The hyperfine interactions with the central proton and with the four nearest halogen nuclei are resolved in the ESR spectrum. In order to resolve hyperfine interactions with other nuclei of the surrounding lattice ENDOR measurements have been performed on U_2 centers in KCl at X-band frequency and 80°K. The large concentration of U_2 centers needed for these measurements was achieved by photo-dissociation of OH^- or HS^- ions with which the crystals had been doped,[2, 3] the latter giving the better results. Using the spin Hamiltonian

$$H_{\text{nucl.}} = g_I \mu_n \vec{H}_o \underset{\wedge}{\vec{I}} + \underset{\text{isotr. HFS}}{a\, \underset{\wedge}{\vec{I}}\, \vec{S}} + \underbrace{b\left(3\underset{\wedge}{I_z} S_z - \underset{\wedge}{\vec{I}}\, \vec{S}\right) + b'\left(\underset{\wedge}{I_x} S_x - \underset{\wedge}{I_y} S_y\right)}_{\text{anistr. HFS}} +$$

$$+ \underbrace{q\left(3\underset{\wedge}{I_z}^2 - I^2\right) \quad + \quad q'\left(\underset{\wedge}{I_x}^2 - \underset{\wedge}{I_y}^2\right)}_{\text{quadrupole interaction}},$$

a somewhat reduced effective electronic spin (because of the large proton coupling) in H_o direction and second order perturbation theory, the following interaction constants, in Mc/s, were taken from the ENDOR spectra:

nearest anions, $^{35}Cl_I$: $a/h = 23.74$ (ESR-value 25)
$b/h = 6.71$ (ESR-value $\approx 1/3\ a/h$)
$3q/h = 0.174$
$z, z' = \langle 111 \rangle$

nearest cations, $^{39}K_I$: $a/h = 0.983$ $b/h = 0.457$
$3q/h = 0.045$ $z, z' = \langle 111 \rangle$

next-nearest cations, : $a/h = 0.123$ $b/h = 0.032$
$b'/h = 0.010$ $\sphericalangle (z, [100]) = \pm 2°$
$^{39}K_{II}$, (1/2, 1/2, 3/2) $3q/h = 0.040$
—positions $q' \approx 0$ $\sphericalangle (z', [100]) = \mp 15°$

Two further chlorine shells could be approximately analyzed. The hyperfine interaction with the (½, ½, 3/2) Cl_{II} nuclei is sufficiently well explained by approximating the electron as a magnetic point dipole at the proton position, but the interaction with the (½, 3/2, 3/2) Cl_{III} nuclei is considerably stronger than estimated on this basis.

The question is being considered if the large ratio of the interactions with anions and cations in equivalent first shell positions can be explained by the different core wavefunctions of these ions, or if it is a true indication of a tetrahedral structure of the U_2-electron envelope function. The relatively large hyperfine interaction with the K_{II} nuclei and the fact, that the principal is almost in ⟨100⟩ direction, may suggest a transmission of the unpaired electron from the neighboring Cl_I nucleus by slight covalent bonding. The quadrupole interactions, especially the relatively large one of the K_{II} nucleus, can be used to determine the displacement of the neighboring ions.

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183 On the K Band in the Alkali Halides*

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A series of experimental and theoretical investigations of the K band in colored alkali halides was undertaken to clarify some features of this absorption and to examine possible theoretical models for the transitions involved. In the case of colored RbCl it was found that, as in KCl and RbBr, there is appreciable photoconductivity only in the high energy tail of the K band. Experimental evidence was also found indicating that the K band in RbCl is neither symmetric nor Gaussian, contrary to what has been assumed. Together with the work of Schnatterly[1] and other investigators, these observations suggest that the K band may not arise from a single transition, but rather from allowed transitions of the F center to a series of bound states above the first excited state, but below the conduction band. To test this conjecture, a detailed calculation of the energy levels of the F center based on a semicontinuum model was undertaken. It was found possible to reproduce the main features of the F and K bands of RbCl from the solution of a physically reasonable Simpson-type model potential assuming only emperical absorption band widths. A satisfactory fit to the transition energies was found for a potential with a Jost cavity of radius 66% of the nearest neighbor distance, a well depth 77% of the Madelung energy and a dielectric constant 37% greater than the observed high frequency value. The differences of these values from those derived on the basis of theories by Simpson, and Krumhansl and Schwartz are thought to reflect the finite size of the ions and the dependence of dielectric constant on the distance between the electron and the vacancy. These results together with the presently available experimental evidence suggests that the Mott-Gurney model for the K band[2] is essentially correct and that it provides a consistent picture of the optical properties and temperature dependence of the K band, and the associated photoconductivity. This work further suggests that some other centers may have spectra consisting of a strong primary transition followed by a K band-like high energy tail. Presumably, the major differences between such spectra would arise because of the different "core corrections" associated with the details of the crystal potential near the specific absorbing center.

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184 Electron-Phonon Coupling of Color Centers in Magnesium Oxide

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The electron-phonon coupling in shallow (but not deep) electron traps is well understood through their relation to conduction band minima. The coupling Hamiltonian for deep traps is usually assumed to be the linear term in the Taylor series expansion with respect to nuclear displacements of the potential seen by the electron. Other sources of the electron-phonon coupling were studied in the particle in a box model for which the Taylor's series expansion is not possible. The "walls" are assumed to be impenetrable oscillating ions coupled by springs to the lattice. The model, solvable in the adiabatic approximation, exhibits several sources of electron-phonon coupling: breakdown of the Condon approximation, nonadiabatic terms, and dependence of ionic vibrational frequency on electronic states. Their contribution to the line shapes is obtainable. We have also studied the origin of the phenomenological interaction Hamiltonian of McCumber, Kane, Schawlow, and others. The basic idea is that used in the deformation potential analysis, namely, that the same interaction Hamiltonian describes the effects of uniaxial stress on the electronic transition frequency and the electron-acoustic phonon interaction. Optical phonons can be introduced by a modification of Reik's argument. The resulting effective interaction is formally symmetric in acoustic and optical modes. This electron-phonon coupling has Kane's form and is also given by the deformable ion model. Separation of the electron and the lattice coordinates is achieved by assuming that all phonon wavelengths are larger than the dimensions of the electron wave function. This form of the interaction Hamiltonian[1] has been used to deduce the effective phonon density and the average magnitude of the electron-phonon coupling from the one-phonon infrared absorption spectrum[2] of color centers in neutron-irradiated MgO. Preliminary data for a Kaplyanski analysis of uniaxial stress induced shift of the infrared zero-phonon line yields a similar value for the coupling.

