

Analysis of Magnetic Field Effects on $K\alpha$ And $K\beta$ XRF Spectra of Selenide Compounds

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Abstract

In this work, EDXRF are used to demonstrate the effect of an applied magnetic field, on the determination of energy of X-ray line, full width at half maximum (FWHM), asymmetry index (AI) and intensity ratio values. To this end, various initial magnetic fields were induced on a selenide compounds, and for each level of residual magnetic field, their corresponding $K\alpha$ and $K\beta$ spectra were collected from a Si(Li) detector. The results showed a strong correlation between the residual sample magnetic field and the atomic parameters such as energy shifts and asymmetry indices. It was observed that the chemical shift values increases with applying the sample magnetic field but FWHM values starts decreasing with higher levels of initial residual magnetic fields.

Keywords: EDXRF, External Magnetic Field, Intensity Ratio

1. INTRODUCTION

The particular change in X-ray absorption edge position of given compound from the metal surface is due to formation of chemical bond by the metal which changes the binding energy of core electron slightly. This term is known as chemical shift and is defined as $\Delta E = E_{\text{metal}} - E_{\text{compound}}$, where the terms E_{metal} and E_{compound} refer to the energy in the given metal and compound. Therefore the change in absorption edge which could be attributed to different chemical environments of a metal ion having same oxidation state is generally known as chemical effects.

Many workers have observed [1–4] the chemical shift is governed by many factors also, nature of the ligands to the metal ion, coordination numbers, covalent character of the bond, electronegativity of the anion, etc. or in other words the chemical environment of the metal ion. For 3d transition elements, $K\alpha$ and $K\beta$ spectrum shows a clear sensitivity to the chemical environment. The L shell fluorescence parameters of some medium and high Z elements and their compounds have been determined by many researchers using proton beam, gamma radiation as well as synchrotron radiations [5–8]. From the survey of literature we notice that the measured L shell fluorescence parameters are strongly influenced by various chemical environments. Kumar and Puri [9] have measured L X-ray intensity ratios of some compounds of Dy by creating L shell vacancy with 22.6 keV and 59.4 keV gamma photons to understand the chemical environment on intensity ratios and also dependence of intensity ratios on excitation energy. Krishnananda

et al. [10] have shown that the measurement of *L* subshell fluorescence yields of some rare earth elements depends on chemical bonding and crystal structures.

Characterizing the oxidation state and the electronic configuration is a challenge typically found when studying and developing new complex materials since magnetic and electrical properties are strongly related to the local electronic structure [11]. Demir and Şahin [12] have investigated external magnetic field on the *L3* subshell fluorescence yield, level widths, X-ray fluorescence cross-sections and intensity ratios of Ta, W, Tl, Th and U using 59.5 keV photons. Porikli et al. [13] have conducted measurements using pure Copper (Cu) and Zinc (Zn) and their compounds with the aim of a better understanding of the chemical effect and external magnetic field effect. They have determined characteristic quantities such as position of line maxima, full widths at half maximum (FWHM), indices of asymmetry and intensity ratio values in the values of external magnetic field 0.6 T and 1.2 T.

We have undertaken a systematic study under well-defined experimental conditions to investigate the effect of a magnetic field on *Kα* and *Kβ* spectra using an energy-dispersive x-ray fluorescence (EDXRF) spectrometer with a Si(Li) detector. CrSe, FeSe, NiSe, CuSe, ZnSe and SnSe were analyzed to study the both two effect. All of the lines were excited using a 100 mCi ²⁴¹Am annular radioactive source and the fluorescent x-rays emitted from the targets were analyzed by a Si(Li) detector (effective area 12.5 mm², thickness 3 mm, Be window thickness 0.025 mm). Particle size effects were circumvented. Peak areas were determined using Gaussian fitting procedures and the errors in various corrections such as self-absorption and detector efficiency were minimized. Moreover, characteristic quantities, such as positions of line maximum, line widths and indices of asymmetry are determined. These careful measurements show that the position of the line maximum and the full width at half maximum (FWHM) of selenide compounds depend on the magnetic field.

