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Effects of the external magnetic field and chemical combination on Kβ/Kα X-ray intensity ratios of some nickel and cobalt compounds

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ABSTRACT

A systematic study of X-ray intensity ratios of the K-series lines was made on compounds of nickel and cobalt to examine the influence of chemical state and 0.6 and 1.2 T external magnetic fields on energy-dispersive X-ray fluorescence analysis. The samples were excited by 22.69 keV X-rays emitted from a Cd-109 radioisotope source and characteristic K X-rays emitted from the samples were counted by means of an Si(Li) detector. For $B = 0$, the present experimental results were compared with the experimental and theoretical data in literature. The results demonstrate a clear dependence of the Kβ/Kα intensity ratios on the chemical state of the element in the sample and values of external magnetic field.

1. Introduction

The Kα X-rays (from L→K transitions) and the Kβ X-rays (from M→K transitions) are the two main components of the K emission lines of an atom when its K-shell electrons are ejected by γ-rays or other energetic particles. Kα and Kβ lines can be easily resolved by a Si(Li) or Ge X-ray detector for 3d elements. The 3d transition metal borides, carbides, nitrides, oxides and sulfides, which form a class of refractory hard metals, possess intriguing metallic properties combined with chemical inertness, hardness, brittleness and extremely high-melting temperatures. Since they combine properties found in insulators with those of metals, these compounds are not only valuable technological materials but are also of special theoretical interest, in particular with regard to their electronic structure. Many studies of the Kβ/Kα intensity ratios of the 3d elements in different chemical compounds have been done (Raghavaiah et al., 1992; Hölzer et al., 1997; Mukoyama et al., 2000; Küçükönder et al., 2003). An exact knowledge of this parameter is important for X-ray emission analysis as it can help in the deconvolution of the highly overlapping X-ray spectra arising from adjacent elements and to test the theoretical models used to predict the relative transition probability for the K-shell vacancies (Scofield, 1974; Jankowski and Polasik, 1989).

Tamaki et al. (1975, 1979) reported a general increase in the Kβ/Kα intensity ratio with increasing formal oxidation number and a large spread of the intensity ratio for different compounds at a fixed oxidation number. Brunner et al. (1982) found deviation of up to 5% for different compounds of Cr, Mn, Fe and Cu by precise PIXE measurements and explained the results by the change in screening of 3p electrons by a varying 3d valance charge and polarization effects. Mukoyama et al. (1986) investigated Mn and Cr and showed that the Kβ/Kα intensity ratio of compounds with tetrahedral symmetry is in general larger than those with octahedral symmetry. Their experimental data are in good agreement with their theoretical calculations based on the discrete variational Xα molecular orbital method. They used a dipole approximation with molecular wavefunctions to evaluate the X-ray intensities. This was confirmed by the studies of Taniguchi et al. (1987) and Küçükönder et al. (1993). Chang et al. (1994) observed a significantly higher Kβ/Kα intensity ratio for strongly covalent V compounds. However, Dhal and Padhi (1994) were not able to observe significant deviations between different alloys of Mn, Ni and Cu.

Several experiments have been performed on the external magnetic field effect on the K shell X-ray emission lines. Demir and Şahin (2006) determined how the radiative transitions and the structures of the atoms in a strong magnetic field are affected, Kα and Kβ X-ray production cross sections, the K-shell fluorescence yields and I(Kβ/Kα) intensity ratios for ferromagnetic Nd, Gd and Dy and paramagnetic Eu and Ho were investigated using the 59.5 keV incident photon energy in the external magnetic fields intensities ±0.75 T. On the other hand, Demir and Şahin (2006) measured L_3 subshell fluorescence yields and level widths for Gd, Dy, Hg and Pb at 59.5 keV incident photon energy in the external magnetic field of intensities ±0.75 T.

As mentioned above, there were too many studies to determine the Kβ/Kα intensity ratio. The most common radioactive source

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used in the laboratories for the EDXRF techniques is Am-241 ($T_{1/2} = 458$ years), which emits gamma rays of 59.54 keV photon energies. We have used the X-rays of 22.69 keV from a 10 mCi Cd-109 point source (providing $5.0 \times 10^3\ sr^{-1}$ photon flux of Ag *X*-radiation) to ionize the target atoms. With the aim of a better understanding of the chemical effect and external magnetic field effect, we conduct measurements using pure nickel (Ni) and cobalt (Co) and their compounds. Kβ/Kα intensity ratio values are determined in the external magnetic field of intensities 0.6 and 1.2 T. The measured values for $B = 0$ were compared with other experimental and theoretical results. To our knowledge, Kβ/Kα intensity ratio values of Ni and Co in the external magnetic field have not been reported in the literature and appear to have been measured here for the first time.

2. Experimental work

Cobalt metal is a silver or gray ferromagnetic element of atomic number 27. In nature, it is frequently associated with nickel, and both are characteristic ingredients of meteoric iron. Common oxidation states of Co include +2 and +3, although compounds with oxidation state +1 are also well developed. The Co ion is also 6-coordinated by F^-, Cl^- and Br^- ions in CoF_3, $CoCl_2$ and $CoBr_2$, respectively (Suzuki et al., 1998). Ni is one of the five ferromagnetic elements. The most common oxidation state of Ni is +2, though 0, +1, +3 and +4 Ni complexes are observed. It is also thought that a +6 oxidation state may exist; however, results are inconclusive. Many Ni (II) compounds are paramagnetic, due to the presence of two unpaired electrons on each metal center. Square planar Ni complexes are, however, diamagnetic.

