STUDY OF CHEMICAL BONDS BY WAVELENGTH DISPERSIVE X-RAY SPECTROSCOPY

Seminar

Author: Nataša Grlj
Mentor: dr. Matjaž Kavčič

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Abstract

The basic principles of the wavelength dispersive X-ray spectroscopy employing crystal spectrometers is described in this seminar. Some effects of chemical bonding on the emitted X-ray spectra of the excited atom are presented and its potential use for the chemical-state analysis. Finally chemical state analysis of sulphur in samples of environmental interest employing high resolution crystal spectrometer at the J. Stefan Institute is demonstrated.
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1 Introduction

Radiative transitions between inner shell electrons result in emission of X-ray photons in the keV energy region. In the spectroscopy of these X-ray transitions, we typically measure X-rays in the energy region of 1 - 30 keV. Solid state detectors, such as Si(Li) detector, usually applied in such spectroscopy, have energy resolution in the order of 130 - 150 eV. This is two order of magnitude larger value than the natural linewidths of the measured transitions. In order to observe fine structure in the emitted X-ray spectra at the eV scale, a high resolution spectrometer is required. For photons in the energy region of 1 keV up to few hundreds of keV, the best resolution can be obtained with crystal spectrometers.

In the following seminar the basic principle of operation of such spectrometers is described. This is followed by the general description of some typical effects of chemical bonding in X-ray spectra. More emphasis is given towards the change in the intensity distribution of the satellite lines induced in collisions with heavy ions and its potential use for chemical-state analysis.

At the end the experimental set-up at the Microanalytical center of the J. Stefan Institute will be described through the measurements of high-resolution proton induced X-ray spectra for the chemical state analysis of S in samples of environmental interest, in particular of the aerosol samples. The presented experimental results will clearly demonstrate the feasibility of quantitative chemical state speciation by employing high resolution proton induced X-ray spectra.

2 Crystal spectrometers

Crystal spectrometers use the fact that a photon beam hitting a crystal is reflected if an integer multiple N of the wavelength $\lambda$ and the incidence angle $\Theta_B$ fulfill the Bragg’s condition

$$2d\sin\Theta_B = N\lambda,$$

where $d$ is the reflecting crystal lattice spacing and $N$ the order of reflection. The photon’s wavelength $\lambda$ and energy $E$ are connected through the known relation

$$E = \frac{hc}{\lambda}.$$

To measure the X-ray spectrum using this method, the incident beam has to be collimated, and the detector is placed at the corresponding position on the opposite side of the normal. The system effectively selects all rays which are incident at the appropriate Bragg angle. If the angle of incidence is then varied, which is normally done by rotating the crystal through a controllable angle and the detector by twice this amount, the detector will receive radiation over a range of wavelengths and a spectrum will be obtained. When a position sensitive detector is used to detect diffracted photons (see Fig. 1) we can record an energy spectrum at a fixed crystal/detector position. The energy acceptance is usually limited by the lateral dimensions of the detector.

The most important parameter of such spectrometer is its energy resolution which is given by the angular resolution of the spectrometer. By differentiating equation 1, we get

$$Nd\lambda = 2d\cos\Theta_B d\Theta_B.$$

Thus, the angular dispersion of the crystal spectrometer is given by

$$\frac{d\Theta}{d\lambda} = \frac{N}{2d\cos\Theta_B} = \frac{\tan\Theta_B}{\lambda}.$$
The resolving power of the crystal spectrometer (taken with the smallest detectable wavelength separation $\Delta \lambda$) is defined as [10]

$$R = \frac{E}{dE} = \frac{\lambda}{\Delta \lambda} = \frac{\tan \Theta_B}{\Delta \Theta}.$$  

(2)

$\Delta \Theta$ is the FWHM (Full Width Half Maximum) of the recorded spectrum of monoenergetic line and depends on the structure of the crystal and on the experimental parameters.

