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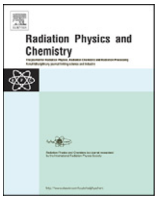

Chemical shift and intensity ratio values of dyspersium, holmium and erbium L X-ray emission lines

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ABSTRACT

A systematic study of L X-ray spectrum has been made on the elements Dy, Ho and Er in the pure form elements and compounds to look into the influence of chemical effect. The vacancies were created by 59.54 keV γ-rays from an ^{241}Am radioactive source. The L X-ray emission spectra of heavy elements taken with the currently available Si(Li) detectors show four or five distinct peaks. Corrections for sample absorption and spectrometer efficiency were applied to the measured relative intensities. The results show agreement with the theoretical predictions of Scofield (Scofield, 1974a).

1. Introduction

Chemical environment of an element affects and modifies the various characteristics of its X-ray emission spectrum. Most of the works suffer from neglecting chemical influences, and usually theoretical atomic values (Scofield, 1974a; Scofield, 1974b) are used as a reference even for quite different chemical compounds of certain elements. Theoretical calculations for solids and molecules have been done mainly to predict transition energies and line profiles, but evaluation of transition probabilities is uncommon.

It is well known that the low energy X-ray spectra such as L X-ray spectra of transition metals are significantly influenced by the chemical environment. There are studies in the literature, which suggest that there are chemical effects on L X-rays (Söğüt et al., 2002). Han et al. (2010) investigated the $L\alpha$, $L\beta$ and total L shell XRF cross sections for Zr, Nb, Mo, Ag, Cd, In, Sn, Sb and I using ^{55}Fe point source at 5.96 keV. Iiahara et al. (1993) measured the L X-ray intensity ratios for some Nb and Mo compounds. When the measured $L\gamma_1/L\beta_1$ ratios were plotted as a function of the effective number of 4d electrons, they found that the experimental data are almost on a straight line. However, it should be noted that the $4d \rightarrow 2p$ transitions are allowed dipole transition and the 4d electron is the valance shell electron, which participates directly in the X-ray emission. In this case the X-ray emission rate is proportional to the number of 4d electrons and increases with increasing effective number of 4d electrons.

Several studies on L shell X-ray relative intensities have been reported (İsmail and Malhi, 2000), which show fairly good agreement between the experimental results and theory. First, the X-ray production cross sections for various groups of lines are needed for quantitative estimation of the elements in various types of samples using the photon induced X-ray fluorescence technique. Second, these measurements serve to provide a check on the theoretical calculations of some of the fundamental physical parameters such as L subshell photo ionization cross sections (Shantendra et al., 1985a), fluorescence yields (Shantendra et al., 1985b), Coster–Kronig transition probabilities (Hallak, 2000) and radiative decay rates (Mann et al., 1991), the direct determination of which render (presents) many difficulties. Several attempts have been made for measuring the L X-ray fluorescence cross-sections σ_i^x, fluorescence yield w_i ($i{=}K, L, M, \ldots$) and intensity ratio values. L XRF cross sections and fluorescence yields are important for developing more reliable theoretical models describing the fundamental inner shell process. But these quantities are not available for all elements in all photon energies, because the L X-ray spectra is somewhat less precise and a little more complicated in nature since it originates from a shell, which has three subshells.

L X-ray spectra, induced by electron impact on the elements with $73 \le Z \le 83$, were measured by Goldberg with a curved crystal spectrometer, and the relative intensities of the L X-ray satellite and diagram lines were estimated by Salgueiro et al. (1974). Salgueiro et al. studied the spectra in 1965 and in 1974; these studies led to a measurement of the L_1-subshell CK and fluorescence yields for some of the elements, which was quoted by Bambeynek (1985) and Krause (1979). Demir and Şahin (2006) measured L_3 subshell fluorescence yields and level widths for Gd,

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Dy, Hg and Pb at 59.5 keV incident photon energy in the external magnetic field of intensities ± 0.75 T. Porikli (2011) conduct measurements under identical conditions using Si(Li) detector and ^{241}Am as the source of excitation to determine the energy shifts and relative intensities of $L\alpha$, $L\beta$ and $L\gamma$ components in La, Ce and Pr, which were in the beginning of lanthanide group. The purpose of their measurements was to characterize the dependence of the line position and line width with the chemical environment changes.

XRF is an analytical method to determine the chemical composition of all kinds of materials (Berenyi et al., 1978; Rao et al., 1986; Arndt et al., 1982). The materials can be in solid, liquid, powder, filtered or other form. XRF can also sometimes be used to determine the thickness and composition of layers and coatings. Applications are very broad and they include the metal, cement, oil, polymer, plastic, food industries, along with mining, mineralogy and geology. Beside environmental analysis of water and waste materials can be included to these applications.

The purpose of this paper is to study chemical effects and discuss their applications to Dy, Ho and Er in various compounds. This paper presents and discusses the measured spectra using an energy dispersive X-ray spectrometer (EDXRF). The effect of chemical state on the $L\alpha$, $L\beta$, $L\gamma$ and Ll X-ray energies and $L\alpha/L\beta_1$, $L\alpha/L\gamma$ and $L\alpha/Ll$ intensity ratio values has been investigated using the 59.54 keV gamma-rays from ^{241}Am.