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185 Calculation of Electronic States of the F′ Center*

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The ground and first excited singlet and triplet states of F′ center in KCl and KBr have been calculated using a two-parameter variation-type wave function. Good agreement with the experimental F′ absorption edge has been obtained.

The lattice is treated as a lattice of point ions. Corrections to this approximation due to the finite size of the core orbitals and to the necessity of orthogonalizing the F′ wave function to the crystal wavefunctions are calculated using the Austin form of the pseudopotential. The coulomb and exchange interactions between the two electrons are taken into account. Correlation between the two electrons of different spin is calculated according to the method of Mitler using the free electron gas appproximation of Wigner to work out an approximate correlation operator. Ionic polarization, which for this charged center is considerable, is calculated on the basis of a semicontinuum model assuming that the lattice plus vacancy is replaced by a polarizable medium plus a spherical hole of radius equal to the nearest neighbor separation; and that the ions follow the average value of the electronic motion. For the electronic part of the polarization, it is assumed that (in the manner of Krumhansl and Schwartz) the core orbitals follow the instantaneous position of the electrons. A correction is made due to the penetration of the core orbitals into the vacancy. All spin interactions (except exchange) are neglected.

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186 Purification of Potassium Chloride by Zone Refining*

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Reagent grade KCl was zone refined in a halogen atmosphere with the specific intent of reducing the sodium and bromine contamination. Purification with respect to these impurities was readily obtained, accompanied by an expected reduction in the total impurity content.

Reagent grade KCl was used directly without preliminary chemical purification. Zone melting was carried out in a high purity quartz boat under a purified atmosphere of 2% HCl in argon. The ratio of ingot length to molten zone length was varied from 6.8 to 9, and the zone speed was 2.0 inches/hour. The apparatus used has been described elsewhere.[1]

Na and Br concentrations were determined by neutron activation analyses. Five mg specimens were irradiated and then placed directly atop a zirconium tungstate resin bed. Br^{82} was eluted with 5 ml 0.01 M NH_4Cl followed by elution of Na^{24} with 10 ml 0.1 M NH_4Cl containing Na^{22} tracer.

Zone melting KCl in a halogen atmosphere simultaneously removed Br contamination through segregation from the melt, distillation and displacement. Analytical data for Br were fit to a computer-programmed solution of the zone refining equation. An effective segregation coefficient of 0.7 was calculated for Br in KCl. The value for Na in KCl was between 0.1 and 0.2. Both values are in agreement with Inoue and Mizuno.[2]

For typical reagent grade KCl (Baker and Adamson Co.), Br = 97 to 163 μg/g and Na = 7 μg/g. For Harshaw, single crystal KCl, Br = 92 μg/g and Na = 3.5 to 6 μg/g. Thirty-eight passes of the molten zone reduced Br to 4.8 μg/g and Na to <0.1 μg/g.

Single crystals were subsequently regrown by pulling from the melt without Na or Br recontamination.

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* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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187 Optical Excitation Spectrum of the F_t Center and Relationship to Calcium Oxide Absorption Bands*

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Subsequent to earlier experiments,[1] in which only broadband light was used, we have been able to detect the ESR spectrum of the CaO F_t-center triplet state as excited by monochromatized light at 1.8°K, giving some information on the nature of the F_t absorption band and its relation to other bands. Though the signal-to-noise ratio in these observations was poor owing to the monochromator insertion loss, we were able to see that the excited ESR intensity peaks up definitely near 3700 Å, falling below our detectability outside the limits 4000 and 3200 Å. Comparison with the absorption spectrum of the CaO samples is interesting. In the region 4500–3000 Å our spectra show two almost resolved strong bands peaked at 3720 and 3400 Å respectively, the second being the stronger. Recent work on the F band location, λ_F, in MgO gave an experimental[2] λ_F about 4% smaller (higher energy) than an earlier estimate, in which λ_F for all the alkaline earth oxides were estimated theoretically.[3] If the CaO value from reference (3) is shifted 4% to higher energy one expects $\lambda_F = 3200$ Å for CaO. It is interesting that the observed 3400 Å band, which is closest to this extrapolated estimate, as seen at low temperatures has sharp structure on its low-energy side (i.e. between the 3400 and 3720 Å peaks), with the general appearance of phonon structure. Since as far as we know it is uncommon to see phonon structure of F centers (though seen in other defects) we are cautious about assigning the 3400 Å band, specifically, to the F center. Conforming with our model for the F_t center, the F_t band should overlie the F band, with maybe some displacement plus excited state splittings. In any event, our opinion is that both the F and F_t band peaks are now confined to within the region 3200–3900 Å, essentially that covered by the two known peaks and the F_t triplet-state excitation.

In some other observations we found by heating samples over the range 350–550°C that the F_t is thermally less stable than the F center, as might be expected for a center of the aggregate-vacancy type. After one hour at 550°C the F center ESR signal was scarcely reduced, while the F_t signal was reduced by a factor of over 50.

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* Supported by the U. S. Air Force.