The energy resolution $\Delta E$ as a function of the energy $E$ is given by

$$\Delta E = \frac{E^2}{NE_{cry}} \sqrt{1 - \left(\frac{NE_{cry}}{E}\right)^2} \Delta \Theta,$$

(3)

where we have introduced a parameter $E_{cry} = \frac{hc}{2d}$ which depends only on the crystal used. When the energy of the photons is increasing (and the reflection angles are becoming small, so $\sin \Theta_B \to 0 \Rightarrow \frac{NE_{cry}}{E} \ll 1$), the energy resolution can be approximated with

$$\Delta E \approx \frac{E^2}{NE_{cry}} \Delta \Theta.$$  

(4)

This has a consequence that for high energy photons the resolution decreases drastically and in the region around 1 MeV it usually becomes comparable to that of a solid state detector.

Let's try to estimate the angular resolution of a typical crystal spectrometer. The dominant contribution is usually the finite spatial resolution with which we are detecting the diffracted photons. Just for estimation I will use the strongest line of the $Fe^{55}$ source which is at the energy of 5.899 keV. One of the most commonly used crystals in this energy range is a LiF (200) crystal with a lattice spacing $2d = 4.027$ Å. The Bragg angle for this line is though $31.46^\circ$.

The angular resolution can be simply estimated just as a ratio between spatial resolution for the detection of reflected photons and a distance between the target and the detector. This two values are tipically around $100 \mu m$ and $0.5 - 1 m$, respectively. This yields a factor of around $10^{-4}$ for angular resolution demonstrating that with crystals spectrometers a resolving power of few thousands can be achieved (in our case, $R \sim 6000$).

Since the incident monochromatic radiation is reflected only within a small angle $\Delta \omega$ the crystal spectrometers have usually low efficiency. The reflectance for the incident beam is determined
by the crystal rocking curve which is characteristic for the specific crystal, the wavelength, and the order of reflection. It also limits the resolution of the corresponding flat single crystal spectrometer since the Bragg condition is fulfilled only for a very narrow region of the crystal.

![Bragg reflection](image)

**Figure 2:** Bragg reflection on the flat crystal. The monochromatic radiation is effectively reflected only within the angular range $\Delta \omega$. The shape of the reflected line determines the crystal rocking curve.

In order to increase the efficiency, focusing curved crystal spectrometers are used. Figure 3 shows the basic idea of such spectrometers. If the diameter of the circle (called the Rowland circle) where the point source S lies is precisely the radius of crystal curvature R, then the radiation from the source meets the Bragg condition for the entire crystal simultaneously. The (monochromatic) radiation is so focused into an image D (again at the Rowland circle). In this way, the efficiency can be increased up to two orders of magnitude.

In case of high energy photons (above 20 keV) the transmission geometry is usually applied. In this case the crystal planes are oriented perpendicular to the crystal surface while the crystal surface itself is bent along a Rowland circle. Here the divergent beam is diffracted into an extended detector situated on the other side of the crystal.

![Focusing crystal arrangements](image)

**Figure 3:** Schematic principle of focusing crystal arrangements. On the left side the reflection (Bragg) geometry usually used for photons with energies less than 20 keV is presented. The transmission (Laue) geometry used for photons with energies above 20 keV is displayed on the right side.

The next table shows some basic parameters of few typical crystals most commonly used in crystal spectrometers. (TIAP stands for Thallium Acid Phthalate and E.D.d.T. for Ethylene Dihydrogen Dextrotartrate.)
### 3 Chemical effects in X-ray spectra

As I stated before, one thing that can be observed when high experimental energy resolution is available, are the changes in the fine structure of the emitted spectra due to the changes in chemical environment. These effects in the K and L lines of the X-ray spectra can be observed through various aspects: energy shifts of the spectral lines, changes in the intensity ratios, changes in linewidths, satellite formation and peak profile changes. They are difficult to be calculated analytically and this is usually done via different numerical methods (look section 3.2). However, changes in the intensity ratios can be understood with the use of some simple calculations and I will explain this below.

#### 3.1 Change in the intensity distribution of satellite lines

In the collision of heavy ion with the atom several inner shell electrons can be ejected as a result of direct Coulomb interaction of the projectile with the target electrons. In this case, we have a simultaneous ionization of the K shell plus some (N) L shell electrons and we can resolve the KL\(^N\) satellite lines in the K X-ray spectra (corresponding to the 1\(s\)-2\(p\) transition in \(KL^N\) ionized atom). These satellite lines are situated on the high energy tail of the diagram line corresponding to transition in singly ionized atom (see below).

