

IVAR KUUSIK

Soft X-ray spectroscopy of insulators



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- I. Kuusik, I., Käämbre, T., Kooser, K., Kikas, A. Electronic structure of LBO and BBO as revealed by boron and oxygen RIXS spectra (2013) *Journal of Electron Spectroscopy and Related Phenomena*, 188, pp. 32–37.
- II. Kukli, K., Dimri, M. C., Tamm, A., Kemell, M., Käämbre, T., Vehkamäki, M., Puttaswami, M., Stern, R., Kuusik, I., Kikas, A., Tallarida, M., Schmeißer, D., Ritala, M., Leskelä, M. Structural and magnetic studies on iron oxide and iron-magnesium oxide thin films deposited using ferrocene and (dimethylaminomethyl) ferrocene precursors (2013) *ECS Journal of Solid State Science and Technology*, 2 (3), pp. N45–N54
- III. V. Yu. Ivanov, V. A. Pustovarov, A. Kikas, T. Käämbre, I. Kuusik, M. Kirm and E. I. Zinin Vacuum ultraviolet and X-ray emission spectroscopy of anion and cation excitons in oxide crystals (2012) *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques* 6 (1), pp. 100–105
- IV. Kuusik, I., Käämbre, T., Kooser, K., Pustovarov, V., Ivanov, V., Kuk, E., Kikas, A. The sub-bandgap energy loss satellites in the RIXS spectra of beryllium compounds (2011) *Journal of Electron Spectroscopy and Related Phenomena*, 184 (7), pp. 366–370.

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Pärna, R., Joost, U., Nõmmiste, E., Käämbre, T., Kikas, A., Kuusik, I., Hirsimäki, M., Kink, I., Kisand, V. Effect of different annealing temperatures and SiO₂/Si(100) substrate on the properties of nickel containing titania thin sol-gel films (2012) *Physica Status Solidi (A) Applications and Materials Science*, 209 (5), pp. 953–965.

Pärna, R., Joost, U., Nõmmiste, E., Käämbre, T., Kikas, A., Kuusik, I., Hirsimäki, M., Kink, I., Kisand, V. Effect of cobalt doping and annealing on properties of titania thin films prepared by sol-gel process (2011) *Applied Surface Science*, 257 (15), pp. 6897–6907.

Kikas, A., Käämbre, T., Kooser, K., Kuusik, I., Kisand, V., Nõmmiste, E., Kirm, M., Feldbach, E., Ivanov, V., Pustovarov, V., Martinson, I. Resonant inelastic X-ray scattering and UV-VUV luminescence at the Be 1s edge in BeO. (2010) *Journal of physics. Condensed matter*, 22 (37), 375505.

Author's contribution

Papers I, IV. Participated in the experimental work. The author is responsible for the data analysis, figures and the manuscript.

Paper III. Participated in the experimental work.

Paper II. Participated in the XAS measurements. The author contributed to the XAS data analysis and interpretation.

I. INTRODUCTION

Most people know that X-rays are in everyday use because of their good imaging properties – for example medical imaging, tomography and quality control in the different industries. However the fact, that spectroscopy with X-rays is also possible and fruitful, is less known. Contrary to optical spectroscopy, which was already in use before X-rays were discovered, X-ray spectroscopy is even younger still.

In 1901 Röntgen received the first ever Nobel Prize in physics for his discovery of the X-rays. Since then science and technology have much benefited from this radiation. X-ray emission from matter was studied soon after the discovery of this radiation.

1909 Barkla and Sadler discovered characteristic X-rays of atoms. Barkla receives the Nobel Prize in physics in 1917 for his work on X-rays. In 1913 father and son Bragg built the first X-ray spectrometer (based on a NaCl crystal). Later they earned the Nobel Prize in Physics of 1915 for their services in the analysis of crystal structure by means of X-rays. The same year Henry Moseley establishes the relation between atomic number and the specific X-ray wavelength of elements (Moseley's law) which is the cornerstone of X-ray fluorescence spectroscopy. The Nobel Prize in physics of 1924 was awarded to Manne Siegbahn for his discoveries and research in the field of X-ray spectroscopy. Manne's son, Kai Siegbahn, was a pioneer of X-ray photoelectron spectroscopy and also a Nobel Prize in physics recipient.

X-ray diffraction was discovered in 1912 by von Laue, Friedrich, and Knipping. The 1914 Nobel Prize in physics was awarded to von Laue for this discovery. Although discovered a little later than X-ray emission, initially X-ray diffraction had more practical value than X-ray spectroscopy – one of the first applications of X-rays was in crystallography, the technique is known as X-ray diffraction (XRD). Structural information from simple crystals like CuSO_4 to complex biomolecules like haemoglobin can be found by XRD.

While the invention and utilization of the X-ray techniques of diffraction and photoemission were awarded with Nobel Prizes, Maurice de Broglie's first observation of an (X-ray) absorption edge in 1913 and the subsequent invention of X-ray absorption spectroscopy, were not [1].

The optical analogue of resonant inelastic X-ray scattering (RIXS) – Raman scattering – was feasible immediately at the time of its discovery (the Nobel Prize of 1930 was awarded to Raman for this discovery), while resonant inelastic X-ray scattering (the main spectroscopic technique under focus in this thesis) experiments became possible only with the use of synchrotron radiation in the 1980s. The pioneering modern experiment of RIXS (also called resonant X-ray Raman scattering or resonant X-ray emission) was conducted in 1976 [2]. However subjectively, the interesting results started coming only in the 1980s.

To physicists X-rays are light with shorter wavelength and higher photon energies than visible light. X-rays are very sensitive to the electron densities in

matter, can be used to distinguish between different chemical elements and can be used to “look into” the bulk of matter. For these and many other beneficial properties of X-rays, spectroscopy with X-rays is able to provide rich information about matter. The spectroscopic use of X-rays is mostly used in the different fields of science – geology, physics, chemistry and environmental science.

Intense and monochromatic (i.e. limited spectral bandwidth) X-rays are needed for spectroscopy. The development of synchrotron radiation sources in the past 20 years has revolutionized the different X-ray spectroscopies like X-ray absorption spectroscopy (XAS), near edge X-ray absorption spectroscopy (NEXAFS), extended X-ray absorption fine structure (EXAFS), X-ray photoelectron spectroscopy (XPS), X-ray emission spectroscopy (XES), resonant Auger electron spectroscopy (RAES) and resonant inelastic X-ray scattering because of the unique properties on synchrotron radiation.

We are still learning about X-rays more than 100 years after Röntgen’s original discovery – Riccardo Giacconi received the Nobel Prize in physics in 2002 for his pioneering contributions to astrophysics, which have led to the discovery of cosmic X-ray sources.

2. THEORETICAL TREATMENT

The relationship between spectroscopy and physics is well known. Most spectroscopic methods probe the electron structure of matter thus they enable better understanding of physics. Spectroscopic techniques use interactions between particles to probe the electronic structure and the energy distribution of different states in matter. Spectroscopic methods allow the determination of chemical, physical, nuclear and mechanical properties on matter. Consequently, spectroscopy is nowadays one of the most powerful tools in modern physics.

Also, advances in spectroscopy and its discoveries will enhance our understanding and theories about matter. For example, the measurement of the hydrogen spectrum by Anders Jonas Ångström in Uppsala, which was described by the famous Balmer series, was very important for the birth of quantum mechanics [3].

The wavelengths of X-rays are approximately from 20nm to 0.1 Å (0.01nm). The spectral range just below the X-rays is called the (vacuum) ultraviolet (VUV) band. As the wavelengths and energies of X-rays span many orders of magnitude, the X-rays are usually further divided into soft and hard X-rays. Soft X-rays have energies less than 1 keV (kilo-electronvolts) and wavelengths longer than 1nm (these two definitions don't agree exactly). Hard X-rays span the rest of the X-ray scale up to gamma rays. However, the distinction between hard X-rays and gamma rays is rather vague.

The interaction of radiation with matter can be divided into three categories: absorption, emission and scattering. Absorption is the transfer of the photon energy to the atoms or molecules of matter that leads to rotational, vibrational or electronic excitations or to electron emission (ionization) in the vacuum ultraviolet or the X-ray spectral range. Emission is the reverse process of absorption. Scattering can be thought of absorption followed by emission in the simplest case. Scattering is said to be elastic when the scattered particle (electron, neutron, photon) has the same energy as the incident particle. Otherwise the scattering is said to be inelastic.

When the term “resonance” is used in (X-ray) spectroscopy it means that the energies of the incoming X-rays are equal to some transition energy of the atoms under study – for example the minimum energy required to remove one of the two innermost electrons of beryllium, boron, carbon, oxygen and silicon are around 112, 188, 284, 530 and 1839 eV (electronvolts) respectively. The binding energy differences between (adjacent) elements are quite large; therefore resonances in the X-ray regime are highly element specific. The absorption and scattering intensities are also greatly enhanced on resonance. The exact resonance energy is dependent on the chemical environment of the elements.

In X-ray spectroscopy, it is customary to label atomic core levels (also called shells) $n=1, 2, 3, 4, \dots$ with letters K, L, M, N,

The typical processes associated with X-rays are shown in Figure 1. In the case of XAS, the absorption cross section is monitored as a function of incident X-ray energy. In case of XPS and AES the electrons emitted from the sample are monitored as a function of their energy. And in the case of XES, the X-rays emitted from matter are registered as a function of their energy (or wavelength). Therefore all of these common X-ray spectroscopies need different experimental equipment.

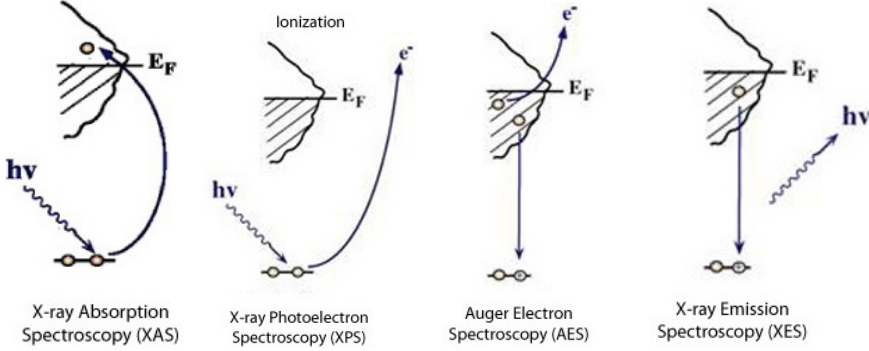


Figure 1. Principles of some important X-ray spectroscopies. XAS, XPS, AES and XES. Figures used with permission from ref [4].

In both XAS and core-level XPS, a core-hole is present in the final state. The subsequent de-excitation or decay of the core-hole can take place via two competing mechanisms: X-ray emission or Auger electron emission (Auger decay). For light elements (low Z) the Auger process is dominant and the X-ray emission has generally a very low yield. For heavier elements (high Z) and higher energies X-ray emission gradually becomes stronger.

This thesis focuses on soft X-ray XAS and RIXS.

2.1. Mathematical background

The theoretical description of X-ray spectroscopy starts with the Dirac Hamiltonian of an electron (eq. (1.1)) in the Gaussian system of units (CGS):

$$H = c\alpha \cdot \left[\left(p - \frac{e}{c} A \right) + \beta mc \right] + V \quad (1.1)$$

Here α and β are the Dirac matrices and A is the vector potential describing the electromagnetic fields, c is the speed of light. The electron momentum operator is denoted by p , its charge by e (elementary charge) and the rest mass is m . V is the potential of the nucleus and the other electrons combined (the so

called central potential or Hartree-Fock approximation). Since the energies involved are much smaller than the electron rest mass mc^2 (511 keV) the use of the non-relativistic approximation to the Dirac Hamiltonian (accurate to order $1/c^2$) is possible [5]:

$$H = \frac{[(p - \frac{e}{c}A]^2}{2m} + \frac{p^4}{8m^3c^2} - \frac{e\hbar}{mc} s \cdot B - \frac{e\hbar}{2m^2c^2} s \cdot (E \times (p - \frac{e}{c}A)) + V + \frac{e\hbar^2}{8m^2c^2} \nabla \cdot E \quad (1.2)$$

Here $\hbar$ is the Planck constant and s is the electron spin operator. The second term is the first relativistic correction to the energy and can be neglected in the soft X-ray regime. The third term describes the interaction of the spin with the magnetic field (B) and is responsible for the Zeeman effect. However this effect is not under study in this thesis. The fourth term represents the spin-orbit interaction and is very important in core level spectroscopy. The fourth term also describes magnetic scattering, but its intensity is small in the X-ray regime and it will be neglected [6]. For the radiation fields considered here the last term vanishes due to $\nabla \cdot E = 0$, however because of the electric field (E) of the nucleus this term describes a relativistic energy correction (the Darwin correction term) to s symmetry orbitals. Using the Coulomb gauge $\nabla \cdot A = 0$ the first term can be expanded:

$$\frac{[(p - \frac{e}{c}A]^2}{2m} = \frac{p^2}{2m} - \frac{e}{mc} A \cdot p + \frac{e^2}{2mc^2} A^2$$

Neglecting the spin-orbit interaction for the moment, the interaction due to the radiation is therefore given by:

$$H' = \frac{e^2}{2mc^2} A^2 - \frac{e}{mc} A \cdot p \quad (1.3)$$

Incredibly these two interaction terms (called the A^2 and the Ap term respectively) explain most of the optical and X-ray spectroscopies like XAS, XPS, RIXS and XRD.

In most cases the field of the radiation acting on the electron(s) is weaker than the field of the nucleus, the interaction due to the radiation can then be taken as a perturbation. According to Fermi's golden rule of time-dependent perturbation theory, the number of transitions per unit time (transition rate w) from the initial state to the final state is then proportional to:

$$w_{if} = \frac{2\pi}{\hbar} \left| \langle f | H' | i \rangle + \sum_n \frac{\langle f | H'_1 | n \rangle \langle n | H'_2 | i \rangle}{\hbar\omega - (E_i - E_n) - \frac{n}{2}} \right|^2 \delta(E_f - E_i - (\hbar\omega_1 - \hbar\omega_2)) \quad (1.4)$$

Here i refers to the initial state, n is the intermediate state, f is the final state, $\hbar\omega_1$ and $\hbar\omega_2$ refer to the incoming and outgoing photon energies respectively, Γ_n is the width of the intermediate state, the delta function ensures energy conservation. If there are many final states in close energy proximity (or even a continuum) the delta function is replaced by the density of states function. The contributions from all participating electrons should be included, but for simplicity only one electron (one electron picture) is described throughout this chapter. The principles discussed in this chapter apply also to spectroscopy of solids, if the independent particle approximation is made and the Bloch wavefunctions are used. It should also be kept in mind, that the electron states in solids are crystal momentum (and spin) dependent. However, the simplest case is considered in this work.

After expansion of the perturbation (H') there are 4 terms – the two interaction terms working in first and second order perturbation theory. The A_p term in first order gives an absorption or emission process with one participating photon, while in second order it describes Raman or X-ray scattering.

The A^2 interaction term describes elastic scattering (Thomson scattering) and non-resonant inelastic X-ray Raman scattering for hard X-rays. In a non-relativistic treatment, the A^2 interaction term is also responsible for Compton scattering [7]. The distinction between the (A^2) elastic, inelastic and Compton scattering is to do with the ratio of the X-ray and electron momentum. When the photon momentum is small compared to the electron momentum then Thomson scattering dominates. As the X-ray energy and momentum increase (compared to the electron momentum) so does the intensity of the Compton scattering. Due to relativistic effects both the Thomson and Compton scattering become less effective at very high photon energies.

The fourth possibility – second order perturbation of the A^2 term involves already 4 photons and this will not be pursued.

The transition rate covered so far is not a good physical quantity, because it is not normalized to the excitation intensity. The cross section describes the system under study much better and is defined as the transition rate (transitions per unit time) normalized to excitation intensity. This can be done by either normalizing to the number of incident photons (n) or their energy (intensity). The transition rate divided by number of photons unit per area per unit time (n) is used here:

$$\sigma = \frac{w}{n} \quad (1.5)$$

The incoming photon flux is also related to the magnitude of the classical vector potential through $\left|A_1\right|^2 = \frac{2\pi\hbar c}{\omega_1} n$, with ω_1 denoting their angular frequency.

When the final state involves the emission of a photon or an electron which both have a continuous energy spectrum the transition rate to some specific final state f does not make too much sense. The transition rate is then integrated over the final states in the energy range dE . Consequently, the cross section is multiplied by the density of states for the scattered photon in the scattered direction (solid angle $d\Omega$) and energy range (dE).

The normalization to the scattered photons can be done using the fact that the magnitude of the vector potential of a single photon (normalized to volume

V , angular frequency ω_2) is $\left|A_2\right| = \sqrt{\frac{2\pi\hbar c^2}{V\omega_2}}$ [8], which is also the normalization

factor for the vector potential written using the creation (a) and annihilation (a^+) operators of photons:

$$A(r, t) = \sum_{k, \alpha} \sqrt{\frac{2\pi\hbar c^2}{V\omega_k}} (a_{k\alpha} e^{ikr} e^{-i\omega_k t} \varepsilon_{\alpha} + a_{k\alpha}^{\dagger} e^{-ikr} e^{i\omega_k t} \varepsilon_{\alpha}^*) \quad [9]. \quad \text{Here } \alpha$$

denotes one of the possible two perpendicular polarizations of the waves. However, the second quantization formalism will not be pursued in this thesis.

Thus the general formulas for the cross section and the density of final states are given by:

$$d\sigma = \frac{w^* d\rho(E)}{n} \quad (1.6)$$

$$d\rho(E) = \frac{V^* \omega_2^2}{(2\pi)^3 \hbar c^3} dE d\Omega$$

2.1.1. Ap interaction term in first order perturbation

The absorption (emission) of X-rays is described by the first order Ap term [7] and the transition rate is:

$$\begin{aligned} w_{if} &= \frac{2\pi}{\hbar} \left| \left\langle f \left| \frac{e}{mc} A \cdot p \right| i \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega) = \\ &= \frac{2\pi}{\hbar} \frac{e^2}{m^2 c^2} |A|^2 \left| \left\langle f \left| e^{ikr} \varepsilon \cdot p \right| i \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \end{aligned} \quad (2.1)$$

The light wave is taken to be a plane wave with amplitude A and the spatial part of $e^{ikr} \cdot \varepsilon$, ε is the polarization unit vector of the wave. For near-threshold X-rays the dipole approximation $e^{ikr} \approx 1$ is very good as $kr \ll 1$. If the electronic energy part of the Hamiltonian is local then the momentum (p) operator of the electron is simply proportional to the electron coordinate r [6, 7]. This is also known as transferring the matrix element from the velocity form to length form. The resulting expression is usually referred to simply as a (electric) dipole transition:

$$w_{if} = \frac{2\pi}{\hbar} \frac{e^2 \omega^2}{c^2} |A|^2 \left| \left\langle f \left| \varepsilon \cdot r \right| i \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \quad (2.2)$$

For emission of photons by excited atoms the final state involves a photon and therefore normalization to the photon density of states should be done. The differential cross section is:

$$\frac{d\sigma}{d(\hbar\omega)d\Omega} = \frac{e^2 \omega^3}{2\pi \hbar c^3} \left| \left\langle f \left| \varepsilon \cdot r \right| i \right\rangle \right|^2 \delta(E_f - E_i - \hbar\omega) \quad (2.3)$$

Because of this relationship, sometimes the measured spectra are sometimes divided by $E^3 = (\hbar\omega)^3 \sim \omega^3$ to obtain spectra proportional to the transition matrix element [10–14], which often is of primary interest. However, due to the narrow emission energy range, which is of most interest in the present work, this has not been done.

In the case of X-ray absorption the final state involves a photoelectron in the continuum. In this case the normalization to the photoelectron density of states and the incoming photon flux should be done and the differential cross section is:

$$\frac{d\sigma}{dE d\Omega} = \frac{e^2 m^2 \omega}{2\pi \hbar c^3} |v| \left| \left\langle f \left| \varepsilon \cdot r \right| i \right\rangle \right|^2 \delta(E_k + E_b - \hbar\omega) \quad (2.4)$$

In this nonrelativistic formula v is the photoelectron velocity. The final and initial state energy difference is replaced by the so called binding ($\approx$ ionization) energy E_b – the energy required to create the core-hole that is present after the absorption of light – plus the photoelectron kinetic energy E_k . By definition, the ionization energy of the i 'th state is the minimum energy required to remove this electron from the atom. According to the Koopmans theorem the ionization energy is just the orbital energy of the corresponding electron. Therefore the binding energies give information about the electron orbitals of the system or in case of solids the binding energies reflect the band structure. This is the underlying principle of XPS.