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188 Volume Changes Connected with the Formation of F Centers from U Centers in Potassium Chloride

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It is well known that F centers can be formed from U centers by means of ionizing radiation whereby the hydrogen atom is ejected into an interstitial position. At room temperature the configuration of the hydrogen interstitial is not known with certainty. It is believed that it joins another interstitial hydrogen atom to form an interstitial hydrogen molecule. On this assumption, the volume change connected with the reaction $U \xrightarrow{\text{irrad.}} F + (1/2)\ (H_2)$ can be written

$$\Delta V = -\Delta V_U + \Delta V_F + (1/2)\,\Delta V_I,$$

where ΔV_U is the volume change which occurs when a halogen ion in a perfect crystal is replaced by a negative hydrogen ion. ΔV_F and ΔV_I are the volume changes due to the lattice relaxation around an F center and an interstitial hydrogen molecule respectively. ΔV was found experimentally to be $(1.12 \pm 0.03)\ a^3$, a being the interionic distance.[1] ΔV_F and ΔV_U were estimated theoretically: An approximative vacancy-centered wave function for the F-center ground state was determined using effective potentials for the interaction between the F electron and the lattice ions. The repulsive interaction of the hydrogen ion in a U center with its nearest neighbors was expressed in the form $V(r) = A \exp(-r/\rho)$, where ρ was taken as 0.333 Å and A was determined from the experimentally value of ΔV_U in KBr. The lattice distortion around a defect was calculated adopting an approximate procedure, in which the atomistic structure of the crystal is taken into account only in the vicinity of the defect, whereas the remainder of the crystal is treated as an elastic continuum. Calculation of the volume change was performed using a method which requires knowledge only of the displacements of those ions which are in direct interaction with the defect. The results were $\Delta V_F = 0.31\ a^3$, $\Delta V_U = -0.13a^3$. This leads to $\Delta V_I = 1.36a^3$. The approximate accuracy of the latter figure is believed to be $\pm 0.4\ a^3$.

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[1] A. Bleckmann and K. Thommen, see Abstract No. 17.

189 Experimental and Theoretical Investigation of the Sidebands of the Local-Mode Absorption of the U Center

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The sidebands of the U center local mode (infrared) were measured at helium temperatures in KBr and KI containing H^- and D^- ions. The sideband spectra for the two isotopes are identical. The gap between the optical and acoustical branches can be seen between 95 and 100 cm^{-1} in KBr and between 69 and 87 cm^{-1} in KI. This agrees very well with the position of the gap determined by slow neutron scattering in KBr. Several peaks are present and are particularly strong in the acoustical region.

Our theory treats the U center as a local mode vibrating in, say, the x direction, which is anharmonically coupled to its nearest neighbors in the ± x directions. The U center frequency is thus dependent on X, the even parity combination of the x displacements of these neighbors. As X oscillates, it modulates the U center frequency giving sidebands, whose shape depends on $\rho_x(\omega^2)$, the power spectrum for the motion of X. This spectrum can be calculated using a Green's function technique if the change in harmonic central force constant ΔF between the U center and its nearest neighbors is known.

The appropriate Green's functions for KBr have been calculated from the phonon frequencies and eigenvectors of Cowley, Cochrane, Brockhouse, and Woods. The resulting $\rho_x(\omega^2)$ fits the experimental data very well if a fairly large negative ΔF is assumed. The fit is poor for $\Delta F = 0$. In this model, the observed peak at 44.5 cm^{-1} is due to an even parity "resonance" motion of the nearest neighbors and is not at all caused by the 41.8 cm^{-1} TA(100) Van Hove singularity. On the other hand, the observed peak at 81 cm^{-1} really mirrors a peak in the unperturbed LA density of states at 83 cm^{-1}. The shift of 2 cm^{-1} is caused by the decrease in force constant.

190 Photochemical Conversion of F Centers to F_A Centers in Potassium Chloride Crystals Containing Sodium

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The F centers in KCl:Na single crystals were excited with intense flashes of 3 μsec duration at temperatures near −10°C. Changes in optical absorptions and photo after-currents under application of ac fields were simultaneously recorded.

Since the number of F′ centers formed by one flash was found to be independent of the Na^+ content of the crystals, it was confirmed that the ionized electrons were not trapped at Na^+, but at other F centers, forming F′ centers. The decay time of the absorption at 967 mμ was attributed only to the F′ center, whereas the decay time at 719 mμ was composed of two components: the decay times of the F′ and the F_A' centers. Further, it was found that F_A' centers were formed directly during the lifetime of the F′ centers. In a specimen which contains $1.5 \times 10^{17}/cm^3$ F centers and $6.2 \times 10^{19}/cm^3$ Na^+, 36% of the F centers were converted to F_A centers at +10°C under irradiation of one flash, while the amount of the photocurrent was smaller by about 30% than that in a specimen containing no Na^+.

If an F′ center moves towards a Na^+ ion, resulting in the formation of an F_A' center, the decay of the F′ center is determined by probabilities of its thermal ionization as well as its reaction with Na^+. In this process, the observed photocurrent may decrease by the amount of the reaction, since the F_A' center hardly contributes to the current because of its very long lifetime and since the contribution by the migration of the F′ center is very small owing to the small distances between the F′ center and Na^+. Thus, it was concluded that the F′ center had moved towards Na^+ under the influence of the effective potential of Na^+, forming the F_A' center directly.

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191 Thermoluminescence in Lithium Fluoride*

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Thermoluminescence has been studied in LiF crystals which were produced by a variety of growth conditions. X ray, Co^{60} gamma ray, and/or optical excitation has been used to both populate and/or produce defects. Collectively, as many as 28 different glow peaks are observed in the range 20–550°K. However, in any one sample only about 15 of these peaks occur. The glow curves cover a range in intensity, the ratio of the strongest to weakest peaks is about 10^4, and the strongest thermoluminescence occurs near 140°K. Not one peak is common to all samples but at least one of three prominent peaks near 140°K is always observed. The reasons for the presence or absence of a glow peak will be mentioned.

The activation energies for the major peaks have been determined by several methods and the four peaks at 115, 147, 154, 255°K and possibly others follow first order kinetics. Typical peak temperatures (°K), pre-exponential factors (sec^{-1}) and activation energies (eV) are 119, 2.7×10^{10}, 0.28, 133, 3.1×10^3, 0.14; 147, 8.3×10^3, 0.17; 154, 3.4×10^7, 0.29; 194, 1.8×10^6, 0.31; 255, 4.7×10^8, 0.53.

The peaks at 115, 154, 194 and 255°K, and possibly others, result from electron untrapping since they can be obtained by both x-ray irradiation and by electrons obtained by irradiating a colored crystal with F-band light. One center at 68°K, has been observed only after optical re-excitation. Several of the glow peaks have been correlated with impurities, ESR data, etc.