2. EXPERIMENTAL DETAILS

A selenide is a chemical compound containing a selenium anion with oxidation number of -2 (Se^{2-}), much as sulphur does in a sulphide. The chemistry of the selenides and sulphides is similar. Similar to sulphide, in aqueous solution, the selenide ion, Se^{2-} , is prevalent only in very basic conditions. Quantum dots based on metal selenides have been extensively for their distinctive spectral properties. Core-shell alloys of cadmium sulfide and selenide are of interest in imaging and phototherapy [14].

The experiments were carried out using high purity CrSe, FeSe, NiSe, CuSe, ZnSe and SnSe compounds (in powder form). For powdered samples, particle size effects have a strong influence on the quantitative analysis of infinitely thick specimens. Even for specimens of intermediate thickness, in which category the specimens analyzed in the present study fall, these effects can be significant. Therefore, in order to circumvent particle size effects all samples were grounded and sieved through a -400 mesh ($<37 \mu\text{m}$) sieve. A 10 ton hydraulic press was used to compress the sample powder into a thin pellet of 13 mm diameter. The pellet was kept in the 10-15 mg cm^{-2} range.

The geometry and shielding of the experimental setup are shown in Figure 1.

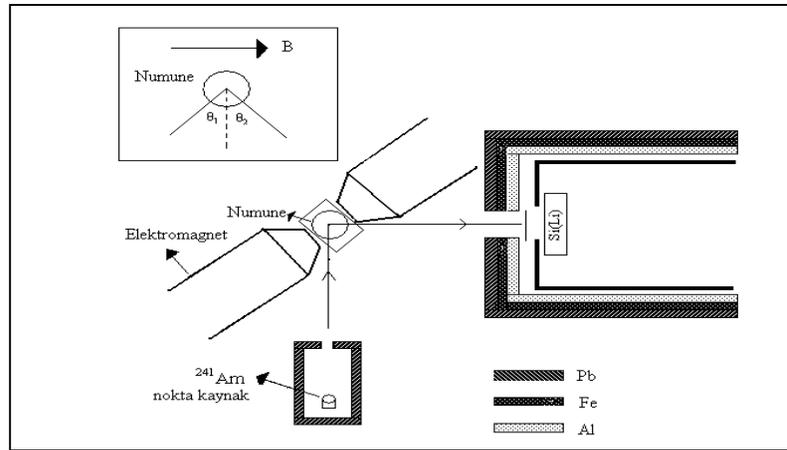


Figure 1. Experimental geometry

A graded conical shield of Al and Pb was used between the sample and the detector to obtain a large beam of emergent radiation and to avoid the interaction of the x-rays emitted by the component elements of the radioactive capsule and detector. The detector was shielded by a graded filter of Pb, Fe and Al to obtain a thin beam of photons scattered from the target and to absorb undesirable radiation shielded the detector.

The sample-detector and excitation source-sample distances were optimized to get maximum count rate in the fluorescent peaks. The sample was placed approximately at 45° to the source-plane as well as to the detector-plane so that the intensity of scattered radiation could be minimized. The count rate kept below $1000 \text{ counts s}^{-1}$ in order to avoid peak broadening, energy shift and non-linearity. The data were collected into 16384 channels of a digital spectrum analyzer DSA-1000. The samples were mounted in a sample holder placed between the pole pieces of an electromagnet capable of producing the magnetic field of approximately 2.8 T at 2 mm pole range. During the study, the magnetic field intensities of 0.5 T and 1.0 T were applied to the samples. An ammeter monitored the continuity and stability of the currents feeding the electromagnet.

3. DATA ANALYSIS

The line parameters, i.e., full width at half maximum (FWHM), index of asymmetry and integrated intensity were determined and are critically compared with previous measurements, where available. The peak position was determined at the center point of the 9/10 intensity of the smoothed line shape. It was known from our experience that the standard deviation of the peak position was determined using the peak top. Figure 2 shows the K x-ray spectra of the CrSe at the 0.5 T.