Accounting for also the energy required to remove an electron from a solid – work function Φ – the delta function actually represents the Einstein formula for photoemission:

$$E_k = \hbar\omega - E_b - \Phi \quad (2.5)$$

This formula is used to calculate the binding energies of electrons after measuring their kinetic energy E_k and is the basis of XPS.

Most of the information about the system under study is given by the matrix elements of type $\langle b | \epsilon \cdot r | a \rangle$ in eq. (2.2) and eq. (2.3). Although the a or b can be some of the valence or conduction band states and can have many different symmetries it is important to point out that if either of the states connected by the dipole operator involves a core level then the so-called dipole selection rules apply. This is because of the fact that the core levels have well-defined and definite atomic-like symmetry due to their strong localization and small overlap with valence states. This means that, for example, the probability of reaching the Ti^{4+} ion d-symmetry states from the 1s core level (K edge) is small, but large for the absorption around Ti 2p edge (L edge). Also, in the case of X-ray emission spectra of boron atoms, the spectra reflect mostly the boron 2p derived states and the boron 2s derived states are suppressed. This is also the reason why valence emission spectra represent the local partial density of states (DOS) based on dipole selection rule governing the radiative transition of a valence electron “dropping” to fill a core-hole [14].

2.1.2. A^2 interaction term

Next the transitions induced by the A^2 interaction term are considered. The A^2 operator describes both two-photon absorption and emission. It also describes the absorption and subsequent emission or vice versa of a photon by an electron. The A_1 and A_2 describe the incoming and outgoing waves (photons) involved in the scattering.

$$w_{if} = \frac{2\pi}{\hbar} \left| \left\langle f \left| \frac{e^2}{2mc^2} (A_1 + A_2)(A_1 + A_2)^* \right| i \right\rangle \right|^2 \delta(E_f - E_i - (\hbar\omega_1 - \hbar\omega_2)) =$$

$$\frac{2\pi}{\hbar} \left| \left\langle f \left| \frac{e^2}{2mc^2} (A_1 A_1^* + A_1 A_2^* + A_2 A_1^* + A_2 A_2^*) \right| i \right\rangle \right|^2 \delta(E_f - E_i - (\hbar\omega_1 - \hbar\omega_2)) \quad (3.1)$$

Therefore there will be 4 different terms that contribute (after squaring):

$$|A_1|^4 + |A_2|^4 + |A_1|^2 |A_2|^2 + |A_2|^2 |A_1|^2$$

The first and second will be neglected, as they are captured by the third or fourth term when $A_1=A_2$. The third and fourth term describe absorption followed by emission or vice-versa. Quantum mechanics and symmetry arguments predict that both sequences are possible and equally probable. To account for this symmetry only one of those is used and the matrix element is multiplied by two. The transition rate is:

$$w_{if} = \frac{2\pi}{\hbar} \left(\frac{e^2}{mc^2} \right)^2 |A_1|^2 |A_2|^2 \left| \left\langle f \left| e^{ik_1 r} e^{-ik_2 r} \varepsilon_1 \cdot \varepsilon_2 \right| i \right\rangle \right|^2 \delta(E_f - E_i - (\hbar\omega_1 - \hbar\omega_2)) =$$

$$\frac{2\pi}{\hbar} \left(\frac{e^2}{mc^2} \right)^2 |A_1|^2 |A_2|^2 \varepsilon \left| \left\langle f \left| e^{iqr} \right| i \right\rangle \right|^2 \delta(E_f - E_i - (\hbar\omega_1 - \hbar\omega_2)) \quad (3.2)$$

The q vector is called the momentum transfer vector and describes the “kick” to the electronic system during scattering and is equal to the difference of the wave vectors ($q=k_1-k_2$) describing the incoming and outgoing photons.

The polarizations of the two photons involved is described with $\varepsilon = (\varepsilon_1 \cdot \varepsilon_2)^2$.

Applying the dipole approximation leads to

$$w_{if} \approx |\langle f | i \rangle|^2 \approx \delta_{if}$$

Because of the orthogonality of the electronic states $\langle \Psi_f | \Psi_i \rangle = \delta_{if}$ the A^2 interaction term cannot induce dipole transitions. The A^2 interaction term

involves two photons so it can not produce one photon transitions. Therefore it is more important in the hard X-ray regime where multipole transitions are possible. It forms the basis for X-ray Raman scattering and non-resonant inelastic X-ray scattering.

The next term in the expansion of the e^{iqr} exponent is iqr .

$$w_{if} = \frac{2\pi}{\hbar} \left(\frac{e^2}{mc^2} \right)^2 |A_1|^2 |A_2|^2 \varepsilon |\langle f | e^{iqr} | i \rangle|^2 \delta(E_f - E_i - (\hbar\omega_1 - \hbar\omega_2)) \quad (3.3)$$

The matrix element of the resulting expression is quite similar to the dipole absorption formula above (2.2) with q replacing ε [15]. In fact, X-ray Raman scattering can provide similar (and more) information as X-ray absorption spectroscopy.

To obtain the non-resonant inelastic X-ray scattering differential cross section, normalization to the final states and the incident flux has to be done:

$$\frac{d\sigma_{inelastic}}{d(\hbar\omega_2)d\Omega} = \left(\frac{e^2}{mc^2} \right)^2 \frac{\omega_2}{\omega_1} \varepsilon \sum_f |\langle f | e^{iqr} | i \rangle|^2 \delta(E_f - E_i - (\hbar\omega_1 - \hbar\omega_2)) \quad (3.4)$$

The matrix element under discussion is called the dynamic structure factor. The dynamic structure factor is also a convolution of the initial and final electron states in momentum space [16].

$$S(q, \omega) = \sum_f \left| \langle f | e^{iqr} | \Psi_0 \rangle \right|^2 \delta(E_f - E_0 - (\hbar\omega_1 - \hbar\omega_2)) = \sum_f \left| \int \Psi_f(p-q) \Psi_0(p) dp \right|^2 \delta(E_f - E_0 - (\hbar\omega_1 - \hbar\omega_2)) \quad (3.5)$$

The A^2 interaction term is also responsible for most of the elastic X-ray scattering (Thomson scattering) when $A_1=A_2$.

$$\frac{d\sigma_{elastic}}{d(\hbar\omega)d\Omega} = \left(\frac{e^2}{mc^2} \right)^2 \varepsilon \left| \langle \Psi_0 | e^{iqr} | \Psi_0 \rangle \right|^2 \quad (3.6)$$

The square of the elastic scattering matrix element involved is called the atomic form factor (also Patterson function) and is the Fourier transform of the ground state electron density – i.e the momentum distribution. For a crystal with periodic electron density the overall scattering intensity depends on both the properties of the individual scattering atom and the discrete reciprocal lattice vectors. The well-know Bragg diffraction law is recovered [5]. If it were possible to experimentally measure the phase of the scattered photon then the

ground state electron density would be simply the inverse Fourier transform of the results of the scattering experiment. In reality however, due to several constraints and symmetries, the electron density can be found even without the phase information. Therefore elastic scattering described by the A^2 interaction term is the basis of XRD.

The characteristic cross section for the A^2 scattering is therefore on the order of the classical electron radius squared $\sigma \sim r^2 \sim \frac{e^4}{m^2 c^4}$ or about $10^{-29} m^2$ per electron – much smaller than the size of a typical atom.

To illustrate the elastic scattering due to the A^2 interaction term, the analytically calculated atomic form factor of the hydrogen atom is presented in Figure 2. Generally the form factor depends on the orientation of the scattering atom and momentum transfer vector, but for spherically symmetric atoms like noble gases for example, only the dependence on the momentum transfer remains. Both theory and experiment confirm that the matrix element describing elastic scattering falls off as the momentum transfer q is increased and its general shape is very similar [17]. This is the reason why at the same scattering angle the elastic scattering of lower energy photons is stronger compared to higher energy photons (for example hard X-rays). In fact, lower wavelength radiation is scattered coherently by all the electrons of the atom(s) and the atomic form factor equals the number of electrons in the atom.

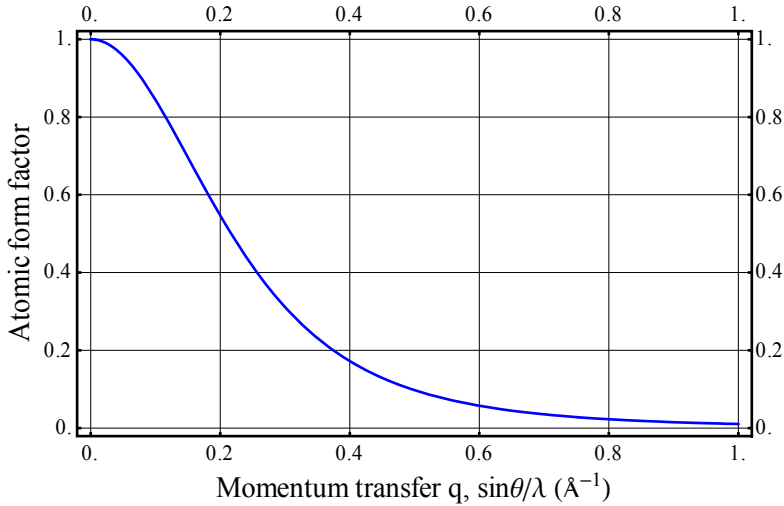


Figure 2. Calculated atomic form factor of hydrogen in the 1s state.

2.1.3. Ap interaction term in second order perturbation

The Ap interaction term in second order perturbation theory describes the focus of this thesis – RIXS. The formula (4.1) is also called the Kramers-Heisenberg formula.

$$w_{if} = \frac{2\pi}{\hbar} \left| \sum_n \frac{\langle f | \frac{e}{mc} \mathbf{A}_2 \cdot \mathbf{p}_2 | n \rangle \langle n | \frac{e}{mc} \mathbf{A}_1 \cdot \mathbf{p}_1 | i \rangle}{\hbar \omega - (E_i - E_n) - \frac{i\Gamma}{2}} \right|^2 \delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2)) =$$

$$\frac{2\pi}{\hbar} \left(\frac{e}{mc} \right)^4 |A_1|^2 |A_2|^2 \left| \sum_n \frac{\langle f | e^{ik_2 r} \varepsilon_2 \cdot \mathbf{p}_2 | n \rangle \langle n | e^{ik_1 r} \varepsilon_1 \cdot \mathbf{p}_1 | i \rangle}{\hbar\omega_1 - (E_i - E_n) - \frac{i\Gamma}{2}} \right|^2 \delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2)) \quad (4.1)$$

The two matrix elements involved in the expression describe absorption and emission of light. The absorption and emission of a photon are time-reversal mirror processes of one-another, their mathematical description is very similar [18]. Therefore the expression above is very similar to two-photon absorption (emission) or classical Raman scattering. Due to symmetry reasons another similar term should be present in the formula (basically A_1 and A_2 reversed), however because it describes a process where a (X-ray) photon is emitted before one is absorbed, its intensity is marginal [19].

As explained before, the dipole approximation is a good approximation in the soft X-ray regime. The resonant scattering rate is then given by:

$$w_{if} = \frac{2\pi}{\hbar} \left(\frac{e}{mc} \right)^4 |A_1|^2 |A_2|^2 \left| \sum_n \frac{\langle f | \varepsilon_2 \cdot \mathbf{p}_2 | n \rangle \langle n | \varepsilon_1 \cdot \mathbf{p}_1 | i \rangle}{\hbar\omega_1 - (E_i - E_n) - \frac{i\Gamma}{2}} \right|^2 \times$$

$$\delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2)) \quad (4.2)$$

The differential cross section for RIXS can now easily be found:

$$\frac{d\sigma_{RIXS}}{d(\hbar\omega_2)d\Omega} = \left(\frac{e^2}{mc^2} \right)^2 \frac{1}{m^2} \frac{\omega_2}{\omega_1} \left| \sum_n \sum_f \frac{\langle f | \varepsilon_2 \cdot \mathbf{p}_2 | n \rangle \langle n | \varepsilon_1 \cdot \mathbf{p}_1 | i \rangle}{\hbar\omega_1 - (E_i - E_n) + \frac{i\Gamma}{2}} \right|^2 \times$$

$$\delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2)) \quad (4.3)$$

The matrix elements can also be written in the length form:

$$\frac{d\sigma_{RIXS}}{d(\hbar\omega_2)d\Omega} = \left(\frac{e^2}{mc^2}\right)^2 m^2 \omega_1 \omega_2^3 \left| \sum_{f,n} \frac{\langle f | \varepsilon_2 \cdot r_2 | n \rangle \langle n | \varepsilon_1 \cdot r_1 | i \rangle}{\hbar\omega_1 - (E_i - E_n) - \frac{i\Gamma_n}{2}} \right|^2 \delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2)) \quad (4.4)$$

If the interference between different scattering channels can be neglected the order of summation and squaring can be interchanged. This scattering is then called a two-step process because the cross section is basically the product of two factors – the matrix elements describing the absorption and emission (4.5). The general formula (4.3) also includes interference terms and is the so-called one-step RIXS process.

$$\frac{d\sigma_{direct}}{d(\hbar\omega_2)d\Omega} = \left(\frac{e^2}{mc^2}\right)^2 \frac{1}{m^2} \frac{\omega_2}{\omega_1} \sum_{f,n} \frac{\langle f | \varepsilon_2 \cdot p_2 | n \rangle^2 \langle n | \varepsilon_1 \cdot p_1 | i \rangle^2}{\left(\hbar\omega_1 - (E_i - E_n)\right)^2 + \frac{\Gamma_n^2}{4}} \delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2)) \quad (4.5)$$

The interference terms represent the interference between different scattering channels and are given by eq. (4.6) [20]. For simplicity, it is assumed that all intermediate states have the same width $\Gamma_i = \Gamma$.

$$\begin{aligned} \frac{d\sigma_i}{d(\hbar\omega_2)d\Omega} &= \left(\frac{e^2}{mc^2}\right)^2 \frac{1}{m^2} \frac{\omega_2}{\omega_1} \times \\ &\times \sum_f \sum_{n' \neq n} \frac{2 \langle f | \varepsilon_2 \cdot p_2 | n' \rangle \langle n' | \varepsilon_1 \cdot p_1 | i \rangle \langle f | \varepsilon_2 \cdot p_2 | n \rangle \langle n | \varepsilon_1 \cdot p_1 | i \rangle}{\left(\hbar\omega_1 - (E_i - E_{n'})\right) \left(\hbar\omega_1 - (E_i - E_n)\right) + \frac{\Gamma^2}{4}} \times \\ &\times \delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2)) \end{aligned} \quad (4.6)$$

The matrix elements can have both positive and negative values, therefore the interference contribution can add to or subtract from certain scattering channels. Due to the so-called optical theorem [21], interference is unable to change the total intensity, it can only redistribute the intensity between different scattering channels.

The resonant behaviour of RIXS is mathematically due to the denominator which “blows up” when the incident photon energy $\hbar\omega_i$ is close to the energy difference of the initial and intermediate state $E_i - E_n$.

The polarization and symmetry dependence and sensitivity of RIXS is due to the properties of the matrix elements and wave vectors in eq. (4.3). RIXS also conserves energy, spin [20] and (crystal) momentum. However, symmetry and momentum sensitivity can be greatly reduced or disappear altogether in real systems because of numerous dephasing, mixing and relaxation processes. All

of this can give valuable information about the system under study. Some examples (and references) are given in chapter 4.3.3.

Therefore the total scattering rate of soft X-rays is given by A^2 interaction term in first order and the Ap term in second order.

$$w = \frac{2\pi}{\hbar} \left| \left(\frac{e^2}{mc^2} \right) \left| A_1 \right| \left| A_2 \right| \left| \langle f | e^{iqr} | i \rangle \right| + \left(\frac{e}{mc} \right)^2 \left| A_1 \right| \left| A_2 \right| \sum_n \frac{\langle f | \varepsilon_2 \cdot p_2 | n \rangle \langle n | \varepsilon_1 \cdot p_1 | i \rangle}{\hbar\omega_1 - (E_i - E_n) - \frac{i\Gamma}{2}} \right|^2 \times \quad (4.7)$$

$$\delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2))$$

As explained before, the inelastic scattering of soft X-rays caused by the A^2 term is negligible, therefore only the elastic part is retained. Often it is also possible to separate the elastic and inelastic parts by assuming they are not interfering with one another. With these approximations the total scattering cross section is the sum of these two channels.

$$\frac{d\sigma_{tot}}{d(\hbar\omega_2)d\Omega} = \left(\frac{e^2}{mc^2} \right)^2 \varepsilon \left| \langle i | e^{iqr} | i \rangle \right|^2 + \quad (4.8)$$

$$+ \left(\frac{e^2}{mc^2} \right)^2 \frac{\omega_2}{\omega_1} \frac{1}{m^2} \left| \sum_{f,n} \frac{\langle f | \varepsilon_2 \cdot p_2 | n \rangle \langle n | \varepsilon_1 \cdot p_1 | i \rangle}{\hbar\omega_1 - (E_i - E_n) - \frac{i\Gamma}{2}} \right|^2 \times$$

$$\times \delta((E_f - E_i) - (\hbar\omega_1 - \hbar\omega_2))$$

Here the first term represents the elastic scattering and the second term explains the RIXS spectrum itself.

So far the description of the scattering process has been in the energy or frequency representation. Heisenberg's uncertainty principle relates the excited

state lifetime to the broadening (Γ) $\tau = \frac{\hbar}{\Gamma}$. The time of the scattering process

can be found in the time-dependent picture. It is found [21] that the duration of the scattering process is dependent of the detuning of the incident photon energy from the resonance energy $-\Omega = \hbar\omega_1 - (E_i - E_n)$.

$$T = \frac{\hbar}{\sqrt{\Gamma^2 + \Omega^2}} \quad (4.9)$$

Thus the scattering time decreases as the excitation energy is tuned away from the resonance. Using this result some important phenomena in RIXS can be explained as will be shown in chapter 4.3.3.

3. SOFT X-RAY SPECTROSCOPY: EXPERIMENTAL CONSIDERATIONS

Having established the underlying theoretical principles of the X-ray spectroscopies their application and experimental considerations are discussed.

3.1. Synchrotron radiation

Synchrotrons are dedicated electron storage rings with their associated accelerators built for generating synchrotron radiation (SR). SR is generated whenever relativistic particles undergo transverse acceleration. Modern synchrotron laboratories use straight sections where dedicated insertion devices are inserted that “wiggle” (bend) the electron beam multiple times strongly – wigglers – or weakly but more coherently – undulators.

Synchrotrons have proven to be powerful tools for a huge number of applications in science and technology. It is the only intense light source tuneable in the range from IR to hard X-rays, roughly a factor of 10^6 energy difference. Nowadays synchrotrons can offer light with high intensity, high degree of collimation, very high brightness, high spatial resolution and high spectral resolution, known (variable) polarization and high photon flux for spectroscopy and diffraction experiments. Also very important for spectroscopy is the possibility to change energy (wavelength) [22]. These advantages lead SR to be a better source than any other in the energy range not (directly) accessible with lasers.

Two very important properties of SR are due to relativistic effects. Namely the forward focussed small radiation cone (angle) and the fact that relativistic electrons traversing a lattice with a spacing on the order of a cm (10^{-2} m, λ_u in Figure 3) emit light with a wavelength on the order of nm (10^{-9} m) is due to several relativistic effects working together.