These correlations suggests specific models for the defects associated with particular glow peaks. The peak at 115°K appears to result from the destruction of the H center. The peak at 133°K is impurity sensitive and is probably caused by the untrapping of a hole from the V_K center. The 255°K can be produced by x-ray irradiation at temperatures below 220°K. However, the ESR signal of the V_F center, which anneals in this range, is not produced by x-ray irradiations above 185°K. Therefore, the 255°K peak is not directly associated with the V_F center. Mg impurity produces the known peaks from 430 to 490°K whereas Mn, Ti, Zr or Ce doping merely enhance the 133°K peak.

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192 Vibration-Induced Splittings of the A and C Absorption Bands of Heavy Metal Ions in Alkali Halides

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A series of experimental studies on the absorption spectra of In, Sn, Tl, Pb, Ga and Ge in alkali halides revealed that the so-called A and C bands have characteristic structures, with two and three components, respectively. These structures can be explained within the framework of the Condon approximation by considering the instantaneous splitting of the degenerate excited states (T_{1u}; $|X\rangle$, $|Y\rangle$ and $|Z\rangle$) due to trigonal lattice vibrations (T_{2g}; Q_4, Q_5, and Q_6). With matrix elements of electron lattice interaction given by $\langle X|V|X\rangle = 0$, $\langle X|V|Y\rangle = cQ_6$ etc., the secular equation for the excited states becomes $(E/cQ)^3 - (E/cQ) - 2\lambda = 0$, where $Q^2 = Q_4^2 + Q_5^2 + Q_6^2$ and $\lambda = Q_4Q_5Q_6/Q^3$. The differential solid angle $d\Omega/d\lambda$ in (Q_4, Q_5, Q_6) — space becomes logarithmically infinite as $|\lambda| \rightarrow 0$, which means that the configurations $\lambda \approx 0$ with the roots $E_0 \approx 0$ and $E_\pm \approx \pm cQ$ make predominant contribution. With the approximation $d\Omega/d\lambda \approx 4\pi\delta(\lambda)$ and the Boltzmann distribution $\exp(-Q^2/\kappa T)$, one easily obtains the line shape function which consists of three components: $F_0(E) = \delta(E)$, $F_+(E) = 4\pi^{-1/2}(c^2\kappa T)^{-3/2}E^2\exp(-E^2/c^2\kappa T)$ (for $E > 0$, zero for $E < 0$) and $F_-(E) = F_+(-E)$. Numerical calculation with exact $d\Omega/d\lambda$ gives the line shape split into three components, of which the central one has logarithmic singularity.

Tetragonal (E_g) lattice mode also removes the degeneracy of the electronic states T_{1u}, but in this case, the resulting line shape is a superposition of three identical Gaussian curves. The observed line shapes of the C bands can be reproduced by mixing smaller amounts of A_{1g} and E_g mode interactions to T_{2g} mode. As long as one takes into account the linear interactions only, the line shape should be symmetric, and independent of temperature if one uses the normalized energy scale $E/\sqrt{\kappa T}$ for the abscissa. This is in qualitative agreement with observations. Any deviations from this rule should be attributed to quadratic and higher order interactions.

The quadratic interaction seems to play an important role in the A bands. Following the Seitz model for the electronic structures of the excited states of the A, B, and C transitions, and taking into account the T_{2g} mode (mentioned above) alone, we get the energy matrix for the A-states $\langle A_x|U|A_x\rangle = -(c^2/4\Delta)(Q^2 + 3Q_4^2)$, $\langle A_x|U|A_y\rangle = -(c/2)Q_6 + (c^2/4\Delta)3Q_4Q_5$ etc. The quadratic terms are second order perturbation through the matrix elements of V between B and A states which have energy difference Δ. Since the secular equation depends on Q_4, Q_5, and

Q_6 through Q and λ only, we again approximate $d\Omega/d\lambda \approx 4\pi\delta(\lambda)$. Putting $\lambda = 0$, we get the three roots: $E_0 = -(c^2/\Delta)Q^2$, $E_\pm = \pm(c/2)Q - (c^2/4\Delta)Q^2$. The resulting line shape is such that the — and 0 components coalesce into a single band, except for very small κT values which will not be realized because of zero-point vibrations. In this way, the asymmetric two-component line shape of the A band, as well as the reversal of the heights of the two peaks as T increases, can be explained with the use of the value of c determined from the splitting of the C band. A part of the shift of the B band as T rises comes from the counterpart of the above mentioned quadratic terms.

193 Color Centers in Ammonium Halides

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A survey of color centers in pure and doped ammonium halides has been carried out. NH_4Cl, $NH_4Cl:Tl$, $NH_4Cl:Pb$, ND_4Cl and NH_4Br crystals were X rayed at temperatures ranging from 12°K to 300°K, and investigated optically and with electron paramagnetic resonance. In crystals irradiated at 78°K two paramagnetic centers were found to be predominant, the V_K center and a second center, the structure of which is not yet known with certainty. The V_K center does not differ significantly from the corresponding center in alkali halides, except therein, that the internuclear axis is along ⟨100⟩ and that the symmetry is exactly tetragonal because the structure of the ammonium halides is of the CsCl-type. The optical properties of the V_K center in NH_4Cl and NH_4Br correspond closely to those in the alkali halides. The π — polarized transition in the ultraviolet and the predominantly σ — polarized transition in the red were found and used to align the centers with polarized light. Doping with Pb and Tl enhances the production rate of V_K centers by X rays. In the pure as well as in the doped NH_4Cl crystals, part of the trapped electrons are released between 77°K and 110°K and annihilate the V_K centers. The V_K centers themselves start to migrate, thermally activated, around 120°K with an activation energy of about 0.3 eV.

The second paramagnetic center has axial symmetry along ⟨111⟩. The basic hfs is due to halogen nuclei. The center undergoes, between 60°K and 180°K, a gradual transition from a low temperature structure with lower symmetry to a high temperature structure of higher symmetry without changing the symmetry axis. Its optical absorption band peaks at 3850 Å and has a half-width of about 1 eV. Attempts to orient this center by means of polarized light were unsuccessful.