**Kα diagram:** \(K(1s) \rightarrow L(2p)\) transition

Energy of the emitted photons is

\[
E_{\text{diag}} = E_K - E_L,
\]

where \(E_K\) and \(E_L\) represents the energy of the K and L shell.

**KαL\(^1\) satellite:** \(KL \rightarrow LL\) transition

The energy of emitted photons in this case is

\[
E_{\text{sat}} = E_{KL} - E_{LL}.
\]

There are two holes in the initial and final state of the atom. We can approximate the energy of this states as:

\[
E_{KL} = E_K + E_L^* \quad E_{LL} = E_L + E_L^{**}.
\]

The change in the effective potential due to the surrounding electrons is smaller in the final state and it follows:

\[
E_{\text{sat}} - E_{\text{diag}} = (E_L^* - E_L^{**}) > 0. \quad (5)
\]

This shows that the **satellite line has higher energy than the main** (diagram) one (see also figures 4, 5 or 7).

Within the independent electron approximation the \(KL^N\) ionization probability can be written as a product of the ionization probability of separate shells, so the corresponding cross section is [1]:

<table>
<thead>
<tr>
<th>crystal</th>
<th>Lithium Fluoride</th>
<th>Quartz</th>
<th>Germanium</th>
<th>TlAP</th>
<th>E.D.d.T.</th>
</tr>
</thead>
<tbody>
<tr>
<td>refl. planes orientations</td>
<td>200</td>
<td>220</td>
<td>420</td>
<td>1011</td>
<td>1010</td>
</tr>
<tr>
<td>2d [nm]</td>
<td>0.403</td>
<td>0.285</td>
<td>0.180</td>
<td>0.669</td>
<td>0.425</td>
</tr>
<tr>
<td>(E_{\text{cry}}[\text{keV}])</td>
<td>3.077</td>
<td>4.350</td>
<td>6.888</td>
<td>1.853</td>
<td>2.917</td>
</tr>
</tbody>
</table>
\[ \sigma_{KL^N} = 2\pi \int_0^\infty P_K(b)P_L(b)b\,db, \quad (6) \]

where \( P_K(b) \) and \( P_L(b) \) are K and L shell ionization probabilities respectively and \( b \) is the impact parameter.

L shell ionization is practically constant for small impact parameters (i.e. for those, where K shell ionization can occur - from L shell point of view such collisions are central). Then the \( KL^N \) ionization cross section is given by

\[ \sigma_{KL^N} \approx 2\pi P_L^N(0) \int_0^\infty P_K(b)b\,db = 2\pi P_L^N(0)\sigma_K. \quad (7) \]

Within the independent electron approximation the multiple L shell ionization probability \( P_L^N(0) \) is given by simple binomial distribution:

\[ P_L^N(0) = \left( \frac{8}{N} \right) p_L^N(0)(1 - p_L^N(0))^{8-N}. \]

The intensity distribution of the \( KL^N \) satellites is therefore well described with the binomial distribution governed by the single electron ionization probability.

In the semiclassical approximation (SCA - where the projectile is treated classically, while the atomic electron is described with quantum wave function) the ionization probability for the isolated atom can be written as

\[ p(b) = \frac{1}{\hbar^2} \left| \int_{-\infty}^{\infty} \exp(i\omega t)\langle \chi_f | V | \chi_i \rangle \right|^2 \, dE_f, \quad (8) \]

where \( V = \frac{Z}{|\vec{r} - \vec{R}_i(t)|} \) and \( \omega = \frac{E_f - E_i}{\hbar} \) (look below).