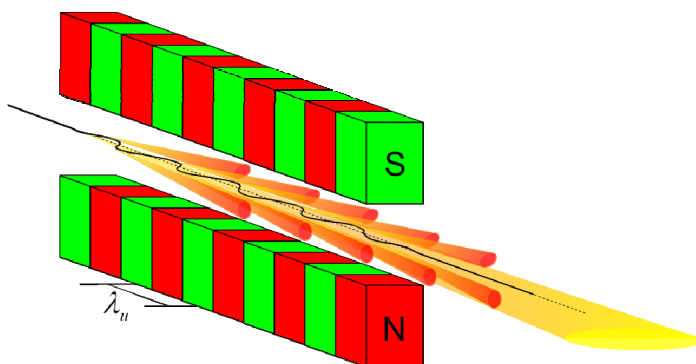


Figure 3. Undulator schematic. The red and green cubes represent magnetic poles, the black line depicts the electron trajectory through the undulator and the orange and yellow represent the emitted synchrotron light.

Detailed information about synchrotrons and SR can be found in [23].

All soft X-ray experiments discussed in this work were done on synchrotrons.

3.2. Beamline I511 at MAX-lab

In order to take advantage of the emitted synchrotron radiation in performing experiments, it has to be guided to a specialized experimental station, where samples under investigation are illuminated. For RIXS experiments it is also necessary to limit the spectral bandwidth of the radiation hitting the sample, i.e. to monochromatize. In the case of an undulator the synchrotron light is already relatively narrow with an absolute width in the order of some electron volts, depending on the tuned energy and the used undulator harmonic. All this is accomplished by a beamline, which consists of a series of high precision optical elements, which direct, monochromatize and focus the radiation onto the sample [3].

The absorption of soft X-ray light by materials is relatively high and correspondingly the reflection at normal incidence extremely low. However, since the index of refraction is slightly less than unity for all materials in the (soft) X-ray range, total external reflection can be used, if sufficiently small incidence angles relative to the surface are employed. Therefore all mirrors (and gratings), which are used as optical elements in a soft X-ray beamline have to be used at grazing incidence angles, i.e. at glancing angles [3]. This means that focusing mirrors with a large radius have to be used, which also means that the overall length of the beamline is large (tens of meters).

Various synchrotron radiation beamlines are designed for different user purposes. In the soft X-ray regime, synchrotron radiation is typically monochromatized by grazing incidence grating monochromators. Generally, grating monochromators are classified based on the shape of the grating, such as toroidal, planar (PGM) and spherical grating monochromators. The different shape gratings used in the monochromators can play different roles in focusing the radiation on samples [3]. Most monochromators for soft X-rays are of plane or spherical grating type. The resolving power is usually used to describe the resolution of a grating monochromator, defined as $R = \lambda/\Delta\lambda$, where λ is the wavelength, $\Delta\lambda$ is the separation of two wavelengths resolved [22].

At beamline I511 of the MAX II storage ring at MAX-lab National Laboratory at Lund University (in Lund, Sweden) a 49 period undulator with a period length of $\lambda_u = 52$ mm is employed as the light source providing linearly polarized photons in the horizontal plane of the laboratory. The undulator light is collected and horizontally focussed by a cylindrical mirror towards the monochromator, which consists of three optical elements. Before illuminating the plane grating the light is further redirected by a plane mirror and after the grating the diffracted light is focused by a spherical mirror towards the exit slit.

Monochromatization of the SR is achieved by a PGM type monochromator of the Zeiss SX700 design covering an effective energy range of 100–1200 eV with one standard grating of 1220 lines/mm. The required photon energy is selected by rotating the plane grating and thereby changing the wavelength, which is dispersed perpendicular to the exit slit. The resolving power of the monochromator is adjustable through the exit slit widths [3]. For the beamline I511 the resolving power can be varied to as high as 10 000 [24] but the normal working mode is around $R \sim 2000$. Behind the monochromator exit slit the I511 beamline splits into two branches with specialized end-stations. The branch used in the presented investigations, I511–3, is dedicated to bulk-sensitive spectroscopy of solids and liquids. A flippable mirror situated directly behind the monochromator exit slit is used to direct the light to one of the end stations. Both branch lines are equipped with refocusing optics, consisting of a so called Kirkpatrick-Baez pair of bendable plane-elliptical mirrors giving a beam spot size at the sample of ca. $20\mu\text{m} \times 30\mu\text{m}$ in vertical and horizontal direction, respectively [3].

The third generation SR facilities can generate radiation with very high brightness (up to 10^{21} photons per second per mm^{-2} per mrad^{-2} (0.1% bandwidth)-1) in this spectral range. However, the photon flux on a sample at the end station can reach as high as 10^{12} – 10^{15} photons/s, depending on resolution and energy. All of the optical elements of the beamline and the X-ray beam itself need to be kept in ultrahigh vacuum ($\sim 10^{-10}$ Torr) owing to the high absorption of air in the soft X-ray region, as well as, to avoid contamination from carbon and oxygen [3].

The soft X-ray emission and resonant inelastic X-ray scattering spectra, presented in the investigations of this thesis, were measured with a Gamdata Scienta XES-350 Rowland type grazing incidence soft X-ray spectrometer. The spherical diffraction grating of a Rowland type spectrometer achieves both the wavelength dispersion and the focusing in a single step. Focusing is achieved if source and detector are placed together with the spherical grating on a circle with half the radius of the grating. Two spherical gratings of 5 and one of 3 meters radius (Figure 4) possess different groove densities (1200, 400 and 300 lines/mm) as well as different grazing incidence angles (1.9, 2.6 and 5.4), respectively to cover an energy range of 50–1000 eV [3]. The spectrometer can be operated with an input slit and in the so-called “slitless” mode where the incidence beam (spot) becomes the optical source and the slit is fully opened.

The prototype of the soft X-ray spectrometer with three gratings is described in [25]. The Scienta XES-300 spectrometer is described in [26]. An overview of beamline I511 at MAX-lab and the X-ray spectrometer can also be found in [3].

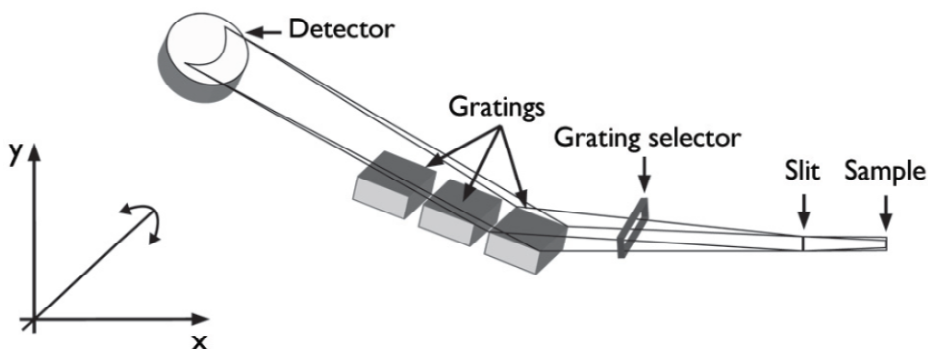


Figure 4. X-ray spectrometer schematic. Figure courtesy of VG Scienta.

3.3. XAS

X-ray absorption spectroscopy studies the intensity of absorption of X-ray photons as a function of the incident photon energy. XAS is generally characterized by many fine spectral features near the absorption edge. In principle, an X-ray absorption spectrum can be distinguished into two parts:

1. The so-called “edge region”, which is extended over about 10 eV from the threshold towards higher energies (NEXAFS, near edge X-ray absorption fine structure). X-ray absorption near edge structure (XANES) refers to the fine structure about 50 eV around the edge [27]. However often these two terms are used synonymously.

The physical origin of the X-ray absorption features in this edge region is different in various classes of matter, Rydberg states in atoms, bound valence states (or bound multiple scattering resonances) in molecules, core excitations in ionic crystals, many-body singularities in metals, bound atom-like localized excitations in solids, etc [22].

2. The region of the photoelectron scattering at higher energies (from 50–1000eV above the edge [27]), which is called the EXAFS (extended X-ray absorption fine structure).

The initial state in the X-ray absorption process is usually the ground state of matter, while the final state is a core excited electronic state – a state with a partially empty core level. Because these measurements involve the excitation of electrons from a core level to partially filled and empty states, the peak positions and spectral line shapes in an XAS spectrum are directly related to the unoccupied electronic states of matter. However, since the corresponding matrix element involves both the initial and final states (eq. (2.2)), initial state information is also present. For example, the spin-orbit splitting of core levels (for example p and d core states) is also observed in the XAS spectra.

“True” XAS spectra (spectra that directly relate to the X-ray absorption cross-section) can be obtained in thin-film transmission experiments. However,

XAS is mostly measured with yield experiments, since transmission experiments in the soft X-ray range often require impractically thin or dilute samples. Thus, XAS spectra are often obtained by measuring either the electron or fluorescence yield as a function of incident photon energy.

3.3.1. XAS measurements in yield mode

Based on the kinetic energies, the electron yield measurement in XAS can be carried out in three ways: Auger electron yield, partial electron yield and total electron yield (TEY). The main difference among the three methods is the relative sensitivity to surface and bulk compositions [22]. The bulk sensitivity of each electron yield method is limited by the mean free path of electrons, which is determined by their kinetic energy.

Auger yield is a technique of high surface sensitivity in the soft X-ray region. TEY method measures the yield of all photoelectrons and Auger electrons, in practice this is usually done by measuring the sample current for conducting samples. The signal in TEY is dominated by the low energy electrons. Thus TEY typically is a technique for sampling the range up to 50–100Å from the surface.

Another way of obtaining XAS is to monitor the radiative decay of core-holes. In the total fluorescence yield (TFY) measured and given as a function of the incident X-ray photon energy.

A simple mathematical model describes the yield signal strength of a thick and flat sample [28] as follows:

$$I_Y(E_1, E_2) \sim I_0 \gamma(E_1) \frac{\mu_Y(E_1)}{\mu_t(E_1) + \mu_t(E_2) \frac{\cos \alpha}{\cos \beta}} \quad (5.1)$$

Here I_0 denotes the incoming X-ray flux, E_1 is the incident X-ray energy, E_2 is the fluorescence photon (or electron) energy, γ is the fluorescence (or electron) quantum yield, α is the incidence angle of the X-rays and β is the escape angle of the detected photon (or electron). Therefore, the yield signal from a thick sample is proportional to the absorption coefficient μ_Y that represents the cross sections for all the processes that the detector is able to record (the specific absorption coefficient), divided by the total absorption coefficient μ_t . The absorption coefficient μ is defined through the Beer-Lambert law:

$$I = I_0 e^{-\mu x} \quad (5.2)$$

Here I_0 denotes the intensity of the wave at distance $x=0$ (for example at the sample surface in case of incidence X-rays).

A number of assumptions have to be made to show in which cases the yield signal is proportional to the absorption coefficient. First, the quantum yield γ must be assumed to be energy independent, then it can be normalized (out) as one can do with the incoming photon flux I_0 . If the first term in the denominator becomes much smaller than the second term then the signal can be approximated as:

$$I_Y(E_1, E_2) \sim \frac{\mu_Y(E_1)}{\mu_t(E_2) \frac{\cos \alpha}{\cos \beta}} \quad (5.3)$$

This condition is enhanced in the case when the incidence X-rays are incident parallel to the surface normal and the detector is at grazing angles to the surface ($\alpha \approx 0$, $\beta \approx 90^\circ$). Now the third assumption has to be made – the absorption coefficient $\mu_t(E_2)$ of the detected fluorescence (or electrons) with energy E_2 varies much slower over the energy range of interest than the absorption coefficient of the incident X-rays with energy E_1 . In that case a signal proportional to $\mu_Y(E_1)$ is obtained. The final assumption that the total cross section is proportional to the partial absorption coefficient – $\sigma_t(E_1) \sim \mu_t(E_1) \sim \mu_Y(E_1)$ – is usually a good one, since the cross section and the absorption coefficient are related through the atomic density ρ_a – number of atoms per unit volume:

$$\mu = \sigma \rho_a \quad (5.4)$$

In the case that the second term in the denominator of eq. (5.1) becomes smaller than the first term then the signal can be approximated as:

$$I_Y(E_1) \sim \frac{\mu_Y(E_1)}{\mu_t(E_1)} \approx \text{const} \quad (5.5)$$

Therefore in that case contrast in the spectra is lost or diminished. This condition is more likely in the measurement geometry in which grazing incident X-rays produce secondary photons or electrons that escape parallel to the surface normal ($\alpha \approx 90^\circ$, $\beta \approx 0^\circ$). It is also possible that the different absorption coefficients $\mu_Y(E)$ and $\mu_t(E)$ can have a very similar energy dependence over the energy region of interest, in which case they cancel and contrast in the spectrum is lost. The manifestation of this in the spectra is called the saturation effect. Even if it is not possible to eliminate the saturation effect, it can be possible to calculate the absorption coefficient of interest by measuring the yield in different geometries [29].

The measured TFY or TEY spectra are not strictly fully proportional to the total absorption coefficient for several reasons. First, the thickness of sample probed depends on the relative penetration depth (attenuation length) of the

incident photons and the escape depth of the emitted electrons (in the case of electron yield) or photons (in the case of fluorescence yield). As the attenuation length varies over an absorption edge, it is possible for the attenuation length to approach the electron escape depth, leading to saturation effects in the TEY and distorting the measured spectra. In the case of TFY measurements of concentrated species, both the total X-ray absorption coefficient and the absorption due to the edge of interest vary strongly, leading to distortions of the spectra referred to as saturation effects or as self-absorption effects. Second, the magnitude of the electron and fluorescence yields both depend on the relative probability, that an excited atom will decay by emitting photons as opposed to electrons. This relative probability differs from atom to atom and edge to edge and is generally not known with great precision. Third, the emission is distributed over a range of electron and photon energies. A given detector will not detect all electron or photon energies with equal efficiency. In addition, the quantum efficiency of the electron yield process (the number of electrons emitted per incident photon) will also vary with photon energy [30].

However, in practice TEY usually gives a spectrum, which is almost equivalent to XAS [22]. This is mainly due to the much larger penetration (escape) depth and smaller absorption coefficient of the incident X-rays compared to the ejected electrons. Therefore the second assumption and eq. (5.3) hold. The third assumption holds because the TEY signal is dominated by (low-energy) secondary electrons.

3.4. XPS, XES and RIXS

X-ray emission can be observed when a core-hole is present in matter. The hole can be created by X-ray absorption, X-ray scattering, electron scattering or some other process. The photon emission is then observed resulting from electronic transitions from occupied (valence) levels to the core vacancy. The emission process cross section is given by eq. (2.3). The initial state in the X-ray emission process is a core excited electronic state and the final state has this initial core-hole filled by an electron from some other state (the valence band), leaving a hole there.

As already mentioned, the emission and absorption of X-rays are reverse processes of one-another. Therefore emission spectra mostly give information about the occupied states. However, since the corresponding matrix element involves both the initial and final states, initial state information is also present. For example, the spin-orbit splitting of core levels (if present, for example p and d core states) is also observed in the valence XES spectra.

XPS and XES both give information about the occupied states. The matrix element of the cross sections of XES and XPS (eq. (2.3) and (2.4)) looks similar. However, one important difference is that the final state of XES is a (valence) hole with definite symmetry, while the final state of XPS is a (core or valence) hole and the photoelectron. This state can have any possible symmetry

due to the involvement of the continuum. XES transitions obey the dipole selection rules for angular momentum and spin. XES is therefore symmetry sensitive and gives information on the partial (local) density of states (PDOS) i.e. states of particular symmetry [14, 31]. For example, if a K vacancy is filled in a valence to core-hole X-ray transition the emission reflects the p density of states of the valence band. Correspondingly, an L core-hole gives rise to an X-ray spectrum that reflects the s and d character of the valence band. Thus, XES is able to decompose the occupied density of states into different core-hole symmetries [31]. Valence band photoemission spectra on the other hand, mostly reflect the total density of states (TDOS) with all symmetries included.

One of the important practical differences between XES and electron spectroscopy is that XES has a larger probe depth, since typically soft X-rays can penetrate (and escape) as deep as a few hundred nm into a solid. The escape depth of the photoelectrons is in the order of 5 nm in XPS or AES. In practice, when measuring electron spectra, this means that the surface of the sample has to be clean on almost a monolayer level, which can be difficult to achieve. The escape depths of X-rays are much larger (hundreds of nm) therefore X-ray emission is (more) bulk sensitive.

The second important practical difference between the two is that while electron spectra from solids have a continuous multiple scattering contribution, the Compton scattering produces a background only in the hard X-ray region. Therefore, (soft) X-ray emission spectra have almost no multiple scattering background. The third important practical difference between XES and electron spectroscopy is the ability to measure insulators. Namely, the tendency of sample charging when studying nonconductive samples, means that special measures have to be taken to obtain the correct spectra, for example: measuring very thin films or nanoparticles, pressing the sample to conductive matrix, using an extra electron flood gun to discharge the sample. XES does not suffer from this limitation. Another important advantage of photon-out spectroscopies is that photons are unaffected by electric and magnetic fields, which makes for example magnetization studies possible. However, the signal strength, the spectrometer efficiency (collecting angle and transmission) and resolution are usually much better in XPS. Therefore XPS spectra can be obtained in less time.

XES can also be observed with electron or ion excitation but with X-ray excitation the distinction between XES and RIXS needs some clarification because their experimental measurement is similar. Since RIXS is a resonant technique, as the excitation energy is increased or decreased far from the resonance the intermediate states are no longer bound states but photoionized states with an outgoing photoelectron. The two step picture is then already valid and because the photoionization dipole matrix element far from the edge or resonance is a rather slowly varying function of the incident energy, the absorption and emission become decoupled from one-another (see also eq. (4.3) and (4.5)). The result is that, very little change in the XES spectra is observed when the incidence X-ray energy is varied. In other words, the shape of the

XES spectra is assumed to be excitation energy and mode (how the core-hole is created) independent, while this may not be the case for RIXS. Therefore, it is possible to observe RIXS near resonances and absorption edges, elsewhere normal X-ray emission is seen. The different spectroscopies are also pictured on Figure 5.

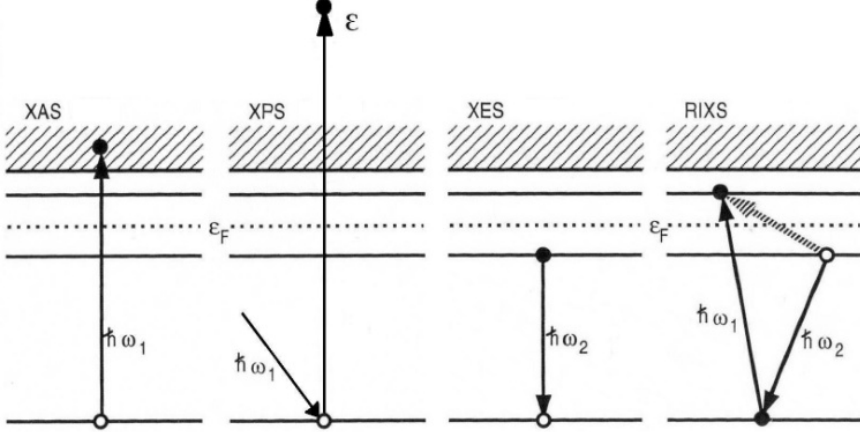


Figure 5. X-ray absorption spectroscopy (XAS), X-ray photoemission spectroscopy (XPS), X-ray emission spectroscopy (XES) and resonant inelastic X-ray scattering (RIXS). $\hbar\omega_1$ denotes the incoming photon (with energy $\hbar\omega_1$), $\hbar\omega_2$ is the emitted photon (energy $\hbar\omega_2$), ε represents the photoelectron.

Another important difference between XAS, XPS, XES and RIXS is the achievable energy resolution. Namely, the energy resolution of XAS, XPS and XES will be limited by the core-hole width or lifetime broadening. The final state of those spectroscopies is a core-hole with a width of Γ , therefore all lines are broadened by Γ . In the case of RIXS and resonant Auger spectroscopy however, there must not be a core-hole in the final state and therefore they do not suffer this limitation. The experimentally studied final state of RIXS is usually a valence excitation (valence hole), which can have a well-defined energy (it can be much narrower than a core-hole), therefore the achievable resolution of RIXS is more limited by the experimental setup and/or solid state broadening than anything else. In fact, under appropriate conditions, it is also possible to obtain the unbroadened (sharper) X-ray absorption spectra (NEXAFS) by measuring X-ray emission intensity at a particular energy (narrow fluorescence yield mode) [32]. The high achievable resolution is also the reason why new X-ray spectrometers are being designed and developed and the research field is quite promising for the future.