194 Splitting of the 5865 Å Zero-Phonon Line in X Irradiated Sodium Fluoride by Uniaxial Stress

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At liquid helium temperature the absorption spectrum of x irradiated NaF exhibits an intense zero-phonon line at 5865 Å on the long wavelength side of the N_1 line.[1] Under stress along ⟨100⟩, ⟨111⟩, ⟨110⟩, and ⟨210⟩ the line splits into 2, 2, 4, and 6 components, respectively. Color centers of monoclinic symmetry (C_{2h}, C_2 and C_s with twofold axis parallel to ⟨110⟩ or reflection plane perpendicular ⟨110⟩) should produce 2, 3, 4, and 6 components, respectively. Lack of 1 component under stress along ⟨111⟩ can be explained by calculating the energetic splittings. Under the assumption of linear dependence on pressure these splittings can be expressed by 4 constants A_0, A_1, A_2, A_3 for different directions of stress P:

$$P \parallel \langle 100 \rangle : \begin{array}{l} A_0 - 2A_1 \\ A_0 + A_1 \end{array} \qquad P \parallel \langle 111 \rangle : \begin{array}{l} A_0 + A_2/3 \pm A_3/3 \\ A_0 - A_2/3 \end{array}$$

$$P \parallel \langle 110 \rangle : \begin{array}{l} A_0 + A_1 \pm A_2/2 \\ A_0 - A_1/2 \pm A_3/4 \end{array} \qquad P \parallel \langle 210 \rangle : \begin{array}{l} A_0 + A_1 \pm 2A_2/5 \\ A_0 + 2A_1/5 \pm A_3/5 \\ A_0 - 7A_1/5 \pm A_3/5 \end{array}$$

Utilizing the experimentally determined ratios $A_1/A_0 = -0.8 \pm 0.3$; $A_2/A_0 = -1.1 \pm 0.3$; $A_3/A_0 = -1.5 \pm 0.5$ one sees that 2 components for stress along ⟨111⟩ cannot be resolved. Therefore the association of monoclinic symmetry to the color center corresponding to the 5865 Å line proves to be consistent. In a recent paper[1] the same symmetry has been found for the N_1 center by splitting the N_1 line. However, from the opposite thermal behavior of both lines one concludes that they are due to transitions in different color centers. Some possible F-aggregate center models for the color center associated with the 5865 Å absorption line have been described earlier,[1] but color centers involving vacancies or impurities cannot be excluded.

[1] G. Johannson, F. Lanzl, W. v. d. Osten, and W. Waidelich, Physics Letters **15**, 110 (1965).

195 The Effect of Colloids on the Thermal Conductivity*

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At the limit where the phonon wavelength is small compared with the size of the inclusion, an inclusion in a crystal is expected to scatter phonons geometrically (i.e., with a scattering cross-section independent of the phonon frequency). On the other hand, when the wavelength is much larger than the inclusion, the scattering follows a Rayleigh law (i.e., with a cross-section proportional to the fourth power of the phonon frequency). The transition from one law to the other as the dominant phonon frequency changes has a marked effect on the thermal conductivity: if the scattering is geometrical the conductivity is proportional to the third power of the temperature, but in the Rayleigh scattering region this is no longer true. Therefore, the thermal conductivity of crystals containing colloids should show a characteristic break if the thermal conductivity is plotted as a function of temperature. This relationship has been found to hold for silver colloids in NaCl whose mean radii vary from 40 Å to 90 Å. Thus, it appears possible to use this characteristic effect as a tool to investigate the presence of colloids in other systems. Preliminary results on KCl crystals irradiated at room temperature reveal the characteristic temperature dependence of the thermal conductivity of a crystal which contains colloids.

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196 Theoretical Transition Energies for Various Transitions of the F_2^+ and F_2 Centers

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Starting from a many-body formulation that includes the phonon field in the proper way, we develop a method of calculating the quantum states of the F_2^+ and F_2 centers. Detailed calculations for the F_2^+ and F_2 centers in KCl are given. The transition energy for the optical transition $1s\sigma - 2p\sigma$ of the F_2^+ center in KCl is predicted to be 0.93 eV, and ~ 0.1 eV less than that given in the previous paper.[1] It turns out that the transition $1s\sigma - 2p\sigma$ of the F_2^+ center may be responsible for the band appearing at 1.4μ in KCl.[2] The calculation for the F_2 center shows that $M(M_1)$ band may be due to the optical transition $(1s\sigma\ 1s\sigma)\,^1\Sigma_g^+ - (1s\sigma\ 2p\sigma)\,^1\Sigma_u^+$ of the F_2 center. The relations between the higher transitions of the F_2 center and the M_2, M_3, M_4 bands in KCl are discussed.

* Present address: University of Waterloo, Waterloo, Ontario, Canada.
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[2] I. Schneider and H. Rabin, Phys. Rev. Letters 13, 690 (1964).

197 Temperature Dependence of the F-Aggregate Center Absorption Bands in Potassium Chloride

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Measurements have been made in KCl, between 4 and 500°K, of the M, R, and N optical absorption bands. The peak position, half width, integrated area, and shape of each band was determined whenever their mutual overlap made this feasible. Three significant results were found.

All of these bands, including the F band, are approximately Gaussian in shape and have a temperature-dependent half-width which can be fit by the expression C $\coth^{1/2} \theta/T$. C is different for each band but θ has a common value of 70°, equal to that found for the F band. This universal value of θ implies that all of the different centers producing these bands are interacting with phonons of the same frequency. Since local mode phonons should have a different frequency for each center, it is likely that the phonons involved are normal lattice phonons. It can be shown that such a distribution of phonons can lead to a good fit of the data.

Because of its isolation from other bands, the M band could be examined closely. Its area is temperature independent. Its shape is not symmetrical, but is skewed in one direction at low temperatures and in the opposite direction at high temperatures. This asymmetry can be interpreted in terms of the curvature of the configuration coordinate curves.

The peak position of the various bands shifts with temperature very much as the F bands does. The broad R_2 band is an exception. Its shift is at least an order of magnitude less than the others and is zero within the experimental error.

198 Color Centers in Magnesium Oxide

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Magnesium oxide, having the rocksalt structure, shows some similarities to the alkali halides, but there are numerous pronounced differences. Since it is much more difficult to obtain in pure form than the alkali halides, one is forced to take into account the effects of impurities on observed electronic properties. This is especially true of iron group ions, some of which may be present in two or three valence states. Iron and chromium ordinarily produce the most prominent effects on the ESR and optical spectra and the thermoluminescence behavior, though manganese is nearly always present. The extra charge of trivalent ions is compensated by incorporation of cation vacancies. The cation vacancy concentration controls impurity valence states as well as the relative intensity of optical bands which are present before or after irradiation with ionizing radiation. The concentration of cation vacancies is determined by the oxygen partial pressure during heating.