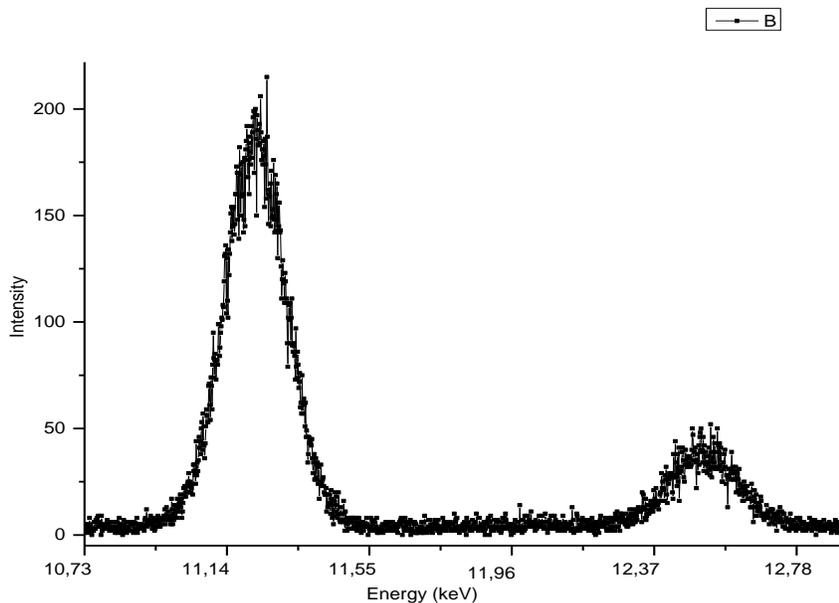


Figure 2. A typical K x-ray spectrum of CrSe at the 0.5 T

The Microcal Origin 8.0 was used for peak resolving background subtraction and determination of the net peak areas of K x-rays. Parameters such as FWHM and asymmetry index were evaluated using the smoothed data. The Savitzky-Golay smoothing method was iteratively processed one time. Spectral smoothing was important for reducing the standard deviation of these parameters. A typical K X-ray spectrum of CrSe, NiSe and CuSe compounds are shown in Figure 3. The Microcal Origin 8.0 was used for peak resolving background subtraction and determination of the net peak areas of K x-rays.

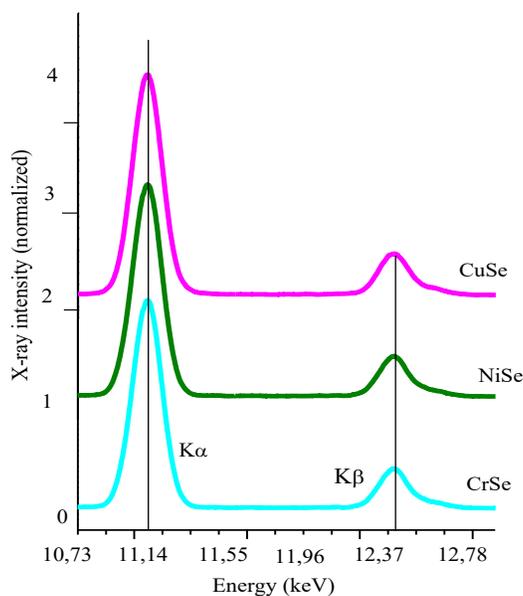


Figure 3. Measured $K\alpha$ and $K\beta$ spectra of CrSe, NiSe and CuSe. The spectra were plotted after smoothing

4. RESULTS AND DISCUSSION

The most intense emission line corresponds to the Se $K\alpha_{1,2}$ diagram line which is unresolvable doublet: $K\alpha_1$ originates from transition $2P_{3/2} \rightarrow 1S_{1/2}$ and $K\alpha_2$ originates from $2P_{1/2} \rightarrow 1S_{1/2}$ transitions. Similarly, Se $K\beta_{1,3}$ ($1S_{1/2} \rightarrow 3P_{1/2,3/2}$) diagram line is unresolvable. The measured chemical shifts (ΔE) in Se $K\alpha$ and $K\beta_{1,3}$ X-ray emission lines are shown in Table 1.