As shown by the gray arrow on Figure 5, the one-step RIXS process can also be considered to be a two-photon transition across the band gap i.e. a valence excitation or a valence to conduction band transition. The energy loss in a RIXS process is related only to the difference between the initial and final states.

Therefore in the first approximation, the minimum energy loss is equal to the band gap of the material.

Similarly to XAS, XES and RIXS may also suffer from the so-called self-absorption effects – i.e the emitted X-ray fluorescence may again be (selectively) absorbed. When the strength of this self-absorption effect is not highly energy-dependent (for example, normal emission) then this will not cause considerable distortions in the measured spectra. However, when there is a strong absorption resonance at some emission energies of interest then the self-absorption effect can cause considerable distortions in the emission spectra. In the spectra considered in this work self-absorption is neglected.

3.5. Core excitons

A very important phenomenon in X-ray spectroscopy is an electronic state that is called a core exciton. It arises when a core electron in a solid is excited to a localized state. The molecular or atomic origin or analogy of the core exciton is a Rydberg state. It is important to realize that the core exciton is a two-particle state – both the core-hole and the excited electron have to be created at the same time. The core exciton can be created by photons, electrons or other charged particles (protons, ions). Because the core-hole is localized to a particular atom, the existence of a core-hole (and/or a localized charge) breaks the symmetry of the crystal [33]. Thus excitons can also be regarded as isolated impurities in an otherwise periodic system. This means that the existence or strength of the core exciton cannot be calculated in the one electron (or simple band structure) model [34]. For example, the core exciton in graphite influences other atoms up to five coordination spheres [35].

However, not all core orbitals in all solids have an associated core exciton. When the excited electron is not sufficiently localized or trapped by the core-hole potential, the electron will become itinerant (i.e a Bloch state), in which case no core exciton can exist. In fact, most core edges and solids do not display a core exciton. For example, in metallic Na the 3s orbitals of one atom overlap those of many neighbouring atoms. When a core-hole is created by removing one of the inner electrons from the Na atom the 3s orbital contracts but they still overlap with the neighbouring atoms [35] and the core-hole potential is unable to “trap” or localize the excited electron. However in the Na halides (NaCl) where the 3s orbital is empty (Na^+) the 3s state can form an exciton with the 2p hole [36]. Thus generally, core excitons are not expected in metals, but rather in semiconductors and insulators.

The binding energy relative to the conduction band minimum is the most important characteristic of a core exciton. The binding energies are roughly around 1 eV, but can reach values as high as 4.2 eV for alkali halides [36]. Larger binding energies imply a higher degree of localization (smaller radius). Like any other atomic-like states, the core exciton also has a definite symmetry. This is an important distinction, as will be discussed in the following sections.

Experimentally core excitons can often be observed (identified) in the NEXAFS spectra. For example the spectra shown in Figure 9 all exhibit strong and sharp peaks near the absorption edge (threshold). This is the primary condition for the existence of the core exciton state. However for simple metals like Na and Al there is little doubt that no true exciton forms, but instead a dynamic screening of the core-hole leads to enhancement of the threshold intensity in both XAS and XES as remnant of “metallic exciton” [35]. A very distinct π^* resonance (exciton) peak can also be seen in the N 1s NEXAFS spectra of LiNO_3 [37]. The core exciton peak can also be weaker like in diamond and be merged with conduction band states (diamond and graphite, see chapter 4.3.1).

It may be possible to observe emission from the core exciton. That can also be possible with electron beam excitation – without the need for synchrotron radiation. Also, the existence of the core exciton may also be seen in the optical/VUV emission (yield) spectra as the incident energy is scanned across the core exciton state [Paper III].

An important subject in RIXS (and also resonant Auger spectroscopy) is the so-called spectator and participator emission (decay). In the participator process the excited electron recombines with the core vacancy, which means that the final electronic state of this process is in the first approximation the electronic ground state (or a valence hole in case of RAES). In the RIXS spectator process one of the valence electrons fills the core vacancy while the excited electron remains in the excited state. Thus the final state after the spectator emission is a valence hole and an excited electron (illustrated on Figure 6). The presence of the spectator electron can change the energy of the (spectator) emission spectra due to screening effects [14].

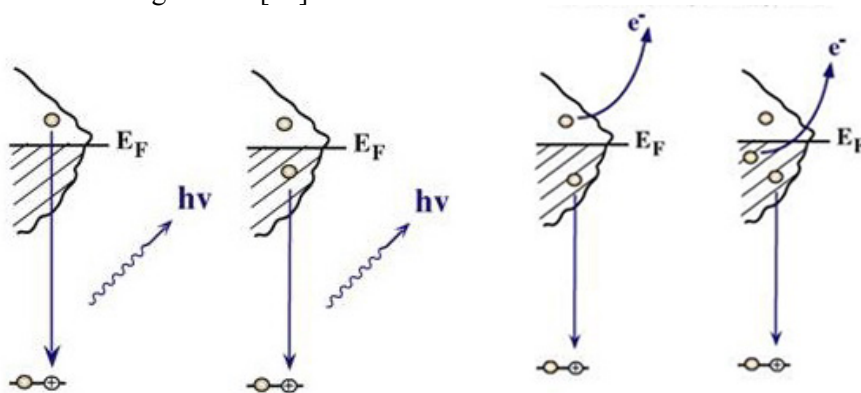


Figure 6. From left to right: participator X-ray emission, spectator X-ray emission, participator Auger decay, spectator Auger decay. Figures used with permission from ref [4].

Core excitons have been observed in many borates, graphite, diamond, BeO , MgO , Al_2O_3 , SiO_2 and in many alkali halides.

3.6. XAS of (3)d compounds

Sharp peaks in the NEXAFS spectra can also be found in the transition metals (probably also f-metals like lanthanides and actinides) NEXAFS spectra. However, these should not be confused with core excitons, as the binding is not achieved by the core-hole effect. As an example, we consider TiO_2 , in which the Ti^{4+} ion should behave as $3d^0$ system – the 3d level should be totally empty in the ground state. In case of $\text{Ti } 2p \rightarrow 3d$ NEXAFS, the final state should include only one 3d electron, therefore the mutual interactions between 3d electrons would not complicate the picture. The results of some previous work on sol-gel prepared TiO_2 thin films [38–40] is discussed here. The more complicated case of iron oxides is considered later.

One of the aims of the studies was to find out how do different dopants of TiO_2 influence the properties of TiO_2 thin films. The sol-gel prepared films were annealed at different temperatures to crystallize the material.

The NEXAFS spectra of Co-, Ni-doped and undoped titania are shown in Figure 7. The rich peak structure near the 2p absorption edge is evident. These peaks are due to absorption to 3d states that are energetically situated in the conduction band, but still have localized character.

The Ti L edge absorption spectra show 4 well separated strong peaks. In pure LS coupling the only atomic transition one would observe is $^1S \rightarrow ^1P$. However in jj-coupling the $j=1$ final state is a mixture of 1P , 3P and 3D LS terms. Both triplet states have equal energy which is lower than the 1P state energy, therefore they are the origin of the weak atomic (Ti^{4+}) pre-peak [41], which in TiO_2 is further split by the crystal field to the pre-peaks P1 and P2. Therefore, the crystal field will be discussed next.

As mentioned in section “3.3. XAS” the X-ray absorption spectra carry information from both the initial and the final state. The Ti 2p initial state is spin-orbit split to $2p_{1/2}$ and $2p_{3/2}$ with an energy difference of 5.4 eV [42]. The final state is mostly Ti 3d derived. In spherical symmetry (isolated ion, for example) the 3d orbitals would be degenerate (no splitting in the first approximation, as discussed previously). However in a crystal, the Ti 3d orbitals are split according to the crystal field symmetry. In octahedral field (O_h) they are split to t_{2g} and e_g symmetry states. The experimentally observed energy difference between the t_{2g} and e_g symmetry states (2 eV) is however not the same as the theoretical $10Dq$ value (3 eV) as shown by De Groot *et al.* [41]. In the simplest picture, with two initial states and two final states 4 transitions should be observed. Since in our case, the crystal field splitting is smaller than the spin-orbit splitting and for octahedral symmetry t_{2g} states are lower in energy than the e_g states, the transitions can be identified as $2p_{3/2} \rightarrow t_{2g}$, $2p_{3/2} \rightarrow e_g$, $2p_{1/2} \rightarrow t_{2g}$, $2p_{1/2} \rightarrow e_g$, corresponding to (A, BC, D, E) labeled peaks in the spectra.

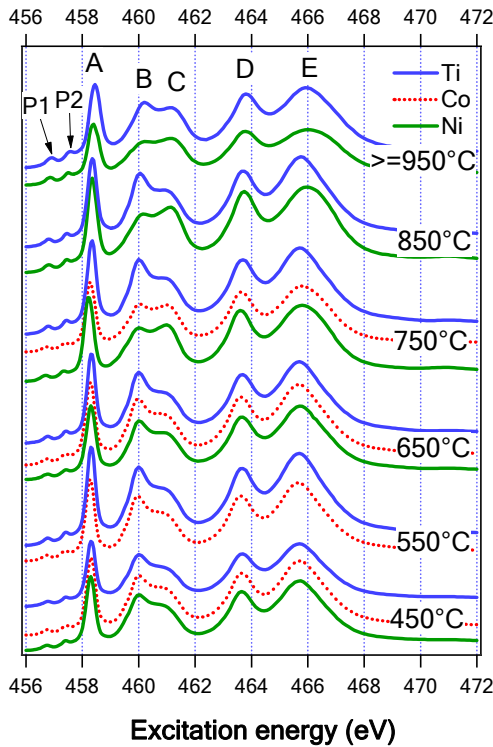


Figure 7. Ti 2p TEY XAS spectra of TiO_2 thin films. Top to bottom in each series: blue lines are the undoped TiO_2 samples, red dots are Co-doped and green lines are Ni-doped titania samples.

More detailed analysis reveals that the symmetry around the Ti^{4+} ion is not fully octahedral, where the B and C peaks would be unsplit [43], but due to distortions the symmetry is lower (rutile D_{2h} , anatase D_{2d} [43]) so that the e_g state splits to B and C peaks. The intensity of the B and C peaks is different for anatase and rutile allowing distinguishing them from the XAS spectra. Namely, in anatase the peak B is stronger than the peak C and vice-versa in rutile [42, 43]. This difference arises in the second peak because it has always a larger hybridization with the ligands [41] and is therefore more sensitive to the environment.

These spectra indicate a phase transition from anatase to rutile in-between 650–750°C for both Co and Ni doped films, while the spectrum of the undoped film shows change only at 950 °C. This is also confirmed by XRD and Raman analysis. The advantage of the XAS technique for phase or local symmetry analysis (when applicable) is that thin films can be measured and the influence of the substrate or other phases present can be minimized, while the disadvantage is that the experiment has to be carried out on a synchrotron.

4. RESULTS AND DISCUSSION

4.1. Results of XAS studies

4.1.1. Fe_2O_3 and Fe_3O_4

Magnetite (Fe_3O_4 : $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$) films can be regarded as transparent magnetic, half-metallic and conductive oxides, which can also demonstrate magnetoresistance, i.e the property of interest in the field of magnetic sensors and data storage. Therefore it is of interest to grow high quality magnetite films [Paper II].

Iron oxide and magnesium-doped iron oxide films were grown by atomic layer deposition in the temperature range of 350–500°C from ferrocene, (dimethylaminomethyl)ferrocene, magnesium β -diketonate and ozone. Fe_3O_4 (magnetite) has a lattice constant approximately twice as large as that of MgO, referring to the possibility to realize substrate-oriented growth and structurally matched interfaces. Also, iron oxide has been combined with other materials, in particular with MgO, in order to modify the properties of the material and, potentially, create magnetic device prototypes [Paper II].

The XAS spectra of iron oxide thin films with different amounts MgO content are shown on Figure 8. The Fe^{3+} ion in hematite ($\alpha\text{-Fe}_2\text{O}_3$) has an electron configuration $2p^63d^5$ and is accommodated at a site with oxygen ligands in octahedral geometry. The octahedral symmetry lowers the 5-fold degeneracy of the 3d state and splits it into a 3-fold degenerate t_{2g} state and a 2-fold degenerate e_g state. Of these two, the e_g (x^2-y^2 and z^2 symmetry) state is oriented towards the oxygen ligand 2p orbitals, has higher energy and the t_{2g} symmetry (xz, xy, yz) orbitals, which are aligned in between these (octahedral) oxygen ligands, have lower energy. Due to Hund's rule coupling, the ground state would be high spin ($3d: t_{2g}^3e_g^2$), with the opposite spin states unoccupied. This half-empty Fe 3d level thus bears some similarity to the Ti^{4+} ion ($3d^0$) configuration described before, and the two sharply split peaks are quite clearly seen (both in the L_3 and in the L_2 part of the Fe 2p absorption spectrum (Figure 8, right panel, bottom curve).

The Fe^{2+} ion has an electron configuration $2p^63d^6$, and is octahedrally coordinated both in the wüstite (FeO) and in magnetite (Fe_3O_4). The octahedral crystal field would split the 3d similarly (with the t_{2g} lower and the e_g higher in energy, but the 3d electron interaction makes the picture less “one-electron-like”, and the splitting is less clearly observed in the spectra. Apart from equal amounts of octahedrally coordinated Fe^{3+} and Fe^{2+} , one third of the iron in magnetite is Fe^{3+} in tetrahedral oxygen coordination, where instead the t_{2g} is oriented towards the ligands and has higher energy than the e_g , which now is oriented away from the ligands and thus requires less energy to accommodate an extra electron in case of absorption. Because of its structure, magnetite is also denoted by $[\text{Fe}^{3+}]_{\text{tet}}[\text{Fe}^{2+}\text{Fe}^{3+}]_{\text{oct}}\text{O}_4$. The lower energy component of the observed Fe 2p NEXAFS spectra obtains more intensity mainly from the Fe^{2+}

absorption being shifted to lower energies with respect to Fe^{3+} , but also from the more prominent t_{2g} component from the tetrahedral sites.

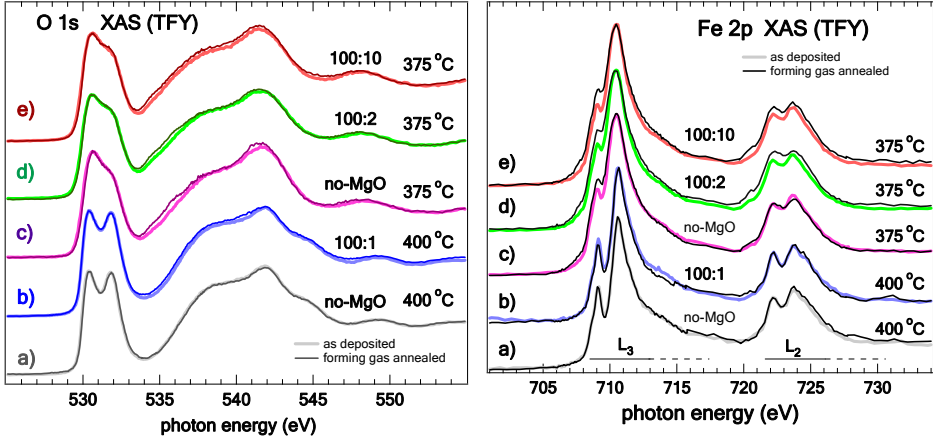


Figure 8. O 1s (left) and Fe 2p (right) NEXAFS spectra of iron oxide thin films. The temperatures near the spectra indicate the growth temperature for the respective sample and the ratio represents the Mg:Fe cycle ratio: i.e 100:1 means the deposition of 100 cycles of iron oxide followed by 1 cycle of Mg oxide until the film was of required thickness.

To further complicate the picture, Fe_2O_3 also has a maghemite ($\gamma\text{-Fe}_2\text{O}_3$) structural phase, which may be seen as a magnetite structure with the Fe^{2+} oxidised to Fe^{3+} due to oxygen uptake. It is subtle, but not impossible to distinguish this phase from magnetite from the Fe 2p absorption spectra. In maghemite the lower energy shoulder becomes decreased, because it now only receives contribution from the tetrahedral Fe^{3+} , and no longer from Fe^{2+} . The difference is more clearly visible in X-ray magnetic dichroism (XMCD) spectra since the electrons in the octahedral and tetrahedral sites order opposingly and the tetrahedral and octahedral site contributions are therefore further resolved.

As explained by de Groot *et al.* [44], the first feature near the oxygen 1s threshold (around 531.0 eV) is due to unfilled oxygen 2p orbitals that are hybridized with the transition metal 3d states. This means that the chemical bond these transition metal oxides also has a covalent character; otherwise the oxygen 2p orbitals would be fully filled. The double peak-like structure of the first feature is mostly due to the crystal-field splitting of the Fe 3d orbitals (t_{2g} , e_g). In the case of hematite, the oxygen 2p states are strongly hybridized with the iron 3d states [45], leading to well resolved splitting in the oxygen 1s NEXAFS spectra. In hematite the exchange interaction of the 3d electrons is stronger than the crystal field perturbation, one would therefore expect the spin-up (arbitrarily chosen) t_{2g} and e_g symmetry states to be fully occupied and therefore the spin-down states to be empty. Therefore the intensity ratio of the

$t_{2g}:e_g$ states in the XAS spectra should be close to the number of unoccupied states $3:2=1.5$, which however is opposite to the experimentally observed intensity ratio (about 0.9, see Figure 8). However, the e_g states have more than 2 times stronger hybridization with the oxygen 2p states than the t_{2g} states therefore the e_g symmetry peak should be much more intense than the t_{2g} symmetry peak [44]. If this is the case, then the experimental ratio after correction for the e_g symmetry peak would be closer to 1.8. Thus the observed e_g symmetry peak is much stronger than predicted statistically and this fact explains part of the discrepancy.

Similarly to TiO_2 , the symmetries of the final states and the intensities of the peaks are not qualitatively easily explainable, as the exchange and charge transfer are mixing different states and e_g symmetry states have larger hybridization with the oxygen 2p orbitals.

The Fe 2p NEXAFS spectra in iron oxides are dominated by the transitions to the empty 3d derived states, like the Ti 2p NEXAFS spectra of TiO_2 . The spin-orbit interaction is stronger in Fe atoms than in Ti atoms (energy separation of about 15 eV). The theoretical calculation by de Groot *et al.* [46] show that the NEXAFS spectra of the Fe^{3+} ion in octahedral field has a more separated first peak of the L_3 part and also a more separated two peaks in the L_2 absorption. Therefore spectra a and b on Figure 8 can be assigned to oxides with dominating Fe^{3+} ions in octahedral symmetry – hematite. This also confirmed by the O 1s edge NEXAFS spectra, where the a and b spectra have clearly separated two peaks near the edge.

It is also important to point out that forming gas annealing (reducing environment) does not change the oxygen spectra, but in the case of Fe 2p NEXAFS, the samples deposited at 375°C and subsequently annealed show a change in both the first peak intensity and also at the low energy shoulder to the L_2 feature. After comparison with reference hematite and magnetite spectra [47], this means that upon forming gas annealing the spectra changed towards magnetite-like. This comparison also indicates that sample spectra labelled c,d,e are more magnetite-like than hematite.

This indicates further conversion to magnetite structure upon forming gas annealing, in agreement with XRD and Raman data. Also, at higher growth temperatures the formation of hematite is observed. Again, this study shows that with XAS it may be possible to identify oxidation states and crystal phases.

4.1.2. Core excitons in NEXAFS spectra

Core excitons have been experimentally identified in many compounds [Papers I, III, IV]. The existence of a core exciton has in some cases been already known before (B_2O_3) and in some cases not (LBO, BBO). Some spectra are shown in Figure 9.