Cation vacancies provide stable trapping sites for positive holes, i.e., the MgO analog of the V_1 center proposed by Seitz. Due to lattice relaxation, this center has tetragonal rather than octahedral symmetry. This is the most important of the intrinsic centers formed in MgO by ionizing irradiation. V_1 centers may also form associated neutral defects. Anion vacancies are much more difficult to generate, requiring neutron irradiation. Most anion vacancies are populated by a single electron during the irradiation process, giving an F center with absorption near 5 eV. The trapped electron is much more localized than in alkali halides. The F center may associate with a cation vacancy (F_2 center) or form more complex F-aggregate structures. In MgO it is ESR spectra which have contributed most to a description of geometry and environment of defects; subsequently some optical and infrared bands have been assigned. Progress has also been made in interpretation of thermoluminescence and charge release peaks.

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199 F-Aggregate Centers in X Rayed Plastically Deformed Potassium Chloride

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Single crystals of KCl, plastically deformed at room temperature, have been x rayed at 78°K and their optical absorption spectra studied before and after warmup to specific temperatures. The color center formation can be divided into two kinds. The first is the "normal" kind occurring in nearly perfect crystals (where the major color center products are F and V_1 centers); the second is the extrinsic, being associated with the introduced lattice defects and quickly reaching its maximum value. The sub-system of extrinsic color centers is relatively independent of the normal color center sub-system. The optical absorption spectra show peaks at 356, 545, 630, 820, 1020, 1250, 1475, 1700 mμ and absorption beyond 2 μ, of which all, but the first absorption peak, correspond to electron centers. The hole center is the Cl_2^- center. Bleaching experiments indicate that the extrinsic electron and Cl_2^- centers are produced in pairs, closer to each other than to F centers. Upon warmup, stepwise changes in the absorption spectra occur which correlate with thermoluminescent glow peaks.

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200 Diffusions Effects in the High Temperature ESR of the F Center[*]

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Saturation measurements on the inhomogeneously broadened magnetic resonance of the KCl F center from 20° to 550°C show $(\gamma H_{1/2})^2 \propto T^2$ up to about 350°C and an exponential dependence on $1/T$, suggesting defect diffusion or ionization, from 400° to 550°C. Above about 470° the saturation curve shape tends systematically toward that expected for a homogeneously broadened resonance. The changes, although not large with an X-band microwave power of 0.4 watt, are present in zone-refined and Harshaw crystals with F-center concentrations of $3 \times 10^{17}/cm^3$ to $2 \times$

$10^{18}/\text{cm}^3$. A transition to homogeneously broadened saturation could reflect an increase of level broadening[1] $\omega_2 = 1/T_2$, but the value of ω_2 required, larger than 10^8 sec^{-1}, makes this unlikely. The behavior is thought to be a result of spectral diffusion, caused either by F-center diffusion: exchange of an F center with one of its 12 nearest neighbor Cl^- ions, or by thermal ionization of the F electron, with spectral diffusion enhanced by quantum-mechanical exchange of free and F center electrons. The saturation data are analyzed on a model of random spectral diffusion,[2] appropriate to the above mechanisms: the resonant frequency of a bound electron, determined by hyperfine interaction with nearby nuclei, is assumed uncorrelated, after a sudden diffusion event, with its initial value. In this case, saturation measurements in the transition range can give the spectral diffusion rate ω_D. This analysis of the data above 470° is consistent with extrapolated values of the spin-lattice relaxation rate ω_1 measured by Feldman et al.[3] The numerical rate and activation energy differ, above 470°C, from those obtained on a simpler analysis. A value $\omega_D = 2 \pm 0.5 \times 10^6$ rad/sec is obtained at 500°C. Between 470° and 550° the activation energy is estimated as $U = 1.45 \pm 0.2$ eV. This large value, and the independence of ω_D on the F-center concentration, favor the mechanism of F-center diffusion.

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[2] E. L. Wolf, Bull. Am. Phys. Soc. 10, 306 (1965).

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201 The Calculation of the Electronic Structure of Lattice Defects in Ionic Crystals*

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We have been developing and using a model for the calculation of the electronic structure, including the associated lattice distortion, of point defects and excitons in ionic crystals. The inclusion of lattice distortion or relaxation makes it possible to calculate the differences between the wave functions and energy levels of the absorbing and emitting states self-consistently within the framework of the model. The model involves a combination of quantum mechanical methods and methods of classical ionic crystal theory. Most of the calculations carried out thus far have considered the detailed electronic structure of only those ions which are nearest neighbors to the defect or are at the defect site (in the case of the excitons). More distant ions, besides having attractive and repulsive interactions with each other, are allowed to be polarized by the defect in a self-consistent manner.

The model will be described briefly, but the results of calculations which have been or are in the process of being carried out with it will be emphasized. For the F center, these include optical (absorption and emission) properties, configuration coordinate and lattice relaxation curves, thermal ionization energies, etc. For the exciton, they include information about the electronic structure of the exciton states and their relaxation in alkali halides. A two-stage relaxation process in which the exciton states just before emission are identical to the states formed when a V_K center captures an electron will be discussed. Various calculated properties of the U center in alkali halides and of the hydrogen interstitial in CaF_2, SrF_2, and BaF_2 will be presented if time permits.

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202 Sidebands to the Infrared Absorption Peak Due to Localized Modes of U Centers in Alkali Halide Crystals*

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Hydrogen or deuterium ions introduced substitutionally into an alkali halide crystal give rise to infrared-active localized vibration modes whose frequencies lie far above the maximum frequency of the perfect host crystal. The observed impurity induced infrared absorption spectra exhibit a prominent peak at the localized mode frequency and two bands symmetrically disposed on either side of the central peak. The central peak has been previously interpreted as due to one (localized mode) phonon absorption processes.

We present a general theory of the sidebands based on two-phonon processes involving a localized mode phonon and a continuum mode phonon, taking account of coupling mechanisms due to both the cubic anharmonicity and the second order electric moment.