Since the K-shell electron is almost independent of change in chemical environment, the K-shell ionization probability is given by equation 8, where \( \chi_i \) is expressed by the wave function for the atomic orbital, but not for the molecular orbital. In addition, a final state can be expressed by the atomic-like wave function, \( \chi_f \), because an out-going electron behaves as a free electron at a distant place. This means that the ionization probability for the K shell can be written within the atomic orbital frame. On the other hand, the wave functions for valence electrons...
or L-shell electrons, $\chi_i$, have to be replaced by the molecular orbital (MO) wave function, $\psi_i$. Then $p^M(b)$ for the molecule is expressed as

$$p^M_L(b) = \int_0^\infty \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \exp(i\omega t)\langle \chi_f | V | \psi_i \rangle^2 dE_f,$$

The MO wave function can be approximated by a linear combination of atomic orbitals for the X L-shell electrons and the related electrons of the surrounding atoms

$$\langle \chi_f | V | \psi_i \rangle = \langle \chi_f | V | C_{X_L} \phi_{X_L} + C_M \phi_M \rangle = C_{X_L} \langle \chi_f | V | \phi_{X_L} \rangle + C_M \langle \chi_f | V | \phi_M \rangle,$$

where $\phi_{X_L}$ and $\phi_M$ are atomic wave functions of X L-shell electrons and related electrons of surrounding atoms, and $C_{X_L}$ and $C_M$ are their expansion coefficients, respectively.

Due to small impact parameters the ionization probability for the surrounding atoms can be neglected, so the upper equation leads to

$$\left| \langle \chi_f | V | \psi_i \rangle \right|^2 = C_{X_L}^2 \langle \chi_f | V | \phi_{X_L} \rangle^2.$$

Ionization probability is now written as

$$p^M_L(b) = C_{X_L}^2 \int_0^\infty \frac{1}{\hbar^2} \int_{-\infty}^{\infty} \exp(i\omega t)\langle \chi_f | V | \phi_{X_L} \rangle^2 dE_f = C_{X_L}^2 p_L(b),$$

and since it depend (through expansion coefficient $X_L$) on the molecular orbital for the L shell electron the $KL^N$ intensity distribution will reflect the chemical state of the atom in the target.
3.2 Energy shifts and other

Other previous stated chemical effects are much more difficult to analyse and they are usually calculated via numerical methods (like Hartree-Fock-Slater method ($X_\alpha$, DV - $X_\alpha$ or Mazalov method . . . ). The results are then compared with experimental data. A lot of researches has been done so far connected to the chemical effects in the emission spectra [1-7]. Typically examined elements are sulphur [1] [2], titanium [4], fluorine [3], silicon [6] and others.

Figure 7: The Si $K\alpha$ X-ray fluorescence spectra of Si compounds, measured by Liu et al. [6]. The energy shift due to the different chemical environment is nicely seen.

On the left is the comparison between XRF S $K\beta$ spectra emitted from ZnS, $Na_2SO_3$ and $Na_2SO_4$ (solid lines) and calculated (via the $X_\alpha$ method) S $K\beta$ spectra for $(SZn_4)^{6+}$, $(SO_3)^2$ and $(SO_4)^2$− clusters (dashed lines). This is an example of peak profile change. Work by Uda et al. [1].
Figure on the left shows observed $F K\alpha$ satellite spectra emitted from a series of alkali fluorides induced by 5.5 MeV $He^+$ ions (solid lines), and deconvoluted components of $K^1L^0$, $K^1L^1$ and $K^1L^2$ (dashed lines). The intensity changes are seen.

4 Chemical-state analysis using high resolution X-ray measurements

As we have seen above effects of chemical bonding are clearly manifested in the X-ray emission spectrum and can therefore be exploited for chemical state analysis. Since these effects are small compared to the resolution of usually applied solid state detectors, high resolution spectroscopy is essential in such analysis.

I have already presented significant chemical effects in the intensity distribution of the $KL^N$ satellite lines. As we have seen the quantitative analysis requires detailed theoretical modeling which is not an easy task. Furthermore, the spectra with intense higher order satellite lines are obtained in collisions with high energy heavy ions which are not commonly applied in analytical methods. Protons with few MeV from the electrostatic accelerators, electrons and bremsstrahlung from an X-ray tube are usually used. In latter cases higher order multiple ionization manifested in strong satellite lines is much less probable. Because of these facts one convenient method for the quantitative chemical state analysis is to measure absolute energy shift of the diagram lines in the X-ray spectra and not the intensity changes.