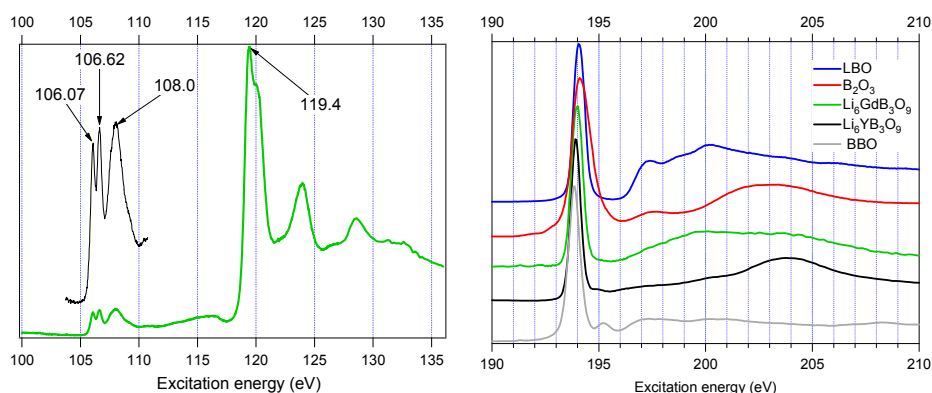


Figure 9. Si 2p and Be 1s absorption edges in phenakite (left) and B 1s absorption edge in different borate crystals (right): from top to bottom LiB_3O_5 (LBO), B_2O_3 , $\text{Li}_6\text{GdB}_3\text{O}_9$ (LGBO), $\text{Li}_6\text{YB}_3\text{O}_9$ (LYBO) and $\beta\text{-BaB}_2\text{O}_4$ (BBO). The black spectrum on the left panel is a magnified view of the Si 2p edge in phenakite.

In the case of the Si 2p edge in phenakite there are two very sharp peaks in the NEXAFS spectra. The width of those peaks (about 0.4 eV fwhm – full width at half maximum) is very narrow for electronic bands in solid state materials, they are rather assigned to core exciton states. Nithianandam *et al.* reported fwhm of about 0.5 eV of the similar exciton double peak in SiO_2 [10]. The difference between the peaks (about 0.6 eV) corresponds well to the Si 2p spin-orbit interaction in SiO_2 [10, 11] and Si [48]. In fact, in all cases shown in Figure 9, there exists a core exciton level that the sharp peak(s) corresponds to. This has been further confirmed by RIXS.

4.2. RIXS studies of borates

4.2.1. General overview

Boron compounds have very interesting properties as will be shown below. The most important boron compound is boron nitride (BN). Both boron and nitrogen are widely available elements. BN has two major phases: sp^2 -bonded hexagonal (h-BN) and sp^3 -bonded cubic (c-BN). c-BN does not exist in nature, like man-made diamond, it was first synthesized at high pressure and high temperature.

Hexagonal BN is the most widely used polymorph. It is produced from boron oxide and ammonia at high pressure and high temperature. It is a good lubricant at both low and high temperatures (up to 900 °C, even in an oxidizing atmosphere). h-BN lubricant is particularly useful when the electrical conductivity or chemical reactivity of graphite (alternative lubricant) would be problematic. Another advantage of h-BN over graphite is that its lubricity does not require water or gas molecules trapped between the layers. Therefore, h-BN

lubricants can be used even in vacuum, e.g. in space applications. The lubricating properties of fine-grained h-BN are used in cosmetics, paints, dental cements, and pencil leads [49]. h-BN is used by nearly all leading producers of cosmetic products for foundations, make-up, eye shadows, blushers, kohl pencils, lipsticks and other skincare products. Because of excellent thermal and chemical stability, boron nitride ceramics are traditionally used as parts of high-temperature equipment. h-BN is isostructural to graphite, but unlike graphite which exhibits semimetallic behaviour, h-BN is a wide bandgap insulator [34].

Cubic boron nitride is widely used as an abrasive. It is ultrahard, has a high melting point and high thermal conductivity. Its usefulness arises from its insolubility in iron, nickel, and related alloys at high temperatures, whereas diamond is soluble in these metals to give carbides. Polycrystalline c-BN abrasives are therefore used for machining steel [34].

Nanotubes of BN can also be produced. BN nanotubes are electrical insulators with a wide bandgap of ~ 5.5 eV (same as diamond).

As c-BN consists of light atoms and is very robust chemically and mechanically, it is one of the popular materials for X-ray membranes: low mass results in small X-ray absorption and good mechanical properties allow usage of thin membranes, thus further reducing the absorption. These membranes (also called “windows”) allow *in situ* measurement of biological, electrochemical or wet samples, for example.

Therefore the properties and applications of h-BN, c-BN and graphite, diamond respectively are very similar. They all have a very covalent bonding character. Both graphite and h-BN have layered hexagonal structure. c-BN adopts a sphalerite crystal structure, which can be constructed by replacing every two carbon atoms in diamond with one boron and one nitrogen atom. The short B-N (1.57 Å) bond is close to the diamond C-C bond length (1.54 Å) and both have similar densities [50].

Boron compounds with optical applications have been studied. The most prominent members of the borate family of crystals that are used for their non-linear optical (NLO) properties are β -BaB₂O₄ (BBO), LiB₃O₅ (LBO), CsB₃O₅ (CBO), CsLiB₆O₁₀ (CLBO), and Li₂B₄O₇ (LTB). LBO and BBO were discovered by Chen *et al.* in the 1980s [51]. They are widely used for frequency conversion (harmonic generation) and generation (optical parametric amplification and oscillation). In the NLO borates, like LBO and BBO, the chemical bond is an ionic bond between the cation (Li, Ba) and a covalently bound anion complex (B₃O₇⁵⁻ and B₃O₆³⁻, correspondingly).

Many studies of the electronic structure of LBO and BBO have been done. The core level (and thus element) specificity of RIXS allows valuable information about the electronic structure of the borates to be gathered and to separate the contributions of oxygen and boron atoms to the electronic properties. This is discussed in Paper I and in the next paragraph.

Also of interest in this work are the crystals Li₆YB₃O₉ (LYBO) and Li₆GdB₃O₉ (LGBO) [52] where a core exciton has been observed [53]

(Figure 9). The yttrium site can obviously be doped with different f-metals and thus the optical properties can be modified to a large degree. Therefore, LYBO and LGBO are known as high efficiency scintillation materials and also neutron detectors.

4.2.2. Molecular picture of BBO

It may be possible to describe and model X-ray spectra of solids using an atomic or molecular picture. For example, the modelling of NEXAFS spectra of some ionic crystals can be done by calculating the atomic multiplet transitions and charge transfer in the corresponding ions, like for example, the 2p→3d NEXAFS spectra in transition metals, as discussed above.

In the case of NLO borate crystals, the anionic group is thought to determine the nonlinear optical coefficient according to the anionic group theory. Two fundamental assumptions are considered in the calculation besides the complete neglect of differential overlap approximations:

(1) the macroscopic NLO coefficient of the crystal is the geometrical superposition of the microscopic second order susceptibility tensor ($\chi^{(2)}$) of the relevant anionic groups, and has nothing to do with essentially spherical cations; and

(2) the microscopic second order susceptibility can be determined from the localized molecular orbitals of the anionic group using quantum chemical calculation [54].

In BBO the anion groups are well separated from each other (Figure 10), therefore it is reasonable to study the anion group as a charged molecule.

It is possible to learn a lot about the molecule and its spectra by studying its symmetry. Namely, group theory is able to predict which transitions in the molecule are allowed and which are forbidden. For example, to calculate electric dipole transitions in a molecule, one needs to find the symmetry of the dipole matrix element: $\langle \Psi_{final} | D | \Psi_{initial} \rangle$, where D is the dipole operator (or more general: the transition operator). The corresponding expression to this matrix element in group theory is the direct product of the irreducible representations corresponding to the initial and final state symmetries and to the symmetry of the dipole operator: $\Gamma_{final} \otimes D \otimes \Gamma_{initial}$. Group theory then is able to predict that, when the decomposition of this expression contains the totally symmetric representation (A_1), the matrix element can be nonzero, however when that is not the case, the matrix element is zero due to symmetry.

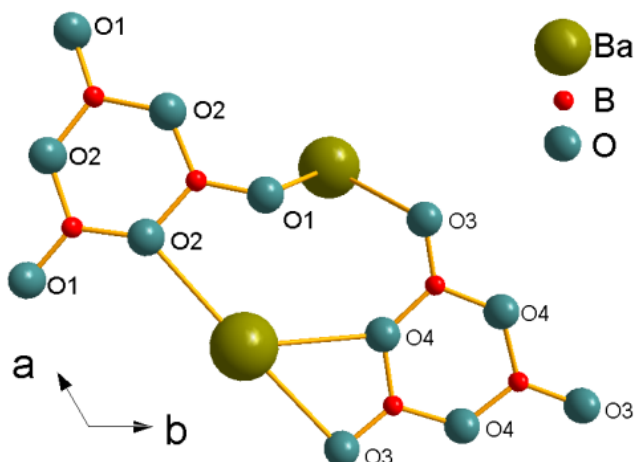


Figure 10. A section of the BBO unit cell, showing the anion groups. The BBO crystal consists of nearly planar $B_3O_6^{3-}$ rings perpendicular to the polar axis c , bonded together through Ba cations.

The symmetry of the $B_3O_6^{3-}$ anion group is described by the D_{3h} point group [55]. The boron and oxygen core electrons are associated with molecular orbitals of e' and a_1' symmetry. Performing the above-mentioned calculation, one finds that only the e' symmetry core orbital can couple via the dipole operator to the e'' symmetry LUMO orbital, which is also the symmetry of the exciton state in solid BBO [Paper I]. This excitation is possible with a z-polarized X-ray photon. Here the z-axis is perpendicular (normal) to the plane of the anion group molecule (i.e. the z axis is parallel to the c -axis of BBO). The core-hole can be filled from MO's with a_1' , a_2' , e' , e'' symmetries. Again, group theory predicts that the e'' states filling the core-hole emit z-polarized photons, all other states emit xy-polarized (polarized in the plane of the anion groups) photons. The MO's with a_1'' , a_2'' symmetry are dipole forbidden to fill the core-hole, however due to electron-phonon coupling, the symmetries of the electronic states can be (inter)mixed and the a_2'' symmetry states may also be experimentally observed.

The high degree of anisotropy in the case of BBO is evident in both the NEXAFS and RIXS spectra and the oxygen atoms can be divided into two groups – the in-ring oxygens (O2 and O4 on Figure 10) and the off-ring oxygens (O1 and O3 on Figure 10). The excitonic effects are only seen with the incident X-rays polarized parallel to the c -axis of the sample [Paper I].

Continuing with the molecular picture (approximation), the 4 peaks that are seen in the oxygen RIXS spectra (A-D, Figure 11 and Paper I) can be assigned from the anion group calculation of Wu *et al.* [55] and French *et al.* [56]. The calculation was based on the negatively charged anion group molecule $B_3O_6^{3-}$. Considering the fact that the emission from the a_2'' symmetry orbitals is

suppressed, as discussed before, the peak A can be assigned to the molecular orbitals $2a_2'$, $9e'$ (non-bonding σ orbitals) and $2e''$ (bonding π orbital), peak D is composed of the bonding $8e'$ and the non-bonding $7a_1'$ σ orbital, peak B is assigned to the molecular orbitals $7e'$, $1e''$ and peak C is derived from the σ molecular orbital $6a_1'$ of the anion group.

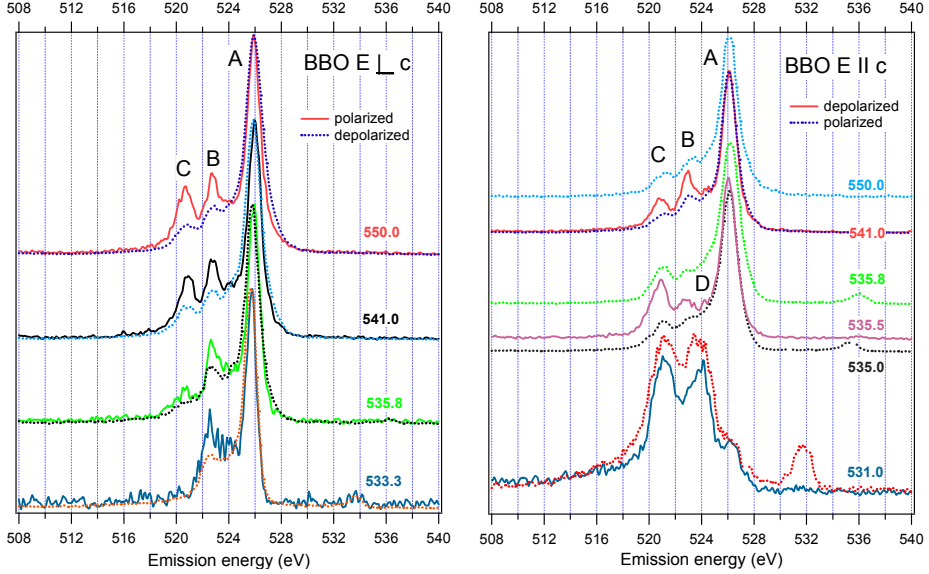


Figure 11. The oxygen RIXS spectra of BBO measured in different polarization and spectrometer orientations. The numbers near the spectra denote the corresponding excitation energy in eV. The incident monochromatic X-rays are either parallel (left panel) or perpendicular (right panel) to the c -axis of the BBO sample and the optical axis of the spectrometer (viewing direction) is either parallel (solid lines) or perpendicular (dotted spectra) to the c -axis of the BBO sample. The spectra have been normalized to equal emission maximum (peak A intensity).

When also considering the fact that emission from the a_2'' symmetry orbitals is suppressed, as discussed above, the peaks A, D, B, C mostly have (a_2' , e' , e''); (e' , a_1'); (e' , e''), a_1' character. Assuming that the corresponding molecular orbitals give rise to the (solid state) emission bands centered at the mean energy of the orbitals, the differences between the D, B, C and the A peak (0.7 eV below the valence band top) can be derived as 2.2 eV, 4 eV and 6.3 eV – therefore overestimating the experimentally measured differences by about 1 eV.

A next approximation deals with the angle dependence of the X-ray emission. Namely, the intensity of the σ orbitals is strongest in the z direction and twice as weak in the other perpendicular directions. The intensity of the π orbitals (e'' symmetry) on the other hand, is zero in the z direction. Due to these

polarization and the symmetry reasons discussed above, when the optical axis of the spectrometer is aligned parallel to the $c(z)$ -axis of the BBO sample, the signal from the e'' symmetry orbitals will weaken significantly and the signal from the other orbitals will be enhanced. Therefore, when changing the X-ray spectrometer viewpoint from along the c -axis of the BBO sample to perpendicular to the c -axis (going from dotted spectra to spectra drawn with solid lines on Figure 11), the A band should have a similar intensity, the D and the C band should roughly double in intensity. Indeed, the C band is always roughly twice as intense in the spectra shown with solid lines and the D band is only (barely) visible (excitation energy 535.5 eV and 541.0 eV) in that geometry. The B band is expected to be 1.5 times stronger in the spectra drawn with solid lines. Experimentally the B band intensifies about 1.7 times (excitation energies 541.0 and 550.0 eV) after the change of the measurement geometry. This indicates that the B band has somewhat more σ than π contribution.

Besides the symmetry and the polarization considerations, the atomic (site) specificity of the RIXS process must also be taken into account. The two different oxygen environments in BBO influence both the XAS and also the RIXS spectra. As shown by both theory and experiment, the C band is mostly derived from the in-ring oxygens [Paper I]. The spectra excited at energies 535.0–535.8 eV ($E||c$ polarization) show an enhancement of the C peak in the RIXS spectra. This is due to the fact that at these energies most of the incident X-rays preferentially excite the in-ring oxygens (due to the resonance) and thus the C peak, that is associated with the in-ring oxygens, is enhanced. The B band, however, has contributions from both oxygen environments – the $7e'$ orbital is mostly associated with off-ring oxygen atoms, while the $1e''$ molecular orbital is associated with in-ring oxygen atoms [55].

With lower excitation energies, when the C band is not yet visible the simple molecular orbital picture predicts that the B band doubles in intensity when the spectrometer viewpoint changes from along the c -axis of the BBO sample to perpendicular to the c -axis. Indeed, the near-threshold spectra excited at 533.3 eV confirm this prediction. The reason for this doubling, is because at low excitation energies only the off-ring oxygen atoms are excited and then the B band is then mostly of e' symmetry.

Group theory thus correctly predicts that the core exciton is only reachable with z -polarized incident light. Also, the angle and polarization dependence of the RIXS spectra agree with the molecular picture of the solid.

4.3. Phonons in RIXS spectra

Phonons cause a temperature-dependent broadening of most types of spectra. If the creation of a core-hole is sudden (i.e. fast with respect to the typical vibrational time scale), phonon broadening can be understood by applying the Franck-Condon principle, i.e. by vertical projection of phonon wave functions of the initial on the final electronic-state manifolds. In the same picture the lattice contribution to the redshift of X-ray emission is easily obtained (Franck-Condon shift) in as much as the core-hole has a long lifetime. In the latter case, absorption and emission are formally equivalent, independent processes. For short core-hole lifetimes, additional complications arise in X-ray and Auger emission, because *incomplete relaxation* of the lattice in the presence of both a core-hole and the excited electron need to be considered [33]. A consistent theoretical description was given independently by Mahan [57] and by Almladh [58] in 1977.

The fingerprint of the lattice relaxation process in the RIXS spectra is a continuous (possibly wide) shoulder at the low energy side of the elastic (participator) peak. This energy loss tail (ELT, also called the low energy shoulder [14]) cannot be explained by anything else, like electronic excitations (dd excitations), magnons, plasmons, because of the continuous and possibly wide nature of the ELT. There are actually not many solids where this has been observed: excitations of carbon in graphite and diamond [59], nitrogen in LiNO_3 [37], lithium in LiBr and LiCl [14], beryllium in simple and composite oxides compounds, boron in many compounds (B_2O_3 , BN , LBO , BBO , $\text{Li}_6\text{YB}_3\text{O}_9$ (LYBO) and $\text{Li}_6\text{GdB}_3\text{O}_9$ (LGBO)). Besides the graphite and diamond C emission spectra ELT has been observed in condensed (bulk) carbohydrate – ethylene [60]. Of course, it is possible to observe this kind of energy loss mechanism also in liquid [61, 62] and gas phase [20, 63]. In gas phase the shoulder is no longer continuous and with sufficient resolution individual vibrational modes can be seen [64]. To the author's knowledge no evidence of phonon losses in RIXS spectra has been found in compounds with heavier atoms than oxygen.

4.3.1. Previous work on diamond and graphite

The ELT in X-ray spectra was first noticed in diamond and graphite [59] and has been studied extensively after that. The graphite C 1s XAS spectra have a very distinct and sharp (about 0.5eV width) π^* feature at the absorption threshold. This is best described by a localized exciton state. The energy loss tail is about 5–6 eV wide and as the optical phonons in diamond have an energy of about 0.16eV, there have to be around 35 phonons generated [59]. This means that the (full) relaxation energy is quite large, theoretically estimated to be $25\hbar\omega = 4\text{eV}$ [65]. The Stokes shift is calculated to be 4.3 eV in the harmonic approximation and 2.9 eV with proper potential energy calculations [33, 66].

The shift of the excited carbon from its equilibrium position towards the (111) direction is very large with an estimated nearest neighbour bond stretch of 28.3% [66] or 30.4% [33]. The latter figure is comparable to the calculated nitrogen impurity induced distortion – 28.2% [33]. In case of these strong distortions the harmonic approximation is not sufficient.

The (fully relaxed) core exciton binding energy in diamond has been estimated as 1.27 eV [67], 1.0 eV (triplet) or 1.1 eV (singlet) [33], higher than 1.1 eV [68], about 1 eV [66] and about 1.3 eV for graphite [67, 69]. The latter figures are again comparable to the nitrogen impurity donor level – 1.7 eV below the conduction band minimum [70]. The theoretically calculated emission spectra agree best with the experiment with $\Gamma=110\text{meV}$ suggesting a 35 fs excited state lifetime [33], while Ma estimated $\Gamma=0.2\text{eV}$ [71].