The experiments were carried out using high-purity Co, $CoCl_2$, $CoCl_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$, CoF_2, $CoSO_4 \cdot 7H_2O$, CuS, $Co(SCN)_2$, Co_2B, $CoCO_3$, CoF_3, $CoF_3 \cdot 4H_2O$, Ni, Ni_2B, Ni_2P, $NiBr_2$, $NiCl_2$, $NiCl_2 \cdot 6H_2O$, $Ni(ClO_4)_2 \cdot 6H_2O$, NiF_2, $NiF_2 \cdot 4H_2O$, $Ni_3(PO_4)_2 \cdot H_2O$, $NiSO_4 \cdot 6H_2O$, NiS, NiSe and NiTe 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 ground and sieved through a −400 mesh ($<37\ \mu m$) sieve. The powder was pelletized to a uniform thickness of 7–12 mg cm^{-2} by a hydraulic press using 10 ton in^{-2} pressure. The diameter of the pellet was 13 mm.

The experimental setup consist of a Si(Li) detector, Cd-109 radioactive source and electromagnet as shown in Fig. 1. 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 . 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 (Giauque et al., 1973). The count rate kept below 1000 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 a magnetic field of approximately 2.8 T at 2 mm pole range. During the study, the magnetic field intensities of 0.6 and 1.2 T were applied to the samples. An ammeter monitored the continuity and stability of

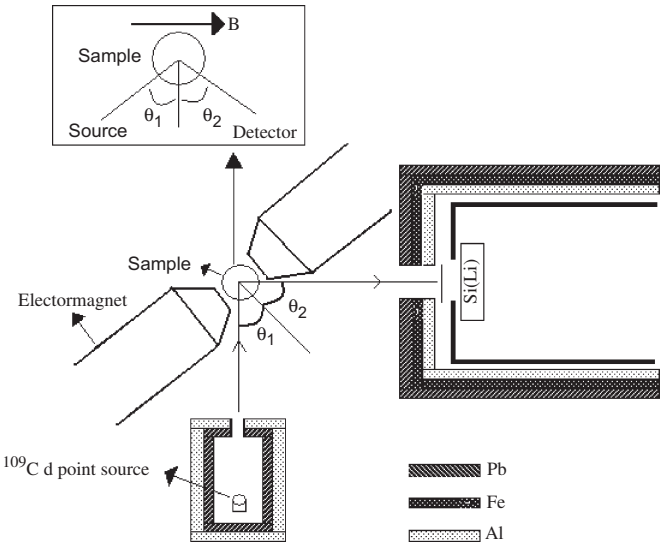

Fig. 1. Experimental setup.

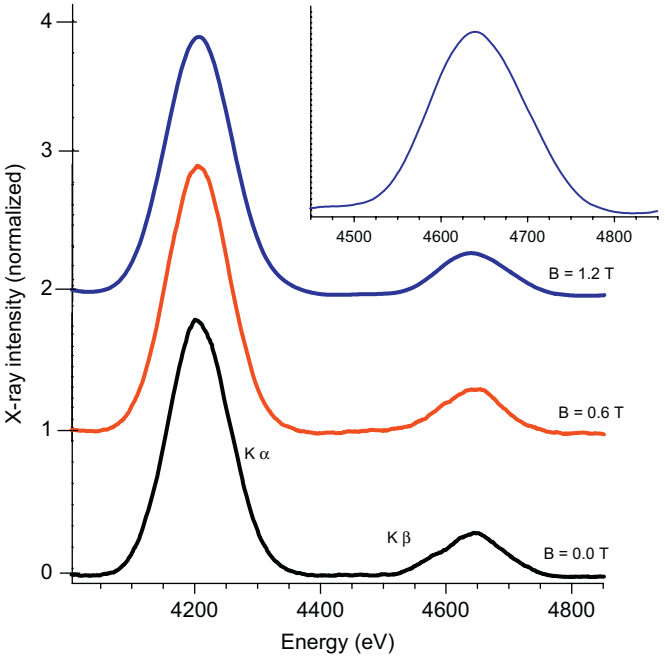

Fig. 2. A typical K X-ray spectrum of the Co target in $B = 0$, $B = 0.6$ T and $B = 1.2$ T magnetic field. The spectra were plotted after smoothing.

the currents feeding the electromagnet. A typical K X-ray spectrum of Co at the 0.6 and 1.2 T is shown in Fig. 2, which was plotted after smoothing. The Microcal Orgin 7.5 was used for peak resolving background subtraction and determination of the net peak areas of K X-rays. The experimental uncertainties were determined taking into account multiple measurements and multiple fits of each spectrum.

The Kβ/Kα intensity ratio values have been calculated by using the following equation:

$$\frac{I(K\beta)}{I(K\alpha)} = \frac{N(K\beta)}{N(K\alpha)} \frac{\varepsilon(K\alpha)}{\varepsilon(K\beta)} \frac{\beta(K\alpha)}{\beta(K\beta)} \quad (1)$$

where $N(K\alpha)$ and $N(K\beta)$ represent the counts under the Kα and Kβ peaks, respectively, $\varepsilon(K\alpha)/\varepsilon(K\beta)$ is the ratio of the detector efficiency values for the Kα and Kβ X-rays, respectively, and $\beta(K\alpha)/\beta(K\beta)$ is the ratio of the target self-absorption correction