One of the most commonly used analytical techniques for determination of elemental concentrations in the investigated sample is Proton Induced X-ray Emission (PIXE). The PIXE method is based on the analysis of the X-ray spectra emitted after the sample irradiation with a MeV proton beam. This technique is very sensitive, non destructive and multielemental. But it can only provides elemental concentrations and gives no information about the chemical state of the element in the sample under investigation. (More detailed description of PIXE can be found in [8].) If we combine proton excitation with the high resolution spectroscopy (high resolution
PIXE or HR-PIXE) chemical effects in the emitted spectra can be exploited for the chemical state speciation.

In the most general case, this speciation is preferably performed via the analysis of the $K\beta_{1,3}$ or $K\beta_2$ lines. These lines, emitted after the transition of valence electrons, are more sensitive to the chemical environment. The energy shifts of the $K\beta$ X-ray emission lines are usually much more pronounced compared to the corresponding ones of the principal $K\alpha$ emission lines, which are expected to be less affected by chemical bonding effects. [2]

Despite of the restrictions imposed by the small energy shifts in the case of the $K\alpha$ lines described above, they are nevertheless crucial for the application of HR-PIXE in the chemical speciation of light elements such as S, mainly due to their higher emission rates compared to the $K\beta$ lines. (The intensity of the $K\beta$ line is around twenty times smaller than that of $K\alpha$.) It is so evident, that a good instrumental resolution of a crystal spectrometer can enhance the potential and applicability of HR-PIXE analysis.

4.1 High resolution PIXE set-up at the Microanalytical center (MIC) of the J. Stefan Institute

HR-PIXE set-up at MIC is described here. The X-rays emitted after the proton bombardment of the target are measured with a high-resolution crystal spectrometer. The spectrometer consists of a target holder, the target shielding which prevents the emitted X-rays to reach the detector directly, a diffraction crystal, bent in Johansson geometry with a Rowland circle radius of 100 cm and a position sensitive detector for the detection of the diffracted X-rays. The diffracted photons are detected by a Peltier cooled (down to $-40^\circ C$) CCD (Charged Coupled Device) detector, which consists of 770 × 1152 pixels, each having a size of 22.5 × 22.5 µm$^2$. Generally, the diffracted X-rays detected by the CCD form a two dimensional image on the detector plane. This image is then projected on the horizontal axis corresponding to the energy axis of the spectrum. The conversion into energy scale is performed off line using the reference calibration line in the spectra. The whole spectrometer is enclosed in a 1.6 × 1.3 × 0.4 m$^3$ stainless steel chamber evacuated by a turbo molecular pump down to $10^{-6}$ mbar.

![Figure 8: Schematic drawing of the experimental set-up.](image1)

![Figure 9: A photograph of the spectrometer.](image2)

What about the energy resolution of the spectrometer? The estimation can be done with the Ti spectrum presented in figure 10. One can successfully fit the $K\alpha_{1,2}$ doublet with the two
Figure 10: The image of the diffracted photons recorded on the CCD camera for the case of TiO$_2$ target bombarded by 2 MeV protons. In order to obtain the final spectrum this image is projected on the horizontal axis corresponding to the energy axis. Note that the energy decrease with the increasing channels so the energy scale is inverted.

Lorentzian lines representing the natural lineshapes (see figure 11). This is already proving a very small influence of the spectrometer on the measured spectra. The width of the measured $K\alpha_1$ line is 2.05 eV, which is approximately 0.9 eV more than the natural linewidth of the measured line, which is 1.16 eV. This difference can also be an estimate of the energy resolution which is therefore below the natural linewidth of the measured $K\alpha$ line, enabling to measure very small energy shifts that can be exploited for the chemical state analysis.

Figure 11: The Ti $K\alpha_{1,2}$ spectrum emitted from the TiO$_2$ target after bombardment with 2 MeV protons. The spectrum is well described by two Lorentzians representing the natural lineshape broadened slightly by the spectrometer response function. [7]

Here, I will present the measurements of the $K\alpha$ diagram lines of titanium and sulphur pure and compound targets using the HR-PIXE setup. Measured $K\alpha$ chemical shifts of sulphur
compounds was then used to specify the chemical state of S in an aerosol sample.