The X-ray absorption process to the core exciton state occurs on a very fast time scale (about 0.1fs) relative to the nuclear motion (about 10fs), therefore the carbon atoms in diamond maintain the same arrangement during the absorption process. The core excited carbon atom is qualitatively equivalent to a nitrogen impurity (so called N+1 approximation) because the valence configuration in both is $2s^2 2p^3$. However, quantitatively the potential acting on the 1s electrons in the N atom is more attractive than in the core-excited C atom. Then in the atomic case, the 2p levels of core-excited C atom are lower than that of N by 0.54 eV, while the 2s levels are higher by 2.34 eV [66]. It is well-known that the nitrogen impurity in diamond produces an A_1 (s-like) and triply degenerate T_2 (F_2 , p-like) state.

The carbon A_1 symmetry core exciton state is still (barely) in the band gap, but the T_2 state is already in the conduction band [33]. However, Mauri and Car's DFT supercell calculations estimate that both exciton states are in the band gap [66]. Because the electronic wave function of the ground state is totally symmetric, transition to the totally symmetric electronic state where the excited electron is delocalized over the four C–C bonds, is not dipole allowed. However the transition to the s-like state becomes possible due to the quasi Jahn-Teller coupling with the conduction band state through the antisymmetric vibration [65]. The other interpretation is that the absorption first proceeds to the T_2 symmetry state which transitions nonradiatively to the A_1 state [33, 66]. The probability of this transition is high because the energy of the longitudinal optical (LO) phonon in diamond is about the same as the energy separation between these electronic states [66]. Either way, that explains why the exciton peak in diamond is quite weak in the NEXAFS spectra.

The system then undergoes the Jahn-Teller distortion: the excited electron becomes localized along one of the C–C bonds and at the same time the excited atom begins to move to an off-center position [59]. This Jahn-Teller distortion involves breaking the symmetry of the system (final symmetry is then C_{3v} instead of T_d [68]) for lower energy [68]. The T_2 state then further splits to A_1 and E symmetry states [68]. The distortion is a competition between the delocalization effect over the four sp^3 orbitals and the localization in one of

them [68]. This distortion is estimated to be happening on the order of 10fs – very quick [65].

The polarization dependence of the RIXS spectra is able to experimentally verify a similar symmetry breaking in graphite [67] where the situation is quite analogous in principle. The p-type core exciton orbitals are Jahn-Teller split to A_1 and B_1 (A_2) symmetries (symmetry lowering from D_{6h} to D_{3h} around the excited atom). The strong quasi Jahn-Teller effect pushes down the s-like lowest branch A_1 state. Again after photoabsorption and the creation of the exciton, a nonradiative transition from the p-derived A_1 symmetry state to the s-derived A_1 state (calculated energy difference 0.2eV) can occur. Then the system starts to relax to a lower energy configuration in the A_1 symmetry state with an associated lattice distortion [69]. Besides the σ^* peak graphite has also a π^* absorption resonance in the NEXAFS spectra, but the exciton-phonon coupling is weak in that state [69]. The qualitative explanation of this is that anti-bonding effects of the electron in the π^* -like graphite orbital are much weaker and the equilibrium position does not shift as much.

The recombination of the core exciton by (participator) X-ray emission will finally leave the system in the electronic ground state, but with the lattice initially distorted. The elastic energy stored in the distortion is released by the emission of phonons which broaden the emission line. This is due to the fact that the lattice distortion occurring after absorption moves the atoms towards the minimum of the core-excited potential energy surface, while pushing them off equilibrium with respect to the ground state potential energy surface [33, 69].

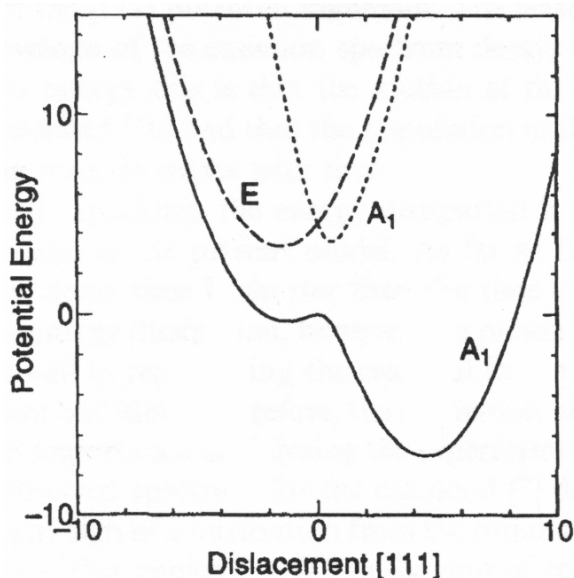


Figure 12. Illustration of the potential energy curves of diamond. Reprinted with with permission of Elsevier from ref [68].

It is also important to point out that this Jahn-Teller distortion changes the strength of the electron coupling to the lattice from weak (just after absorption) to strong. In terms of a simple picture, this is due to the fact that as the system slides down the potential energy surface, the steepness increases (see Figure 12).

The initial exciton state just after the photoabsorption process is less localized (more delocalized) than the final state after the Jahn-Teller distortion [65, 69]. This fact is able to explain the (possible) sharpness of the exciton peak in the NEXAFS spectra, suggesting weak electron-phonon coupling and the (possible) wide and strong peak in the RIXS spectra, indicating strong electron-phonon coupling [65, 70].

The RIXS spectra with the ELT resemble the hot luminescence in the F-centers in alkali halides [68]. This whole process is similar to the hot-luminescence emission from self-trapped excitons in alkali halides. However, the (valence) exciton state lifetime in these systems is much larger (10^{-2} – 10^{-9} s), therefore the relaxation process should be much more complete in case of the F-centers [59].

The second important property of this hot luminescence-like emission is that the ELT can be wider than the total lattice relaxation energy. Again this can be illustrated with Mäder and Baroni's *ab initio* calculations [33] where, as was already mentioned, the total energy loss (Stokes shift) for a very large core-hole lifetime (i.e. normal luminescence) is expected to be 2.9 eV. However, with a realistic core-hole lifetime (but no longer an *ab initio* calculation but rather an empirically corrected harmonic approximation calculation) the calculations show that the ELT can extend to roughly to double this value ≈ 6 eV – in agreement with experiment. Indeed, in the harmonic approximation the largest energy loss is equal to twice the lattice relaxation energy $2\Sigma_{\text{ph}}$ [12–14, 33].

Finally it should be mentioned, that a good theoretical description of this process is difficult [33] due to the highly dynamical and localized-delocalized nature of it. There are elements of weak and strong electron phonon coupling, interaction with different vibrational modes, high degree of anharmonicity, Jahn-Teller and quasi Jahn-Teller interactions, breaking (change) of symmetry, energy dissipation, electron itinerancy (band effect), core-hole effects, possible lifetime-vibrational interaction. The perturbation can be localized while it interacts with the delocalized modes of the crystal [72]. The duration of the process is intermediate so that neither time-dependent nor energy (frequency) dependent picture is best suited. These conflicting tendencies mean that the description of this process is a good challenge for theory.

4.3.2. Modelling the participator emission

To understand the lattice relaxation effect it is of interest to model the shape of the ELT. For that purpose a very simple model has been employed. Only BeO is considered in the following discussion due to the clearly manifested ELT in that system [73].

Details of the model used in the calculations can be found in Paper IV. The model originates from diatomic molecules, whose vibrations can be described by a 1D potential energy curve – the Morse function. Different excited state symmetries, potential energy curves and non-adiabatic transitions between them are not taken into account in this simple model. The benefit of the Morse potential energy curve is that anharmonicity, which is important in this process, is taken into account. Also, if only one excited state potential energy curve is used, it is possible to fit the exciton peak in the NEXAFS spectrum and the emission spectra to the model, thus attaining some consistency. As will be shown, the simple model is able to qualitatively explain the participator emission [Paper IV]. The calculated spectra are published in Paper IV and some further calculations are shown in Figure 13.

According to eq. (4.9) large detuning decreases the scattering time and the wave packet is unable to evolve for a long time [60] and the vibrational motion is effectively suppressed. The reason why the envelope of the emission spectrum decays toward the low energy side is that the population in the core exciton state decreases with time [68] (mainly due to Auger decay). This arises from the time-dependent picture of scattering. However in the frequency (energy) dependent picture, the interference terms are responsible for the weakening of the ELT when the excited state lifetime decreases or detuning increases.

The effect of the interference terms is also called lifetime vibrational interference [60], because the strength of this effect depends on the ratio of Γ to $\hbar\omega$ (vibrational quantum). While it is sufficient to use the direct term (4.5) to account for the band profiles of electronic transitions in the optical or ultraviolet regions, similar band profile calculation in the soft X-ray region, in general, have to include the interference term (4.6). When the energy separation of the vibrational levels of the intermediate state is much larger than the lifetime width Γ , the interference term is negligible and the direct term will determine the band profile [20]. And contrary, the interference terms are more important if the core-hole width is larger, for example they are more important in the case of oxygen core-hole (oxygen excitation) vs carbon core-hole [20]. If a broadband excitation source is used, the excitation probabilities to each vibrational level of the intermediate state depend not only on the Franck-Condon factor between the ground and intermediate state but also on the monochromator function [20]. Therefore the interference effects can still be important even when the energy separation of the vibrational levels of the intermediate state is much larger than the lifetime width Γ . A gaussian monochromator function (0.1 eV fwhm) is assumed in the modelling of the spectra. The calculated emission spectra have

been further gaussian broadened (0.2 eV fwhm) to account for the spectrometer resolution. The effect of the core-hole lifetime, the interference terms and phonon damping are shown in Figure 13.

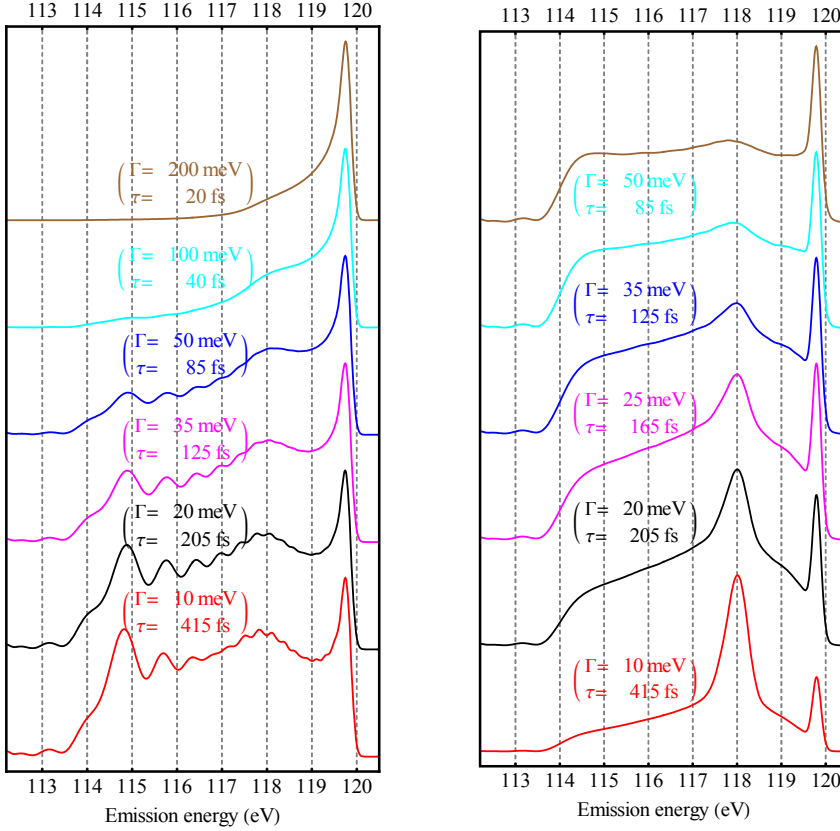


Figure 13. The effect of the excited state lifetime on the participator band spectra of BeO as calculated with the one-step model based on the Kramers-Heisenberg formula (left) and an empirical two-step model with energy dissipation (right). Excitation energy is set to 119.8 eV in all cases; vibrational quantum was chosen to be 0.1 eV. A further Gaussian shape line at the excitation energy has been added to the spectra to mimic A^2 type elastic scattering (see eq. (3.6) and (4.8)). The spectra have been normalized to equal maximum emission intensity.

The overall shape of the coherent spectra calculated according to eq. (4.3) are similar to other results for diamond and graphite [68–70] especially Harada *et al.* [67].

The “ripple” seen in the calculated spectra is also evident in other works [67, 69, 70]. This is qualitatively explained by the phonon wave packet oscillating in the adiabatic potential surface [69]. If there are a large number of coupled phonon modes which have a wide width of the power spectrum, the ripple

structure would be smeared out. However Yasui *et al.* [69] claim that the graphite experimental spectrum also shows ripples.

Also of interest is phonon damping or phonon energy dissipation (actually coupling to other modes). This effect was neglected in the calculation of diamond [69, 70] and graphite [67] RIXS spectra as the lifetime of the core excited state was said to be very short. However, in case of BeO where the ELT is very strong already with large detuning and shows little dispersion and no “ripple”, phonon damping may become important. This is because the excited state lifetime can become long in BeO. For example, in case of atomic $\text{Be}^{(2)+}$ ion Auger decay is impossible. Therefore it is expected that the Auger decay rate is greatly reduced in BeO and thus the excited state lifetime is increased.

Comparing the spectra calculated with the one-step model to the experimental participator emission, it is evident that the peak at 118 eV emission energy is not reproduced correctly in the one-step model. The peak in the experimental BeO RIXS spectra at around 118 eV emission energy that shows little dispersion could be another electronic state (for example a s-like exciton), similar to diamond and graphite where there are many exciton potential energy curves and the system could transfer between them.

However, this fixed emission energy (118 eV) peak could also be due to the emission from the fully relaxed lattice (the Stokes shifted luminescence emission) or a local minimum in the potential energy surface (Figure 12). Thus if phonon damping is indeed strong in BeO, the peak around 118 eV could also be classical (cold) luminescence like peak and in the case of strong phonon damping the importance of the interference terms should decrease significantly as the coherence is lost during dephasing. Therefore a two-step model (see eq. (4.5)) with empirical phonon damping was also developed.

The calculations with the two-step model that uses empirical phonon damping indeed show that phonon damping may be important in BeO, because the calculated spectra reproduce the peak around the 118 eV emission energy (see Figure 14, Paper IV and ref [73]). However, the spectra show too strong ELT width dependence of the excitation energy [Paper IV] and/or altogether too little width of the ELT, in odds with the experimental spectra. The strength of the energy dissipation is unknown, therefore the ratio between the excited state lifetimes and the degree of phonon damping (Figure 13) is somewhat arbitrary in the modelled spectra and only the overall trend not the absolute values should be noticed. Also, a “round” value of 0.1 eV for the phonon energy was chosen in the calculations.

If the 118 eV emission energy peak is indeed pronounced due to phonon damping, then because of the fact that this peak is not near the center of the ELT, a high anharmonicity of the excited state follows. The theoretical modelling also indicates that an anharmonicity is required for reproducing this peak. This is further supported by the fact that the exciton peak in the NEXAFS spectrum is asymmetric in its shape (unpublished data).

4.3.3. The strength of the effect

The lattice relaxation effect is most clearly manifested in BeO [73], where the intensity of the participator emission (the energy loss feature) is comparable to that of the spectator emission. Beryllium is the lightest metal atom after lithium and evidences of phonons in electronic spectra were observed already in the photoemission study of metallic beryllium [74]. There are also at least two self-trapped valence excitons in BeO [Paper III]. Two other beryllium compounds also show a significant ELT (see [Paper IV] and Figure 14).

The intensity of the energy loss shoulder should be compared to the spectator emission band, because the intensity of the elastic peak can change strongly when the beam position on the crystal surface is changed. This shows that the elastic (A^2 interaction, see formula (3.6)) scattering at the surface gives its contribution to the sharp elastic scattering peak, but the intensities of the inelastic processes reflect the fundamental properties of the bulk crystal [Paper IV].

From the NEXAFS spectra (Figure 9 and [59]) it can be seen that the core exciton seems to have a stronger binding energy in the borates (and also the Si 2p core exciton in phenakite) than in the case of diamond and graphite. Also the exciton resonance in the beryllium and boron compounds NEXAFS spectra is not as much asymmetrically broadened as it would be the case if the excited electron could couple with the conduction band [69, 70]. As shown by both theory and experiment (and discussed before) the exciton resonance in diamond and graphite is located in the same energy range as the transition to the conduction band states. For example, Tanaka and Kayanuma predicted large excited electron itinerancy in graphite [65]. Therefore the delocalization and electron itinerancy should be weaker in the more polar compounds discussed below. However, it is expected that the underlying principle and mechanism of the lattice relaxation is the same in the other systems under study. This is confirmed by Yasui *et al.* and Kayanuma *et al.* who calculated the emission spectra of graphite and diamond with the conduction band taken and not taken into account (cluster model) and found that the overall result does not change as much [69, 70].

In a recent work Li *et al.* [75] observed the multiple (vibronic) peak structure of the π^* resonance in h-BN and proposed that the Jahn-Teller effect is operating in that system too, similarly to diamond and graphite. They also suggested that in these dynamic conditions the Born-Oppenheimer approximation and the Franck-Condon principle might break down.

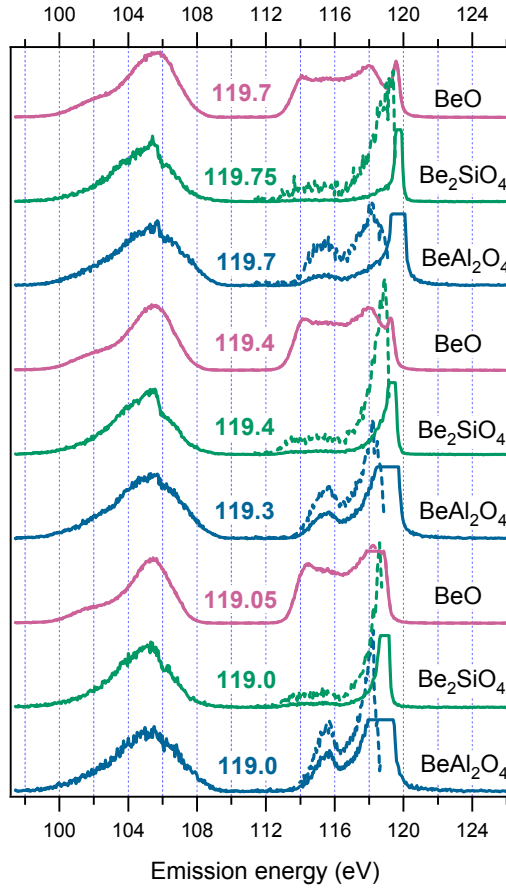


Figure 14. The Be K-edge RIXS spectra showing the ELT in BeO, phenakite (Be_2SiO_4) and chrysoberyl (BeAl_2O_4). The dashed lines are the magnified view of the ELT with the elastic scattering peak suppressed.

As was already shown, the first important parameter that influences the strength of the phonon-relaxation process is the excited state lifetime compared to the phonon vibrational period. The phonon relaxation rate is argued to be well characterized by the frequency of the fastest coupled phonon mode in the material [14]. When the core-hole lifetime is much longer than the typical lattice relaxation times in the (electronic) excited state ($\Gamma \ll \hbar\omega$), the lattice has time to relax completely before emission takes place, and emission can therefore be regarded as a process involving the equilibrium core excited lattice as the initial state and distorted bulk lattice as the final state [33]. In the other extreme, when $\Gamma > \hbar\omega$, then the excited state is short-lived and the lattice has little time to react to the perturbation, a weak and (possibly) wide shoulder should be observed, as a small fraction of the excited atoms “live” long enough for partial phonon relaxation. The case when $\Gamma \approx \hbar\omega$ is the most interesting.

Thus phonon-relaxation effects are important when the phonon-relaxation energy is large and when $\hbar\omega$ is not negligible compared to Γ [13]. However, unfortunately the core-hole lifetimes or widths (Γ) are usually not known with enough precision to estimate the ratio between Γ and $\hbar\omega$ [14].