The theory is applied to the case of U centers in potassium iodide, using a deformation dipole model for the perfect host crystal and a modified mass defect model for the impurity. The latter is assumed to interact through central short-range forces with its nearest neighbors only. The comparative contributions from the two mechanisms have been estimated by only taking into account the cubic anharmonicity of the overlap potential and the second order distortion electric moment due to the overlap forces.

It has been found for the higher frequency sideband that the ratio of the anharmonic contribution to the second order electric moment contribution is a monotonically decreasing function of the frequency whose value is of the order of 10^3 near the localized mode frequency ω_0 and 10 at the frequency $\omega_0 + \omega_L$ where ω_L is the maximum frequency of the perfect host crystal. The spectrum calculated at 4.2°K is in excellent agreement with Timusk's[1] experimental data regarding the frequencies of the various maxima but shows some discrepancy about their relative magnitudes.

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[1] T. Timusk and M. V. Klein, see Abstract No. 189.

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203 The Thermodynamics of M-Center Formation

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Several attempts have been made previously to establish the stoichiometry of the reaction between F and M centers by means of measurement of their equilibrium concentrations.[1, 2, 3] In no case, however, were the observed concentrations actually proven to be characteristic of thermodynamic equilibrium at a known temperature.

We report here an experiment in which F centers in additively colored KCl crystals were brought to equilibrium with M centers in complete darkness at temperatures between 60 and 110°C. Below 60°C, the time for attainment of equilibrium was excessive; above 110°C the equilibrium concentration of M centers was too small for reliable measurement. F-aggregate centers other than M centers were removed initially by quenching from 200°C. The existence of equilibrium at a given temperature was proven by approaching the equilibrium point from both under- and over-saturation with respect to M centers.

Curves of log α_F vs. log α_M, where α is the maximum absorption coefficient measured at equilibrium, had an average slope 1.88, in reasonable agreement with the slope expected if two F centers are used to form one M center. ΔH^0 for the process

$$2F = M$$

was found to be -4.0 kcal (-0.18 eV), from the variation of $K = n_M/n_F^2$ with temperature. At 363°K, taking the standard state as 1 center cm^{-3}, the following values were also obtained:

$$K = 1.0 \times 10^{-19}\ \text{cm}^{-3},\ \Delta G^0 = 31.5\ \text{kcal},\ \Delta S^0 = -98\ \text{cal deg}^{-1}.$$

The entropy change agrees with the configurational entropy change calculated statistically for the formation of one M center from two F centers. If N is the concentration of negative ion sites,

$$\Delta S^0 = R \ln 6/N = -103\ \text{cal deg}^{-1}.$$

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[2] C. Z. van Doorn, Phys. Rev. Letters 4, 236 (1960).

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204 The Electronic Structure of the O_2^- Center

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Using O^{17} enriched oxygen the hyperfine structure of the paramagnetic resonance of the $(O^{17}-O^{16})^-$ centers and $(O^{17}-O^{17})^-$ centers in KCl, KBr and KI has been studied. The tensor of the hyperfine interaction expressed in Mcps is given in the following table. The internuclear axis is designated by z, and the x axis is taken along the lobes of the p function of the unpaired electron.

	A_{xx}	A_{yy}	A_{zz}
KCl	189.0	0	55.2
KBr	181.3	0	71.1
KI	184.1	0	64.0

The results confirm the model proposed by Cohen and Känzig[1] according to which the unpaired electron is in a $^2\pi_g$ state. The Hamiltonian of the hyperfine interaction can be written as

$$\begin{aligned}\mathcal{H}_{\mathrm{hfs}} = \gamma_e\gamma_n\Big[&\left(8\pi/3\,|\psi(0)|^2 + 4/5\langle 1/r^3\rangle_s\right)\sqrt{\Delta^2/(\Delta^2+\lambda^2)}\;I_xS_x\\ &+\left(8\pi/3\,|\psi(0)|^2 - 2/5\langle 1/r^3\rangle_s\right)\sqrt{\Delta^2/(\Delta^2+\lambda^2)}\;I_yS_y\\ &+\left(8\pi/3\,|\psi(0)|^2 - 2/5\langle 1/r^3\rangle_s + 2\langle 1/r^3\rangle_l\sqrt{\lambda^2/(\Delta^2+\lambda^2)}\right)I_zS_z\Big]\end{aligned}$$

Here λ designates the spin-orbit coupling parameter and Δ the orthorhombic crystal field parameter of reference (1). The values of

$$\sqrt{\Delta^2/(\Delta^2+\lambda^2)} \quad\text{and}\quad \sqrt{\lambda^2/(\Delta^2+\lambda^2)}$$

can be taken from the analysis of the g factor.[1]

The subscripts s and l refer to the spin density and orbital moment density, respectively. Using for $\langle 1/r^3\rangle_s$ and $\langle 1/r^3\rangle_l$ the experimental values for the $^3P_2$ state of the O^{17} atom as quoted by Bessis et al.[2] the thus calculated anisotropic component of the hfs tensor agrees within a few percent with our measurements. The isotopic component corresponds to a value of $|\Psi(o)|^2$ of $1.65 \times 10^{-24}\mathrm{cm}^{-3}$, which can be explained by an admixture of about 3% 2s character.

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205 Color Centers in Alkaline Earth Fluorides

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The stable four-band spectra (580, 400, 335, 225 mμ) normally reported in irradiated CaF_2 is due to a $4d^1$ electron trapped at an yttrium impurity in a cation site. Ionizing radiation converts the non-charge compensated Y^{3+} to Y^{2+}. Pure SrF_2 and BaF_2 exhibits no coloration when subjected to irradiation. Coloration in CaF_2 decreases as the Y concentration. An ultra-pure Vinor Laboratory CaF_2, containing less than parts per billion of Y, was found to be highly resistant to coloration. Absorption coefficients less than 0.01 cm^{-1} were measured after the crystals had been subjected to 10^7 rad of 3MeV electron irradiation. This is better than a factor of 10 smaller than the best crystal reported.[1] Irradiated SrF_2 and BaF_2 doped with YF_3 possess the same bands as $CaF_2(Y)$; however, all the bands shift to longer wavelengths, as the lattice constant increases. Isoelectronic ions, such as $Ti^{3+}(3d^1)$ and $La^{2+}(5d^1)$, exhibit similar absorption spectra as $Y^{2+}(4d^1)$ in CaF_2. Except for the case of Ti^{3+}, irradiation is necessary to trap the single d electron at the impurity ion. These data are consistent with the fact that all trivalent rare earth ions can be reduced to their divalent state in CaF_2. No color centers analogous to the F center in the alkali halides were observed.