4.2 Chemical-state analysis of S and Ti pure and compound targets

The measurements of proton induced $K\alpha$ X-ray emission spectra of titanium and sulphur pure and compound targets was performed with the set-up described above. The proton incidence and X-ray emission angle relative to the target surface was $45^\circ$. The photons emitted from the S targets were reflected in the first order of reflection by the $(10\bar{1}0)$ reflecting planes of the $SiO_2$ crystal ($2d = 8.5096$ Å), while the second order of reflection on the same crystal was used for the Ti targets. In order to reduce the background a $6\mu m$ mylar foil was inserted in front of the CCD detector. From these measurements, the energy shifts of the $K\alpha$ lines in the compound targets, relative to the pure ones, were experimentally determined. The results demonstrate a clear dependence of the $K\alpha$ energy shifts on the chemical state of the element in the sample.

![Figure 12: Measured spectra of $K\alpha$ diagram lines of different S compounds induced with 2 MeV protons. The chemical shifts are clearly exhibited. [7]](image)

![Figure 13: Measured [7] energy shifts of the $K\alpha$ diagram line as a function of S oxidation state. A linear dependence has been found with a slope of approximate $0.25\Gamma_{nat}/oxidation\;state$.](image)

4.3 Chemical-state analysis of S in aerosol samples

Sulphur and its compounds consist one of the most important pollutants emitted in the atmosphere with the anthropogenic emissions to account for the moment for the 75% of the total. The wide range of sulphur oxidation states in the air particulate matter determines its chemical reactivity in the environment and the variety of the sulphur compounds that can be formed. Analytical techniques based on the detection of the fluorescent radiation emitted from the analysed sample (PIXE, XRF) have been successfully applied for many years in the quantification of samples with environmental importance. In particular, the PIXE technique has established itself as a routine analytical technique in the environmental studies being a multi-elemental, sensitive, fast, non-destructive and relatively inexpensive technique, requiring very little sample preparation [8]. However, like already mentioned, the above conventional X-ray analytical techniques are capable to analyze only the elemental content of the sample and not their chemical environment. HR-PIXE can be therefore applied.

One such analysis of sulphur in aerosol sample has been done at MIC. They have used the previously measured energy shifts of the $K\alpha$ diagram line and tried to specify the chemical
state of sulphur in an aerosol sample [7] collected near Koper [8]. Total aerosol loading mass was approximately 0.4mg/cm². The total S concentration of this specific sample was determined by the standard PIXE technique and it was equal to 28.1µg/cm².

Figure 14: Measured Kα diagram line (left) and the expected energy shift of Kα line due to the different chemical environment (right). [7]

According to the measured energy of the Kα diagram line one could clearly identify the chemical state of sulphur in the aerosol sample as a sulphate (\([SO_4]^{2–}\)). The graphical presentation of this speciation is presented on the figure 14 and demonstrates the feasibility of the described method.

5 Conclusion

During this seminar, I’ve described the chemical effects in the emission spectra as a tool for chemical speciation when high resolution spectrometers are available. Although these effects are exhibited through various aspects, I’ve stuck with the two mostly used. We have seen different approaches to the topic (the measurements of intensity changes, satellite formation, measurements of the energy shifts of Kα or Kβ ...). In the third part of my seminar, I’ve described high resolution PIXE set-up at the MIC and their work related to the topic. In this part, the chemical speciation with HR-PIXE was described more in detail.

HR-PIXE or any other method that use changes in the emitted spectra are of course not the only physical methods used for chemical state analysis. However, they all use the same principle, the fact that the energy and the electron orbitals changes with the change of the chemical environment. In XANES (X-ray Absorption Near Edge Structure) analysis, the shape of the absorption edge is examined in high resolution scan and can give the information of the valence state of the atom [14]. ESCA (Electron Spectroscopy for Chemical Analysis) on the other hand is based on the photoelectric effect, but is highly surface specific due to the short range of the photoelectrons that are excited from the solid [15].

Each method has its advantages and disadvantages, and they are difficult to compare. I have described HR-PIXE more in detail because it is one of the commonly used ion-beam analytical techniques and is also available at the J. Stefan Institute. HR-PIXE employing crystal spectrometers enables also chemical state speciation and therefore even further enhance the applicability
of the PIXE technique.

References