According to formula (4.9) the duration of the RIXS process is also strongly influenced by the degree of detuning of the incident radiation energy from the resonance energy. Since the time available to phonon-relaxation is dependent upon the scattering duration, as explained above, the degree of detuning should influence the ELT in the RIXS spectra. This is indeed the case and is clearly seen on the chrysoberyl RIXS spectra [Paper IV]. First, the overall intensity of the ELT follows the NEXAFS spectrum i.e. it is strongest at resonance and weaker off-resonance and disappears completely when there is no core-exciton created. Thus the intensity of the energy loss feature seems to reflect the (exciton) absorption cross section. However, because of the fact that the RIXS spectra are normalized to constant spectator emission intensity, the intensity variations actually show a gradual change of the branching ratio between the spectator and the inelastic participator emission. Using Gel'mukhanov and Ågren's relation between scattering time and detuning (eq (4.9)) one is able to interpret this as follows. The scattering process is the shorter the further the excitation energy is from the resonance (larger Ω), which means that less time is available for initiating the movement of the atoms and hence less total energy transfer occurs to the lattice. For example, comparing chrysoberyl emission spectra excited at energies 119.3, 119.7 and 120.0 eV the weakening and flattening (also somewhat widening) of the spectra is seen. The same effect is also seen in the modeled spectra in Figure 13 as the lifetime width (Γ) increases. Although Γ and Ω are different in their nature, their effect on the scattering time is similar (see eq (4.9)).

The influence of the excitation energy detuning to scattering time is a well-known, important and useful property of RIXS. For example, large detuning is able to suppress vibrational mixing of different symmetries [76] and decrease the influence of vibrations [64]. Vice-versa, small detuning may allow final states with ungerade symmetries when purely electronic transitions would disallow this [60, 61, 77] i.e. an apparent violation of the parity selection rule. In other words, the (apparent) validity of electronic selection rules may be influenced by detuning.

Using the static dielectric constant of ϵ_0 (due to electronic and ionic polarizability) and the high-frequency dielectric constant of ϵ_∞ (due to electronic polarizability) of the compound one can estimate the phonon relaxation energy Σ_{ph} (also called the phonon self-energy [72]) [12, 14, 48, 78] of the lattice assuming that the core-hole is completely localized:

$$\Sigma_{ph} = S \times \hbar\omega = e^2 \sqrt{\frac{6}{\pi V}} \left[\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right] \quad (6.1)$$

Here ϵ_0 should not be confused with the dielectric permittivity of free space or vacuum permittivity in SI system of units, which in CGS (esu) is unity. V denotes the primitive cell volume. It was assumed that the relaxation energy appears as S longitudinal-optical phonons of a single frequency ω [48]. The polar coupling results from the long-range Coulomb interaction of the core-hole with the ionic polarizability of the medium. For insulators, core electron excitations couple most strongly with longitudinal-optical (LO) phonons [13] and, since these bands have little dispersion in ionic solids, an Einstein lattice is an excellent approximation [12, 14].

It is known that this simple model with a single phonon mode (LO) underestimates the relaxation energy [12, 14, 72], therefore an empirical correction factor of 2 should be used, as suggested by Mahan [72]. Miyano *et al.* used a scaling factor of 1.7 [14]. However, because of the empirical nature of the calculations done in this work, a systematic underestimation is of small importance in the following discussion.

The formula (6.1) is also used in the context of polaron theory. In fact, the small Fröhlich polaron in the strong coupling regime, the self-trapped exciton (or polaron) and the core excitons share some similarities in their interaction with the lattice.

In polar materials the lattice relaxation effect is expected to be strongest, as the (extra) charge of the core-hole interacts strongly with the other charges. Also, the excited state lifetimes are larger in metal oxides as the Auger decay rate is reduced. This is due to the higher ionicity of the oxides and the smaller overlap of the valence electrons with the cation core-hole [14]. The effect is expected to be weaker in metals, as the free electrons are able to screen the core-hole very effectively. In non-polar materials like diamond for example, the interaction is through induced charges on the neighbouring atoms and is expected to be weakest [13, 48]. However, as explained before, after the symmetry breaking, the interaction can be much stronger in non-polar materials also (like diamond). The electron-phonon coupling also depends on the strength of the excitation. For full core level ionization the coupling constant is larger than for core-excitons [79].

According to Toyozawa [80] the electron-phonon coupling constant V_q for polarons is:

$$V_q = \frac{\sqrt{4\pi\alpha\hbar\omega}}{\sqrt{k_p V q}} \quad (6.2)$$

Here, α is the dimensionless polaron coupling constant and k_p the reciprocal radius of the polaron, V the unit cell volume, $\hbar\omega$ the (longitudinal optical) phonon energy and q the magnitude of its wave vector. The coupling constant V_q defined in this way has the dimension of energy and is used in the interaction Hamiltonian of the polaron.

α and k_p are defined as:

$$\alpha = \frac{e^2 k_p}{8\pi\hbar\omega} \left[\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right]$$

$$k_p = \sqrt{\frac{2m\omega}{\hbar}}$$

As was stated before, the polarons in the strong coupling limit and excitons share many similarities and couple to the LO phonons. The scattering rate from polarons is proportional to the square of the electron-phonon coupling constant V_q and so is the strength of the electron-phonon interaction itself [80]. The (core-)hole-phonon interaction matrix element as used by Mahan [72] is very similar and justifies my assumption that the width of the ELT in the RIXS spectra (Θ) is proportional to the square of the electron-phonon coupling constant:

$$\Theta \sim \frac{2\pi}{\hbar} \left| V_q \right|^2 \rho \sim \left| V_q \right|^2 \sim \Sigma_{ph} \hbar\omega$$

Here q is assumed to be the wave-vector of a low-wavelength LO at the zone boundary. Here, the fact that the relaxation energy Σ_{ph} , the phonon energy $\hbar\omega$ and the coupling constant V_q are approximately related by the following equation [81] was used:

$$\Sigma_{ph} \cong \frac{\left| V_q \right|^2}{\hbar\omega} \quad (6.3)$$

Therefore the proposed empirical formula to estimate the width of the ELT is given by the following equation:

$$\Theta = \frac{C}{\hbar} \Sigma_{ph} \times \hbar\omega \quad (6.4)$$

The prefactor C is a dimensionless scaling or normalization constant. Here it is important to point out that the dimension of Θ as defined above, is energy per time. Since the timescale of the scattering process is in the femtosecond (10^{-15} s) rather than second scale, a low value of C (22×10^{-15}) was used to make the calculated values of Θ directly comparable to the experimental widths. One still has to bear in mind that because of the way Θ has been defined the comparison is made between parameters of different dimensions and their similar value is for convenience only, since the experimental RIXS spectra do not directly carry any information about the timescale of the emission process.

Phonons, created in both the absorption and emission process, result in a temperature-dependent broadening of the spectra [48]. A similar theory with linear electron-phonon coupling and the Einstein lattice with (longitudinal optical) phonon energy $\hbar\omega$ also predicts gaussian shape broadening of the spectral lines with standard deviation σ [10, 12, 48]:

$$\sigma^2 = S \times (\hbar\omega)^2 \coth\left(\frac{\hbar\omega}{2kT}\right) = \sum_{ph} \times \hbar\omega \times \coth\left(\frac{\hbar\omega}{2kT}\right) \quad (6.5)$$

Here S is again the dimensionless electron phonon coupling constant equal to the mean number of phonons created in the transition. It is assumed that S is large enough that the line shape will be gaussian [78]. Thus the relaxation energy times the phonon energy also appears in eq. (6.5), confirming its importance.

However more detailed analysis shows that the core-hole actually couples with all phonon modes (TA, LA, TO, LO) [72]. Also, the holes on the anion and cation sites experience different amount of phonon broadening and relaxation because their different coupling to the phonon modes [72]. The simple model is still enough to estimate the strength of the effect.

The relevant data and calculations have been collected to Table 1. The parameters have been obtained from various sources, but mainly from handbooks [82–84]. Crystallographic structure data is mostly taken from ref. [82]. In some cases, the Lorentz–Lorenz equation (also known as the Clausius–Mossotti relation or the Maxwell’s formula) has been used to calculate the dielectric permittivity from polarizabilities given in ref. [85]:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N\alpha' \quad (6.6)$$

Here n denotes the refractive index, α' is the mean polarizability (of the cell) and N is the density of the polarizability units. The magnetic permeability was assumed to be unity so that $\epsilon_\infty = n^2$ and thus ϵ_∞ could be estimated from optical refractive indices. In case of hexagonal, tetragonal or orthorhombic (LBO) crystals the weighted mean of the dielectric constants in different directions has been used.

In some cases there is a considerable wide range of values given in the literature, therefore the calculated values have been rounded accordingly.

The estimation of the relaxation energy for diamond is somewhat complicated because the static dielectric constant is given as 5.5–10. Many sources give the static permittivity value of 5.6. If this is the case then $\epsilon_0 \approx \epsilon_\infty$ and the lattice relaxation energy is almost zero. This is the expected result for a covalent non-ionic system like diamond. However graphite has a static relative permittivity of 12–15. Using this graphite upper value the relaxation energy calculates as 1.0 eV, this agrees very well with the theoretical calculations cited above (see chapter 4.3.1).

Table 1. Some measured, calculated and qualitative properties of several systems of interest.

	Linear thermal expansion α at 300K (10^{-6}K^{-1})	Thermal conductivity κ at 300K ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	LO phonon energy (eV)	Estimated Σ_{ph} (eV) (This work)	Other estimations Σ_{ph} (eV)	Estimated S (This work)	Estimated Θ (eV/s) (This work)	Observed width and/or strength of the ELI
Al_2O_3	3.9–4.3[86] 7.1–8.3[84]	35–39[84] 38[87]	0.11[83]	1.1	1.6[13]	10	4	2–4eV [88]
Beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$)	–2.9–2.6[89]	4.2–5.5	0.13 [90]	0.6–0.7 [85, 87]		5	3	3–4eV (unpublished data)
BeO	5.3–6[86] 7.5–8.5[84]	370[87] 245–250[84]	0.14[83, 86]	1.5–1.6		11	7	Strongest (5–6eV)
Chrysoberyl (BeAl_2O_4)	6.6–7.6[89]	23[91]	0.12 (931 cm^{-1}) [90]	1.2–1.3 [92]		10	5	Very strong ($\approx 5\text{eV}$)
Phenakite (Be_2SiO_4)	5.2–6.4[89]	35[93]	0.11 (880–950 cm^{-1}) [90]	0.9[85]		8	3	Very wide but weak in the Be site Medium in the Si site (3–4eV)
(BeSe) BeTe			≈ 0.07 (500–550 cm^{-1}) [94, 95]	0.2		3	0.3	Existing exciton but very weak or missing lattice relaxation [96]
B_2O_3			≈ 0.17 ($\approx 1400\text{cm}^{-1}$) [97]	0.5–0.6 [97]		3	3	3–4eV [98]
BBO ($\beta\text{-BaB}_2\text{O}_4$)	4(L c) [99] 36(II c) [99]	1.2 (L c) 1.6 (II c) [99]	0.17–0.18 (1400–1500 cm^{-1})	0.6–0.7 [100]		4	3.5	3–4eV

Table 1. Continuation

	Linear thermal expansion α at 300K (10^{-6}K^{-1})	Thermal conductivity κ at 300K ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	LO phonon energy (eV)	Estimated Σ_{ph} (eV) (This work)	Other estimations Σ_{ph} (eV)	Estimated S (This work)	Estimated Θ (eV/s) (This work)	Observed width and/or strength of the ELT
BBO ($\beta\text{-BaB}_2\text{O}_4$)	4(Lc) [99] 36(Ilc) [99]	1.2 (Lc) 1.6 (Ilc) [99]	0.17–0.18 (1400–1500 cm^{-1})	0.6–0.7 [100]		4	3.5	3–4eV
BN	3.5	760[93] 1300[87]	0.16[83]	0.6[82]		3–4	3	3–4eV [101]
C (graphite and diamond)	–0.6–1[87] 2.16[84]	2000[87] 3000[93]	0.16[83]	0–1	1.5–1.8 [33]	0–6	0–5	Very Strong (6eV) [59]
LBO (LiB_3O_5)	18 (mean) [99]	2.7–4.5[99]	0.17?	0.7–1.0 [82, 100]		4	4	3–4eV
LiCl LiBr	44–50[102]	2.5[103] 1.3[103]	0.029[14]	1.54	1.54 [14]	53	1	Weak (1–2eV) [14]
MgO	9.5–10.5[86] 11.52[84]	60[93] 40[87]	0.09[83, 86]	1.6	1.5–1.6 [12, 13]	18	4.5	?
$\beta\text{-SiC}$ (cubic)	2.8 [84]	300–490[93]	0.12[83]	0.3		2–3	1	Weak or missing [104]
($\alpha\beta$)- Si_3N_4	3	150	0.12 ($\approx 1000\text{cm}^{-1}$) [105]	0.4		3	1.6	Weak? (weak in γ -phase [106])
SiO_2	0.49–0.55[87]	1.5–1.8[84]	0.15[83]	1.0–1.1	<1.0 [13] 1–2[10]	7	5	Medium 3–5eV [10, 88]
TiO_2 (rutile)	7.14[84]	7.4–10.4[84]	0.1[83]	0.7–0.8 [87]	1.3 [107]	7–8	2.4	No exciton [108]

After examining the data in Table 1 one can notice that none of the (standard) properties values correlates well with the observed strength of the phonon relaxation. For example: the two crystals with the strongest ELT – BeO and diamond also have a large thermal conductivity. However, SiC also has a large thermal conductivity (and is very hard, similar to diamond) but a very small width of the ELT. Thus, the correlation between thermal expansion or thermal conductivity and the strength of the effect is small. LiCl (and also many other alkali halides) has a large dimensionless electron-phonon coupling constant but a small width of the ELT. LiCl also has equal estimated phonon relaxation energy with BeO but a much narrower ELT. The boron compounds have the largest phonon energies, but not the largest width of the ELT.

It can be seen that the calculated parameter Θ correlates well with the observed width of the ELT. The simple formula predicts a strong effect in BeO, chrysoberyl and graphite, in agreement with experiment. It also predicts that the effect will be weak in BeTe, LiCl, SiC, Si₃N₄, TiO₂. It is also interesting to point out that the borate compounds B₂O₃, BBO, BN and LBO (also LYBO and LGBO [53]) have similar calculated Θ values and measured widths of the lattice relaxation effect (also beryl). In phenakite there is a core exciton state on both the Be and Si site. The ELT in the Be site exciton emission is rather weak in intensity but very wide, while the emission ELT of the exciton centered on the Si atom is somewhat narrower but stronger. As explained before, the lattice relaxation energy depends on which atom the extra charge is (for example, cation or anion). Thus this is the reason why the predicted strength of the effect in phenakite lies in-between the two observed exciton emission ELT widths.

However, the simple formula somewhat overestimates the width of the ELT in SiO₂ and Al₂O₃ as can be seen when comparing the data in Table 1. This could be due to the fact that the effect was observed in the L edge exciton rather than the K edge exciton.

It is also important to notice that the correlation between the strength of the effect and the parameter Θ is not strictly linear and for low values of Θ the lattice relaxation effect may not be experimentally observable at all.

Also of interest is the superconducting layered boron compound MgB₂. The crystal structure of MgB₂ may be regarded as that of completely intercalated graphite with carbon replaced by boron, its neighbour in the periodic table [109]. Or in other words: hexagonal boron layers separated by hexagonal Mg layers. Mg has almost a charge state of 2+, the electrons have been transferred to the boron atoms, which should behave similarly to carbon atoms in graphite [110]. The predicted phonon relaxation strength (about $\Theta \approx 2.5 \text{ eV/s}$) of MgB₂ should be sufficient to observe weak lattice relaxation; however the boron core exciton is missing due to the metallic behaviour of the compound [110, 111] (see also chapter: 3.5. Core excitons).

Unfortunately no data was found about the phonon relaxation around the L edge exciton in MgO, but according to the table, a medium to large width of the ELT can be expected in that system.

Insufficient data was found to estimate the strength of the effect in lanthanum beryllate ($\text{La}_2\text{Be}_2\text{O}_5$), but in the work published in Paper III, it was determined that the effect in that system is very weak. The single crystal used in that study was grown using the Chohralski method at the Design and Technological Institute of Monocrystals in Novosibirsk. The measurements were performed at room temperature like most of the other studies. These data support the observation that the existence of light elements like Be is not sufficient for the existence of the ELT. Similarly to lanthanum beryllate there was no indication of phonon losses in the Si 2p RIXS spectra of the Y_2SiO_5 crystal.

Tanaka and Kayanuma conjectured that such a large atomic displacement effect is a universal characteristic for light element materials in which the 1s core-hole has a relatively long lifetime and the phonon energy is relatively high [65]. However in the light of this work it seems that the strength of the effect is somewhat more complicated than that – a strong electron-phonon coupling is necessary for the manifestation of the effect.

SUMMARY

The present thesis focuses on soft X-ray spectroscopy of insulators, especially resonant inelastic X-ray scattering (RIXS) experiments. Both experimental and theoretical work on some beryllium and boron compounds has been carried out.

First an overview of relevant X-ray spectroscopies (XAS, XPS, XES, RIXS) was given, then the theoretical cross sections for some processes were derived. The benefits of synchrotron radiation and the layout of the I511 beam-line at the MAX-lab synchrotron radiation facility are briefly described.

The measurement of X-ray absorption spectra in the so-called yield mode is explained. The oxidation state of the cation and the phase composition of Fe oxide [Paper II] thin films has been analysed from the measured XAS spectra. A temperature-dependent phase transition was observed in that system.

RIXS studies show that a boron core exciton has level exists in both LBO and BBO, similarly to BN and B₂O₃. The strong anisotropy of BBO and the small anisotropy of LBO [Paper I] were also evident in their X-ray spectra. It was shown that the measured BBO X-ray spectra can be interpreted remarkably well using a molecular picture of the solid.

And finally and most importantly the strength of the phonon relaxation effect in solids was studied. Experimental work on many systems has been done [Papers I, III, IV]. First, an overview of previous work on two well studied systems – diamond and graphite – was given. A simple model to account for the shape of the emission band was developed [Paper IV]. The results from that model are in agreement with experimental data and with previous theoretical work. Furthermore, a case was made that energy dissipation during the excited state lifetime may be important for the correct description of the shape of the ELT. The strength of the phonon relaxation effect was shown to be empirically well predicted by the electron-phonon interaction strength: the product between the estimated lattice relaxation energy and the energy of the LO phonon.

SUMMARY IN ESTONIAN

Isolaatorite spektroskoopia pehme röntgenkiirguse abil

Käesolev väitekirj keskendub isolaatorite (laia keelutsooniga materjalid) röntgenspektroskoopiale põhitähelepanuga resonantsel röntgenhajumisel (RIXS). Eksperimentaalseid ja teoreetilisi uuringuid on tehtud erinevatel berülliumi ning booriühenditel. Sissejuhatuses kirjeldatakse röntgenspektroskoopia ajalugu ning tuuakse välja mõned olulisemad saavutused selles valdkonnas. Antakse põgus ülevaade olulisematest röntgenspektroskoopia võimalustest (XAS, XPS, XES, RIXS), seejärel tuletatakse teoreetilises osas mõningate protsesside ristlõigete avaldised.

Kirjeldatakse lühidalt sünkrotronkiirguse eeliseid ning I511 kiirekanalit sünkrotronkiirguse keskuses MAX-lab (Lund, Rootsi). Seejärel selgitatakse röntgenneeldumisspektrite mõtmist nn *yield* režiimis.

Raudoksiidi õhukeste kilede katiooni oksüdatsiooniastet ning aine faasi-koostist on püütud määrata mõõdetud röntgenneeldumisspektritest [Artikkel II]. Leiti faasikoostise sõltuvus kile sünteesitemperatuurist.

Resonantse ergastusega röntgenemissioonispektritest selgub, et LBO ja BBO boori aatomitel eksisteerib röntgeneksiton, sarnaselt BN ja B_2O_3 [Artikkel I]. Samuti on töös leitud, et BBO suur anisotroopia ning LBO väike anisotroopia avaldub selgelt ka nende röntgenspektrites. Väitekirjas näidatakse täiendavalt, et BBO RIXS spektreid on võimalik üllatavalt hästi kirjeldada kasutades BBO molekulaarset anioonrühma $B_3O_6^{3-}$.