2. Material and methods

2.1. Experimental arrangement

The studied elements were Dy, $DyBr_3$, $DyCl_3$, DyF_3, $Dy_2(C_2O_3)_3\cdot XH_2O$, Ho, $Ho_2(CO_3)_3\cdot XH_2O$, $Ho(NO_3)_3$, Ho_2O_3, $Ho_2(SO_4)_3$, Er, $ErBr_3$, $ErCl_3\cdot 6H_2O$, $Er(NO_3)_3\cdot 5H_2O$, $Er_2(C_2O_4)_3\cdot H_2O$ and $Er_2(SO_4)_3\cdot 8H_2O$, Er_2O_3. The target samples were prepared by pressing the fine powder of compound to keep the target pure and at constant pressure. The powder was palletized to a uniform thickness of 0.10–0.20 g cm^{-2} range by a hydraulic press using 10 ton in^{-2} pressure. The diameter of the pellet was 13 mm. The experiment was repeated three times for each spectrum, using three identical samples in order to confirm the radiation decomposition effect is negligible during measurements.

The experiments were performed at the Atatürk University, X-Ray Fluorescence (XRF) Laboratory. Compounds were excited by a ^{241}Am annular source with an activity of 100 mCi. The experimental arrangement and the geometry used in the present study are shown in Fig. 1. The produced X-rays were detected by a spectroscopic amplifier (with pile up rejection) and a Si(Li) semiconductor detector with a resolution of 155 eV at 5.9 keV. The X-ray spectrum was acquired in 16384 channels of a digital spectrum analyzer DSA-1000 and the spectra were recorded for time intervals ranging from 7200 to 40000 s in order to achieve better approximation of the X-ray peaks to a Gaussian distribution, avoid peak broadening, energy shift and non-linearity, which were the sources of statistical error. The lifetime of the analyzer was used to set the duration of each measurement and dead times throughout these measurements were always less than 1%. The integrated error including the counting statistics errors were estimated to be less than 1.0 and 1.5%. Count rates were kept enough to avoid any pile-up rejection. The counting time was adjusted all specimens to give a statistical error of <0.2 for the $L\alpha$ and $L\beta$ peak, <0.5 for the $L\gamma$ peak and <1.0 for the Ll peak. Three sets of measurements were carried out for each sample, and an average of the two measurements was found for the L X-ray intensity ratio, which is reported.

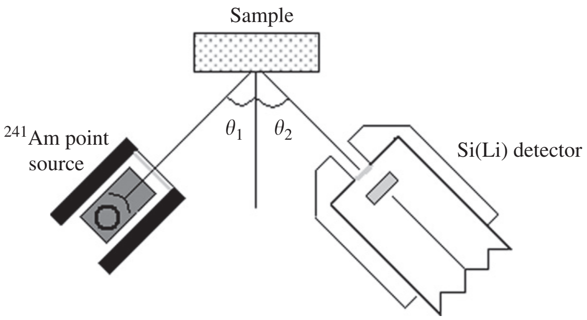

Fig. 1. Experimental setup used for the measurement of $L\alpha/Ll$, $L\alpha/L\beta$ and $L\alpha/L\gamma$ intensity ratios and line parameter changes.

The L X-ray spectra are more complex than the K X-ray spectra and they consist of many peaks, several of which strongly overlap. These complex spectra were analyzed using the least squares fitting procedure using a non-linear background subtraction. The photopeaks were assumed to consist of pure Gaussians and no tailing function. Since there is no escape peak any other undesired effects contributing to the spectrum, the mean count of twenty channels at each side of the peaks used to calculate the background and to define the net peak area. The Microcal Orgin 7.5 was used for peak resolving, background subtraction and determination of the net peak areas of L X-rays. For all the spectra, the background counting rate was approximately 2–4 counts per second. Backgrounds we used to subtract from every spectrum were the lowest counting in the spectral range.

The L X-ray intensity ratios were determined from the fitted peak areas after applying necessary correction to the data. Corrections to the measured ratios mainly come from the difference in the $L\alpha$, $L\beta$, $L\gamma$ and Ll self attenuations in the sample, differences in the efficiency of the Si(Li) detector and air absorption on the path between the sample and the Si(Li) detector window. Our theoretically estimated efficiency was shown to be in good agreement with the measured efficiency. At the energy region of the present interest, the discrepancy between them was found to be quite small.

The peaks due to $L\alpha$, $L\beta$, $L\gamma$ and Ll group of lines are well resolved and an example of the fitted spectra is shown in Fig. 2. Measured numbers of counts are shown as solid black circles, while the red line represents the overall fit. The background is shown as a green line. Fig. 2 shows that the observed spectrum is fitted fairly well with the fitted function, which is also indicated by the residuals being much lower than the $\pm 2\sigma$ limit. The X^2 value for this fitting was 0.95.

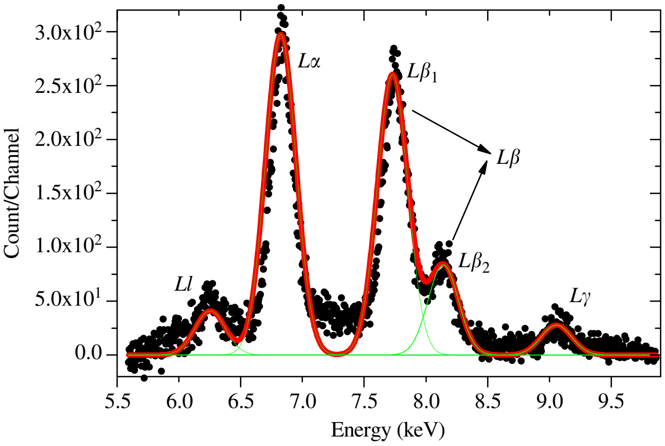

Fig. 2. Measured Ll, $L\alpha$, $L\beta_1$, $L\beta_2$ and $L\gamma$ emission lines of Er.