* Work supported by the National Science Foundation.

† Operated with support from the U.S. Air Force.

[1] J. R. O'Connor and J. H. Chen, Phys. Rev. **130**, 1790 (1963).

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206 Thermoluminescence and Dynamical Jahn-Teller Effects in Irradiated Calcium Fluoride Containing Yttrium

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Coloration of CaF_2 by ionizing radiation has been shown to be due to the trapping of an electron at Y^{3+} sites. Yttrium is a common impurity in fluorite. Normally the extra positive charge of Y^{3+} is compensated by a F^- interstitial. The number of these associated pairs decreases as their separation increases. Upon irradiation, electrons and holes are trapped at Y^{3+} and F^- sites, respectively. Radiative recombination has been observed in terms of thermoluminescent spectra from the first five nearest pairs. Therefore, the remaining Y^{2+}, in essentially cubic sites, are more stable.

EPR measurements indicate an isotropic resonance with $g = 1.971$ above 20°K. At 4.2°K an axial resonance with $g_{\parallel} = 2.00$ and $g_{\perp} = 1.958$ is observed, corresponding to a tetragonal contraction of the lattice.

The behavior of the optical spectra[1] as a function of temperature is also commensurate with the interpretation that the $4d^1$ electron is coupled to the tetragonal and orthorhombic normal modes of the lattice, giving rise to a dynamical J-T effect. This results in the lifting of the degeneracy of the e_g and t_{2g} levels.

* Supported by the National Science Foundation.

† Operated with support from the U.S. Air Force.

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207 ENDOR and ESR Investigation of the S_3^- Sulphur Center in Potassium and Sodium Chloride

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Schneider et al.[1] have found that alkali halide crystals, which have been heated for a long time near their melting point under high pressure sulphur or selenium vapor, show a characteristic ESR spectrum with orthorhombic ⟨110⟩ -symmetry. We have performed ENDOR measurements on such KCl:S and NaCl:S crystals and ESR measurements on $KCl:S^{33}$ (11.56% enriched). The results are:

1. The ENDOR spectra in both KCl:S and NaCl:S show a strongly anisotropic hyperfine and quadrupole interaction with chlorine neighbors. The principal axes are near to z = [001] (center axes z = [001], y = $[1\bar{1}0]$) with a small tilt towards the [111] -direction. Interaction constants (in Mc/s):

$$a/h = 3.94 \quad b/h = 1.54 \quad q/h = 1.6 \quad \varphi \approx 7^\circ \begin{pmatrix}\text{tilting}\\ \text{angle}\end{pmatrix} \quad Cl^{35} \text{ in KCl:S}$$

$$a/h = 9.96 \quad b/h = 3.14 \quad q/h \approx 2 \quad \varphi \approx 6^\circ \quad Cl^{35} \text{ in NaCl:S}$$

2. In NaCl:S an interaction with sodium is resolved. Its principal axis is also near to z = [001], but this time slightly tilted in an oblique direction. Interaction constants:

$$a/h = 6.54 \quad b/h = 0.83 \begin{pmatrix}\text{detectable deviation}\\ \text{from axial symmetry}\end{pmatrix} q/h \approx 0.16 \quad \varphi \approx 7^\circ$$

3. The ESR linewidth in NaCl:S is consistent with the assumption of an interaction with two equivalent Cl-nuclei (1) and four equivalent Na-nuclei (2).

4. The ESR spectrum of $KCl:S^{33}$ shows hyperfine splittings due to one S^{33}-nucleus (I) and two equivalent S^{33}-nuclei (II). Both interactions are almost purely anisotropic with principal axes in [001]-direction. The splittings in this direction are $A_I = 53$ G and $A_{II} = 18$ G. This is in good agreement with results obtained by Schneider et al.,[1] for the analogous selenium centers.

We think that the only model which can explain these facts is a bent S_3^- molecule-ion (angle ≈ 90°) occupying a corresponding KCl_2^- or $NaCl_2^-$ trivacancy. The plane of the molecule is (001). The unpaired electron is localized in a p_π -orbital formed of the sulphur atomic p -orbitals perpendicular to this plane.

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[1] J. Schneider, A. Räuber, and B. Dischler: private communication.

208 Multiplication of Electron Excitations and Formation of Color Centers in Ionic Crystals

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1. The spectra of F-center formation for NaCl–Tl, KCl–Tl, NaBr–Tl, KBr–Tl and KI–Tl crystals in the spectral region 4–21 eV were investigated. The intensity of activator emission accompanying the optical ionization of F centers was considered as a measure of the number of F centers.

2. The comparison of the F-center formation spectra and absorption spectra of ionic crystals leads to the conclusion that F centers are created by electrons released from Tl^+-centers, as well as by excitons and by electron-hole pairs.

3. F centers are generated in NaCl–Tl crystals by ultraviolet radiation in two stages. The first stage reaches the saturation in a short time. At the second stage the number of F centers increases approximately linearly with the irradiation time.

4. The change of photon energy from $h\nu < 2E_g$ to $h\nu > 2E_g$ (E_g — the band gap) causes a sharp increase in the efficiency of F-center formation. It is due to the creation of two electron-hole pairs by one photon. This effect has been examined in detail in NaCl.

5. The phenomenon of photon multiplication by crystals in the optical region was observed for photon energies $h\nu > 2E_g$. One photon of ultraviolet radiation creates two photons of activator emission.[1]

6. The examination of the kinetics of F-centers formation and the excitation of activator emission by photons with $h\nu > 2E_g$ leads us to the conclusion that one such photon generates two electron-hole pairs in close proximity.

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ЦЕНТРЫ ОКРАСКИ В ЩЕЛОЧНО-ГАЛОИДНЫХ КРИСТАЛЛАХ

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