Dissertatsiooni kõige olulisem osa on foononrelaksatsiooni uurimus tahkistes. Nimelt on mõnede ainete (C, BBO, LBO, BeO jt) RIXS spektrites võimalik näha energiakao tiiba elastse hajumise joone kõrval. Antud nähtust on eksperimentaalselt mitmetes süsteemides uuritud [Artiklid I, III, IV]. Töös antakse ülevaade kirjandusest kõige põhjalikumalt uuritud süsteemide – teemant ning grafiit – kohta. Välja on töötatud lihtne mudel, mis kirjeldab emissioonispektrites esineva energiakao „tiiva” kuju [Artikkel IV]. Mudeliga tehtud arvutused on kooskõlas nii eksperimendi kui ka sarnaste eelnevate teoreetiliste arvutustega. Lisaks sellele esitati argumente väite, et foononite energia hajumine ergastatud seisundi eluea jooksul võib olla oluline mõõdetud spektrite kirjeldamisel, kinnitamiseks. Samuti näidati, et nähtuse tugevus on empiiriliselt hästi ennustatud elektron-foonon interaktsiooni tugevusega: ligikaudu võre relaksatsioonienergia korrutis süsteemi LO (optiline pikivõnkumise) foononi energiaga.

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REFERENCES

- [1] H. Wende, Rep. Prog. Phys. 67 (2004) 2105.
- [2] P. Eisenberger, M.P. Platzman, H. Winick, Phys. Rev. Lett. 36 (1976) 623.
- [3] T. Schmitt, Uppsala University, Uppsala, 2004.
- [4] A. Nilsson, vol. 2012, 2012.
- [5] M. Altarelli, Lect. Notes Phys. 697 (2006) 201.
- [6] L.J.P. Ament, Leiden University, Leiden, 2010.
- [7] R. Santra, J. Phys. B: At. Mol. Opt. Phys. 42 (2009) 023001.
- [8] G.W.F. Drake (Ed.), Atomic, Molecular & Optical Physics Handbook, American Institute of Physics, 1996.
- [9] N. Zettili, Quantum Mechanics, John Wiley and Sons, 2001.
- [10] V.J. Nithianandam, S.E. Schnatterly, Phys. Rev. B 38 (1988) 5547.
- [11] W.L. O'Brien, J. Jia, Q.-Y. Dong, T.A. Callcott, J.E. Rubensson, D.L. Mueller, D.L. Ederer, Phys. Rev. B 44 (1991) 1013.
- [12] W.L. O'Brien, J. Jia, Q.-Y. Dong, T.A. Callcott, D.R. Mueller, D.L. Ederer, Phys. Rev. B 45 (1992) 3882.
- [13] W.L. O'Brien, J. Jia, Q.-Y. Dong, T.A. Callcott, K.E. Miyano, D.L. Ederer, D.R. Mueller, C.-C. Kao, Phys. Rev. B 47 (1993) 140.
- [14] K.E. Miyano, D.L. Ederer, T.A. Callcott, Q.-Y. Dong, J.J. Jia, L. Zhou, D.R. Mueller, Phys. Rev. B 49 (1994) 5929.
- [15] J.P. Rueff, in: E. Beaurepaire (Ed.), Magnetism and Synchrotron Radiation, Springer, 2010, p. 263.
- [16] Y. Feng, G.T. Seidler, J.O. Cross, A.T. Macrander, J.J. Rehr, Phys. Rev. B 69 (2004) 125402.
- [17] J.H. Hubbell, W.J. Veigele, E.A. Briggs, R.T. Brown, D.T. Cromer, R.J. Howerton, J. Phys. Chem. Ref. Data 4 (1975) 471.
- [18] P.L. Cowan, in: G. Materlik, C.J. Sparks, K. Fischer (Eds.), Resonant Anomalous X-Ray Scattering Theory and Applications, 1994, p. 449.
- [19] W. Schülke, Electron Dynamics by Inelastic X-ray Scattering, Oxford University Press, 2007.
- [20] P. Skytt, P. Glans, K. Gunnelin, J. Guo, J. Nordgren, Phys. Rev. A 55 (1997) 146.
- [21] F. Gel'mukhanov, H. Agren, Phys. Rep. 312 (1999) 87.
- [22] L. Qian, Uppsala University, Uppsala, 2001.
- [23] A. Hofmann, The Physics of Synchrotron Radiation, Cambridge University Press, 2004.
- [24] R. Denecke, P. Väterlein, M. Bässler, N. Wassdahl, S. Butorin, A. Nilsson, J.E. Rubensson, J. Nordgren, N. Martensson, R. Nyholm, J. Electron Spectrosc. Relat. Phenom. 101–103 (1999) 971.
- [25] J. Nordgren, G. Bray, S. Cramm, R. Nyholm, J.E. Rubensson, Rev. Sci. Instrum. 60 (1989) 1690.
- [26] J. Nordgren, J. Guo, J. Electron Spectrosc. Relat. Phenom. 110–111 (2000) 1.
- [27] K. Tsuji, J. Injuk, R. Van Grieken (Eds.), X-Ray Spectrometry: Recent Technological Advances., John Wiley & Sons, Ltd, 2004.
- [28] L. Tröger, D. Arvantis, K. Baberschke, H. Michaelis, U. Grimm, E. Zschleeh, Phys. Rev. B 46 (1992) 3283.

- [29] S. Eiseblitt, T. Böske, J.E. Rubensson, W. Eberhardt, *Phys. Rev. B* 47 (1993) 14103.
- [30] A.J. Achkar, T.Z. Regier, E.J. Monkman, K.M. Shen, D.G. Hawthorne, *Sci. Rep.* 1 (2011) 182.
- [31] W.L. O'Brien, J. Jia, Q.-Y. Dong, T.A. Callcott, D.L. Mueller, D.L. Ederer, C.-C. Kao, *Phys. Rev. B* 47 (1993) 15482.
- [32] K. Hämäläinen, D.P. Siddons, J.B. Hastings, L.E. Berman, *Phys. Rev. Lett.* 67 (1991) 2850.
- [33] K.A. Mäder, S. Baroni, *Phys. Rev. B* 55 (1997).
- [34] J.B. MacNaughton, A. Moewes, R.G. Wilks, X.T. Zhou, T.K. Sham, T. Taniguchi, K. Watanabe, C.Y. Chan, W.J. Zhang, I. Bello, S.T. Lee, H. Hofsäss, *Phys. Rev. B* 72 (2005) 195113.
- [35] R. Ahuja, P.A. Brühwiler, J.M. Wills, B. Johansson, N. Martensson, O. Eriksson, *Phys. Rev. B* 54 (1996) 14396.
- [36] S.T. Pantelides, *Phys. Rev. B* 11 (1975) 2391.
- [37] A.B. Preobrajenski, A.S. Vinogradov, S.A. Krasnikov, R. Szargan, N. Martensson, *Phys. Rev. B* 69 (2004) 115116.
- [38] V. Kisand, U. Joost, V. Reedo, R. Pärna, T. Tatté, J. Shulga, A. Saar, L. Matisen, A. Kikas, I. Kink, *Appl. Surf. Sci.* 256 (2010) 4538.
- [39] R. Pärna, U. Joost, E. Nõmmiste, T. Käämbre, A. Kikas, I. Kuusik, I. Hirsimäki, I. Kink, V. Kisand, *Appl. Surf. Sci.* 257 (2011) 6897.
- [40] R. Pärna, U. Joost, E. Nõmmiste, T. Käämbre, A. Kikas, I. Kuusik, I. Hirsimäki, I. Kink, V. Kisand, *Phys. Status Solidi (A)* 209 (2012) 953.
- [41] F.M.F. De Groot, J.C. Fuggle, B.T. Thole, G.A. Sawatzky, *Phys. Rev. B* 41 (1990) 928.
- [42] R. Ruus, A. Kikas, A. Saar, A. Ausmees, E. Nõmmiste, J. Aarik, A. Aidla, T. Uustare, I. Martinson, *Solid State Communications* 104 (1997) 199.
- [43] G. van der Laan, *Phys. Rev. B* 41 (1990) 12366.
- [44] F.M.F. De Groot, M. Grioni, J.C. Fuggle, J. Ghijsen, G.A. Sawatzky, H. Petersen, *Phys. Rev. B* 40 (1989) 5715.
- [45] Y. Ma, P.D. Johnson, N. Wassdahl, J. Guo, P. Skytt, J. Nordgren, S.D. Kevan, J.E. Rubensson, T. Böske, W. Eberhardt, *Phys. Rev. B* 48 (1993) 2109.
- [46] F.M.F. De Groot, J.C. Fuggle, B.T. Thole, G.A. Sawatzky, *Phys. Rev. B* 42 (1990) 5459.
- [47] S.J. Broton, R. Shapiro, G. van der Laan, J. Guo, P. Glans, J.M. Ajello, *J. Geophysical Research* 112 (2007) G03004.
- [48] R.D. Carson, S.E. Schnatterly, *Phys. Rev. B* 39 (1989) 1659.
- [49] M. Engler, C. Lasniak, R. Damasch, B. Ruisinger, J. Eichler, *Process Engineering* 84 (2007) e49.
- [50] S.-F. Wang, Y.-F. Hsu, J.-C. Pu, J.C. Sung, L.G. Hwa, *Materials Chemistry and Physics* 85 (2004) 432.
- [51] C. Chen, Y. Wu, A. Jiang, B. Wu, G. You, R. Li, S. Lin, *J. Opt. Soc. Am. B* 6 (1989) 616.
- [52] E.F. Dolzhenkova, V.N. Baumer, A.V. Tolmachev, R.P. Yavetsky, *Materials Research Bulletin* 41 (2006) 530.
- [53] I. Kuusik, T. Käämbre, A. Kikas, V. Pustovarov, V. Ivanov, in: U. Johansson, K. Lilja, A. Nyberg, R. Nyholm (Eds.), *MAX-lab activity report 2010, 2011*, p. 234.

- [54] T. Sasaki, Y. Mori, M. Yoshimura, Y.K. Yap, in: K. Byrappa, T. Ohachi (Eds.), *Crystal Growth Technology*, Springer, New York, 2003, p. 419.
- [55] K. Wu, C. Chen, *Appl. Phys. A* 54 (1992) 209.
- [56] R.H. French, J.W. Ling, F.S. Ohuchi, C.T. Chen, *Phys. Rev. B* 44 (1991) 8496.
- [57] G.D. Mahan, *Phys. Rev. B* 15 (1977) 4587.
- [58] C.-O. Almbladh, *Phys. Rev. B* 16 (1977) 4343.
- [59] Y. Ma, P. Skytt, N. Wassdahl, P. Glans, D.C. Mancini, J. Gou, J. Nordgren, *Phys. Rev. Lett.* 71 (1993) 3725.
- [60] F. Hennies, S. Polyutov, I. Minkov, A. Pietzsch, M. Nagasono, F. Gel'mukhanov, L. Triguero, M.-N. Piancastelli, W. Wurth, H. Agren, A. Föhlisch, *Phys. Rev. Lett.* 95 (2005) 163002.
- [61] F. Hennies, S. Polyutov, I. Minkov, A. Pietzsch, M. Nagasono, H. Ågren, L. Triguero, M.-N. Piancastelli, W. Wurth, F. Gel'mukhanov, A. Föhlisch, *Phys. Rev. A* 76 (2007) 032505.
- [62] Y.-P. Sun, F. Hennies, A. Pietzsch, B. Kennedy, T. Schmitt, V.N. Strocov, J. Andersson, M. Berglund, J.E. Rubensson, K. Aidas, F. Gel'mukhanov, M. Odelius, A. Föhlisch, *Phys. Rev. B* 84 (2011) 132202.
- [63] P. Glans, P. Skytt, K. Gunnelin, J.H. Guo, J. Nordgren, *J. Electron Spectrosc. Relat. Phenom.* 82 (1996) 193.
- [64] F. Hennies, A. Pietzsch, M. Berglund, A. Föhlisch, T. Schmitt, V. Strocov, H. Karlsson, J. Andersson, J.E. Rubensson, *Phys. Rev. Lett.* 104 (2010) 193002.
- [65] S. Tanaka, Y. Kayanuma, *Phys. Rev. B* 71 (2005) 024302.
- [66] F. Mauri, R. Car, *Phys. Rev. Lett.* 73 (1995).
- [67] Y. Harada, T. Tokushima, Y. Takata, T. Takeuchi, Y. Kitajima, S. Tanaka, Y. Kayanuma, S. Shin, *Phys. Rev. Lett.* 93 (2004) 017401.
- [68] S. Tanaka, Y. Kayanuma, *Solid State Communications* 100 (1996) 77.
- [69] A. Yasui, Y. Kayanuma, S. Tanaka, Y. Harada, *Phys. Rev. B* 74 (2006) 205404.
- [70] Y. Kayanuma, S. Tanaka, *J. Electron Spectrosc. Relat. Phenom.* 136 (2004) 167.
- [71] Y. Ma, *Phys. Rev. B* 49 (1994).
- [72] G.D. Mahan, *Phys. Rev. B* 21 (1980) 4791.
- [73] T. Käämbre, A. Kikas, K. Kooser, V. Kisand, M. Kirm, A. Saar, E. Nömmiste, V. Ivanov, V. Pustovarov, M. Martinson, *J. Electron Spectrosc. Relat. Phenom.* 156–158 (2007) 299.
- [74] J.N. Andersen, T. Balusubramanian, C.-O. Almbladh, L.I. Johansson, R. Nyholm, *Phys. Rev. Lett.* 86 (2001) 4398.
- [75] L.H. Li, M. Petracic, B.C.C. Cowie, T. Xing, R. Peter, Y. Chen, C. Si, W. Duan, *Appl. Phys. Lett.* 101 (2012) 191604.
- [76] P. Skytt, P. Glans, J. Guo, K. Gunnelin, C. Sathe, J. Nordgren, F. Gel'mukhanov, A. Cesar, H. Agren, *Phys. Rev. Lett.* 77 (1996) 5035.
- [77] K. Gunnelin, P. Glans, J.E. Rubensson, C. Sathe, J. Nordgren, Y. Li, F. Gel'mukhanov, H. Agren, *Phys. Rev. Lett.* 83 (1999) 1315.
- [78] P.H. Citrin, P. Eisenberger, D.R. Hamann, *Phys. Rev. Lett.* 33 (1974) 965.
- [79] P. Unsworth, J.E. Evans, P. Weightman, A. Takahashi, J.A.D. Matthew, Q.C. Herd, *Phys. Rev. B* 54 (1996) 286.
- [80] Y. Toyozawa, *Optical processes in solids*, Cambridge University Press, New York, 2003.
- [81] J.R. Schrieffer, J.S. Brooks (Eds.), *Handbook of High-Temperature Superconductivity Theory and Experiment*, Springer, New York, 2007.

- [82] W.J. Tropf, M.E. Thomas, T.J. Harris, in: M. Bass (Ed.), *Handbook of Optics*, vol. 4, McGraw-Hill, 2001.
- [83] E.D. Palik, *Optical Parameters for the Materials in HOC I and HOC II* Elsevier Science, 1991.
- [84] W. Martienssen, H. Warlimont, *Handbook of Condensed Matter and Materials Data*, Springer, 2004.
- [85] A.C. Lasaga, R.T. Cygan, *American Mineralogist* 67 (1982) 328.
- [86] T. Hanada, in: T. Yao, S.-K. Hong (Eds.), *Oxide and Nitride Semiconductors*, Springer, 2009.
- [87] R.J.D. Tilley, *Understanding solids: the science of materials*, John Wiley & Sons Inc., 2004.
- [88] W.L. O'Brien, J. Jia, Q.-Y. Dong, T.A. Callcott, J.E. Rubensson, D.R. Mueller, D.L. Ederer, *Nuclear Instruments and Methods in Physics Research B* 56–57 (1991) 320.
- [89] T.J. Ahrens, *Mineral physics and crystallography : a handbook of physical constants*, American Geophysical Union, Washington, 1995.
- [90] J. Jehlicka, P. Vandenabeele, H.G.M. Edwards, *Spectrochimica Acta Part A* 86 (2012) 341.
- [91] C.F. Cline, R.C. Morris, M. Dutoit, P.J. Harget, *Journal of Materials Science* 14 (1979) 941.
- [92] R.D. Shannon, M.A. Subramanian, *Physics and Chemistry of Minerals* 16 (1989) 747.
- [93] S.L. Shinde, J.S. Goela, *High Thermal Conductivity Materials*, Springer, New York, 2006.
- [94] Z. Mameri, A. Zaoui, A. Belabbes, M. Ferhat, *Materials Chemistry and Physics* 123 (2010) 343.
- [95] D.N. Talwar, *Phys. Rev. B* 82 (2010) 085207.
- [96] D. Eich, et al., *Phys. Rev. B* 73 (2006) 115212.
- [97] N.A. El-Alaily, R.M. Mohamed, *Materials Science and Engineering B* 98 (2003) 193.
- [98] A. Mansour, S.E. Schnatterly, *Phys. Rev. Lett.* 59 (1987) 567.
- [99] Cleveland Crystals Inc., <http://www.clevelandcrystals.com/BBOLBO.htm>, vol. 2013, 2013.
- [100] V. Trnovcova, M. Kubliha, A. Kokh, P.P. Fedorov, R.M. Zakalyukin, *Russian Journal of Electrochemistry* 47 (2011) 531.
- [101] J.A. Carlisle, S.R. Blankenship, L.J. Terminello, J. Jia, T.A. Callcott, D.L. Ederer, R.C. Perera, F.J. Himpsel, *J. Electron Spectrosc. Relat. Phenom.* 110-111 (2000) 323.
- [102] D.B. Sirdeshmukh, L. Sirdeshmukh, K.G. Subhadra, *Micro- and Macro-properties of Solids: Thermal, Mechanical and Dielectric Properties*, Springer, New York, 2006.
- [103] S. Pettersson, *J. Phys. C: Solid State Phys.* 20 (1987) 1047.
- [104] J. Lüning, J.E. Rubensson, C. Ellmers, S. Eiseblitt, W. Eberhardt, *Phys. Rev. B* 56 (1997) 13147.
- [105] R. Vogelgesang, M. Grimsditch, J.S. Wallace, *J. Appl. Phys.* 92 (2002) 3103.
- [106] S. Leitch, A. Moewes, L. Ouyang, W.Y. Ching, T. Sekine, *J. Phys.: Condens. Matter* 16 (2004) 6469.

- [107] A.E. Taverner, C. Rayden, S. Warren, A. Gulino, P.A. Cox, R.G. Egdell, *Phys. Rev. B* 51 (1995) 6833.
- [108] J. Jimenez-Mier, J. van Ek, D.L. Ederer, T.A. Callcott, J.J. Jia, *Phys. Rev. B* 59 No. 4 (1999).
- [109] J.K. Burdett, G.J. Miller, *Chemistry of Materials* 2 (1990) 12.
- [110] K.D. Tsuei, H.-J. Lin, L.-C. Lin, T.-Y. Hou, H.-H. Hsieh, *International Journal of Modern Physics B* 16 (2002) 1619.
- [111] A.V. Sokolov, E.Z. Kurmaev, S. Leitch, A. Moewes, J. Kortus, L.D. Finkelstein, N.A. Skorikov, C. Xiao, A. Hirose, *J. Phys.: Condens. Matter* 15 (2003) 2081.

PUBLICATIONS

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2008– Institute of Physics, University of Tartu, engineer.
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Scientific work:

Main area of research is X-ray and electron spectroscopy of insulating materials, especially resonant inelastic X-ray scattering (RIXS). Special interest has been held in evidences of lattice relaxation effects in RIXS spectra. Extensive experience in working on synchrotrons has been obtained. Experience or familiarity with different experimental techniques like XES, RIXS, XAS, PES, XPS, XANES, XRD and XMCD is present.
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Peamine uurimisvaldkond on isolaatorite röntgen- ja elektronspektroskoopia, suurima rõhuasetusega pehme röntgenkiirguse resonantsel hajumisel (resonant inelastic X-ray scattering – RIXS). Eesmärk on uurida kuidas avaldub erinevate ainete resonantsergastusega röntgenfluorestsentsi spektrites võnkerelaksatsioon. Omandatud on sünkrotronil töötamise kogemus. Lisaks on kasutanud või kokku puutunud selliste eksperimentaalmeetoditega nagu XES, RIXS, XAS, PES, XPS, XANES, XRD, XMCD jm.

Publikatsioone: 8 artiklit rahvusvahelistes eelretsenseeritavates teadusajakirjades

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