From the present measurements, it is seen that both positive and negative shifts have been observed in Se $K\alpha$ and $K\beta_{1,3}$ emission peaks. It has been also seen that, when we applied external magnetic field the line-width broadening and asymmetry index parameters are found generally proportional with the chemical shift.

It is seen from Table 1 that SnSe compound shows both positive and negative shift in given Se K shell emission lines.

Tablo 1. MT FDM üstel kalınlıklı disk için β ve $1/k$ değerlerinin kritik dönme hızına olan etkisi

Element	Magnetic Field Values	FWHM (eV)		Asymmetry Index		ΔE (eV)		δE (eV)	
		$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$	$K\alpha$	$K\beta$
CrSe	B=0 T	3.423	3.989	1.452	1.355	-0.389	-0.555	0	0
	B=0.5 T	3.256	3.890	1.252	1.303			0.263	0.138
	B=1.0 T	3.005	3.040	0.974	0.996			0.448	0.396
FeSe	B=0 T	3.455	3.925	0.968	1.268	-0.894	-0.444	0	0
	B=0.5 T	3.187	3.564	0.950	0.973			0.358	0.118
	B=1.0 T	3.054	3.288	0.952	0.964			0.545	0.227
NiSe	B=0 T	3.370	3.822	1.367	1.363	-0.368	-0.390	0	0
	B=0.5 T	3.140	3.433	1.172	1.111			0.438	0.286
	B=1.0 T	3.110	2,999	0.999	0.956			0.593	0.436
CuSe	B=0 T	3.708	3.758	0.997	1.331	0.250	0.305	0	0
	B=0.5 T	3.209	3.299	0.948	1.102			0.395	0.179
	B=1.0 T	3.162	3.082	0.931	0.984			0.574	0.425
ZnSe	B=0 T	3.433	3,730	1.445	1.259	0.331	0.305	0	0
	B=0.5 T	3.256	3.545	1.153	0.975			0.336	0.325
	B=1.0 T	2,899	3.201	1.041	0.939			0.509	0.390
SnSe	B=0 T	3,666	3,912	1.501	1.347	0.203	-0.105	0	0
	B=0.5 T	3.423	3.624	1.325	1.109			0.216	0.330
	B=1.0 T	3.028	3.154	1.153	1.007			0.441	0.356

We see that SnSe compound show some abnormal behaviour. This happens because of different compounds have different valence electronic configuration and oxidation states.

As seen from Table 1, in the presence of an external magnetic field, the asymmetry index of the Se compounds change. The $K\alpha$ and $K\beta$ emission lines asymmetry indices values decrease with external magnetic field. Asymmetry index is the most affected peak parameter from the external magnetic field. When we increased the magnetic field, the peaks began to narrow. For higher values of external magnetic field, we identified that there is relationship between asymmetry indices and FWHM values for the increasing magnetic field intensity. To obtain more definite conclusion, more experimental data are needed for pure Se and Se compounds which crystal structure are different. In our opinion, it would be desirable to

separate chemical effect and external magnetic field effect more clearly. But more experimental data are clearly needed, particularly for different symmetries and for chemical compounds.

5. CONCLUSION

In the present work, external magnetic field effect and chemical effect on the *K* subshell peak parameters of some selenide compounds can be measured accurately using EDXRF spectrometry. For compounds, the chemical environment such as type of bonding and type of crystal structure may play significant role in X-ray emission. From the results, atomic parameters changed symmetrically with the external magnetic field. In our opinion, it would be desirable to separate chemical effect and external magnetic field effect more clearly. From the above data, we understand that the X-ray fluorescence parameters depend on chemical environment such as type of chemical bonding, coordination number, electronegativity as well as crystal structure.

6. ACKNOWLEDGEMENTS

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