Radiation Physics and Chemistry 92 (2013) 1–7

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Review

Effect of applied external magnetic field on the *L* X-ray emission line structures of the lanthanide elements

Sevil Durdağı *

Erzincan University, Faculty of Arts and Sciences, Department of Physics, 24030 Erzincan, Turkey

HIGHLIGHTS

- Changes in external magnetic field affects some parameters.
- Lanthanides electronic structure can change with this effect.
- There is correlation between the intensity ratio changes with atomic number.

ARTICLE INFO

Article history:
Received 11 April 2013
Accepted 27 June 2013
Available online 6 July 2013

Keywords:
Line width
Energy shift
External magnetic field
Intensity ratio
XRF

ABSTRACT

In this work, X-ray emission lines of the $L\alpha$, $L\beta$, $L\gamma$ and Ll groups in elements La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er were studied to examine the influence of 0.6 T and 1.2 T external magnetic field. The measurements were done using an energy dispersive Si(Li) detector with photon excitation by radioisotopes. A significant dependence of the *L* X-ray emission lines was observed for Sm but no discernible effect on the Pr $L\alpha/L\gamma$ intensity ratio was observed. Likewise no significant effect of external magnetic field on the various $L\alpha/Ll$ intensity ratios was observed. For $B=0$, the results are compared with the theoretical data and experimental results in literature. The results demonstrate that the relative intensities are more susceptible to the external magnetic field than the energy shifts.

1. Introduction

Low-energy X-ray spectra such as *L* X-ray spectra of transition metals or lanthanides and their compounds and *K* X-ray spectra of light elements and their compounds are significantly influenced by their environment. Also it is well known that X-ray spectra are sensitive to the chemical states of the emitting atoms and are of great use for studying the atomic and electronic structure in materials. Such a study covering a wide range of elements will be of help in making correlations between theory and experiment.

Several studies, theoretical (Scofield, 1974b; Paič and Pečar, 1976) as well as experimental (Raj et al., 1999, 1998, 2001) have been reported on the influence of solid state or chemical effects on the $K\beta/K\alpha$ ratio. Some papers deal with chemical effects (Berenyi et al., 1978; Rao et al., 1986), mostly in connection with X-ray emission after an electron capture process (EC) and partially after photoionisation (PI). Brunner et al. (1982) explained their experimental results on 3d elements by the change in the screening of 3p electrons by a varying 3d electrons delocalization as well as the polarization effect. Both the line width and the peak shift of the $K\alpha_1$ line are strongly correlated with the number of unpaired 3d electrons or valancy and the ligands in the transition metal compounds (Deutsch and Hart, 1982). Dhal and Padhi (1994) measured the relative *K* X-ray intensities on the elements Mn, Ni, Cu, Ga, Ge, Ag, Cd, Sn and Sb in the form of pure elements, alloys and compounds to look into the influence of solid state effects. Gubanov et al. (1975) have studied the X-ray emission spectra for VO, VN and VC using a high resolution crystal spectrometer. Unfortunately, they only provided the intensity data for $K\beta_{2,5}$. Dobrodey et al. (1993) have calculated $K\beta_{2,5}$ spectra of VO and VO_2 based on molecular-cluster models of VO_6^{10-} and VO_6^{8-} respectively by using a discrete variational method of local density approximation. Harada and Sakurai (1999) investigated the intensity ratios of $K\beta$ X-ray emissions from lanthanide compounds using an energy dispersive configuration and digital detector electronics. In the case of *K* lines for low Z elements and of *L* and *M* lines for higher atomic numbers, some of the spectral features mentioned are particularly evident and can be observed with spectrometers used in routine analysis. Moreover, only a few studies have been reported on the measurement of chemical state effects on the *L* series intensity ratios (Iiahara et al., 1993; Baydaş et al., 2001; Han et al., 2010). These effects should be relatively pronounced owing

* Tel.: +90 446 224 30 97x40041.
E-mail addresses: sporikli@gmail.com, sporikli@msn.com

0969-806X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.radphyschem.2013.06.030

to the involvement of outer orbitals in the emission of *L* X-rays. İsmail and Malhi (2000) report the *L* shell X-ray relative intensities for Sm, Eu, Lu, Hf, Os, Pt, Tl, Pb and Bi using 20.48 keV Rh tube. Olsen et al. (1973) studied the *L* X-ray spectrum of Sn with proton, alfa particles and oxygen ion bombardment and observed the presence of simultaneous multiple vacancies in *M* shell in addition to a vacancy in *L* shell. Bissinger et al. (1974) studied the *K* and *L* X-ray spectra of Au bombarded with 12–50 MeV oxygen ions and observed *L* X-ray cross-sections, intensity ratios and centroid energy shifts.

The chemical environment has a strong effect on the transitions originated in valence band and its influence could clearly be observed in the emission spectrum structure. The chemical behavior of actinide atoms (in particular, that of uranium) is determined by valance *nl*-electrons of three types: 7s, 6d and 5f. Although the bond energies of these electrons are almost equal, their wave-function differs greatly in distribution in the radial direction (Katz et al., 1986; Balasubramanian, 1994).

Several experiments have been performed on the external magnetic field effect on the *K* shell X-ray emission lines. Demir and Şahin (2006; 2007) have defined that how radiative transitions and structures of the atoms in a strong magnetic field is affected. $K\alpha$ and $K\beta$ X-ray production cross-sections, the *K* shell fluorescence yields and $K\beta/K\alpha$ intensity ratios for ferromagnetic Nd, Gd, and Dy and paramagnetic Eu and Ho have been investigated using the 59.54 keV incident photon energy in the external magnetic field of intensities ± 0.75 T. Porikli and Kurucu (2008a; 2008b) conduct measurements using pure Ni, Co, Cu and Zn and their compounds. Characteristic quantities such as position of line maxima, full widths at half maximum (FWHM), indices of asymmetry and intensity ratio values were determined in the values of external magnetic field 0.6 T and 1.2 T. Chemical end external magnetic field effects can be associated with the valancy and/or the ligand environment of the emitting atom, and can be used analytically in speciation to determine chemical state.

In our opinion it would be desirable to know external magnetic field effect more clearly: so we have carried out experiments on the external magnetic field influences on the $L\alpha/L\beta$, $L\alpha/L\gamma$ and $L\alpha/Ll$ intensity ratio in some lanthanides under same excitation conditions. Possible origins of external magnetic field effects are discussed which will be useful in the quantification of the results and their interpretation. We have been working on the elemental analysis of different kinds of materials using the energy dispersive X-ray fluorescence (EDXRF) system. The measurements reported here were made on the elements La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er using a Si(Li) detector. A commercial ^{241}Am radioactive source was used with an activity 100 mCi.

2. Sample preparation—experimental setup

The electronic structure of the lanthanide elements, with minor exceptions is $[Xe]6s^24f^m$. In their compounds, the 6s electrons are lost and the ions have the configuration $[Xe]4\ f^m$. The chemistry of the lanthanides differs from main group elements and transition metals because of the nature of the 4f orbitals. These orbitals are "buried" inside the atom and are shielded from the atom's environment by the 4d and 5p electrons. They have very wide range of coordination numbers (generally 6–12, but numbers of 2, 3 or 4 are known), small crystal-field splitting and very sharp electronic spectra in comparison with the d-block metals. Considering all these features of lanthanides, we have decided to work on lanthanide group elements.

Various compounds of lanthanide group elements were obtained in powder form. Powder samples were sieved for 400 mesh and prepared by supporting 10 and 20 mg cm^{-2} range mass thickness. All the target samples were prepared by pressing compound fine powders at a constant pressure (10 Tm/cm^2).

The experimental arrangement is shown in Figs. 1 and 2. As shown in Fig. 1, the placement of the upper lead shield avoided direct exposure of the detect radiation from the source. The iron lining on its inner side was used to avoid the Pb *L* X-rays and the Al lining was used to suppress *K* X-rays from iron, and collimate the *K* X-rays from the sample (at top). X-ray spectra from various target materials were recorded with a calibrated Si(Li) detector having a thickness of 3 mm and an energy resolution of 155 eV at 5.9 keV coupled to a multichannel analyzer interfaced with a computer on line through a spectroscopy amplifier. The amplifier shaping time constant that resulted in the best resolution and this value was used throughout the measurements. The life time of the analyzer was used to set the duration of each measurement, and dead times throughout this measurements were always less than 1%. The spectra were recorded for time intervals ranging from 7200 to 40,000 s in order to reduce the statistical errors of the measurements. The data were collected into 16,384 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, 0.6 T and 1.2 T were applied to the samples. An ammeter

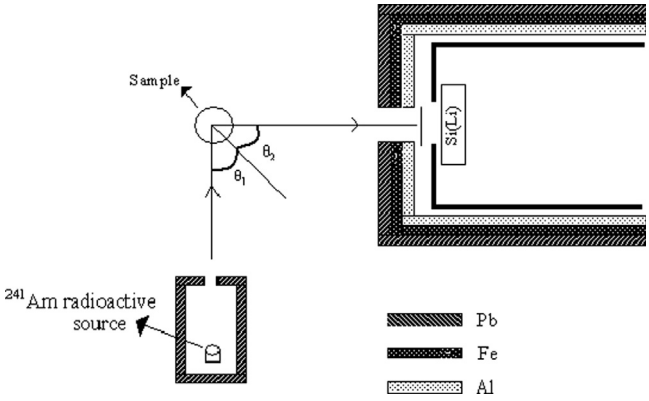

Fig. 1. Experimental set-up.

Fig. 2. Experimental setup used for measurement of $L\alpha/Ll$, $L\alpha/L\beta$ and $L\alpha/L\gamma$ intensity ratio and line parameter changes.