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Figure 1: Fig. 1. X-ray L_{III} absorption spectra in various compounds: A –lanthanum, B –neodymium, V –praseodymium, G –samarium. 1 –peroxide; 2 –oxide; 3 –oxyfluoride; 4 –fluoride

Abstract

Full Text

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X-RAY *L*-ABSORPTION SPECTRA OF LANTHANUM, PRASEODYMIUM, NEODYMIUM, AND SAMARIUM IN OXIDES AND FLUORIDES

(Presented by Academician A. P. Vinogradov on March 9, 1963)

Many compounds and alloys of rare-earth elements (REE) possess a number of remarkable and unusual properties and already find broad application in technology. This stimulates work aimed at their comprehensive study and makes it desirable to obtain various information about their electronic structure. In connection with this, interest in studying the x-ray spectra of REE in compounds of various classes has increased in recent years ($^{1-3}$). However, the number of works in this field is still small.

In the present work, the absorption spectra of a number of REE were studied in compounds with a predominantly ionic character of bonding–peroxides, oxides, oxyfluorides, and fluorides. The peroxides of La, Pr, Nd, and Sm were prepared at our request by L. V. Soboleva. The oxyfluorides and fluorides were obtained from L. R. Batsanova. The x-ray $L_{II,III}$ absorption spectra of the REE were obtained using a focusing tube spectrograph in the second order of reflection from the $(10\bar{1}1)$ plane of a bent quartz crystal. The radius of curvature of

Fig. 1. X-ray L_{III}-absorption spectra in various compounds: **A** –lanthanum, **B** –neodymium, **V** –praseodymium, **G** –samarium. **1** –peroxide; **2** –oxide; **3** –oxyfluoride; **4** –fluoride

the crystal was 330 mm. The dispersion was ~ 6 eV/mm. The resolving power was ~ 7500. The spectra were recorded photographically on a flat cassette placed perpendicular to the direction of the incident x-ray beams. Operating conditions of the x-ray tube: 10-12 kV, 50 mA. The anode was copper. The optimum density of absorbers, selected experimentally, was 4-5 mg/cm^2. The spectra of each REE in different compounds were photometered and, after averaging and conversion to the electron-volt scale, were compared with one another. The experimental results obtained are presented graphically in Fig. 1. Their consideration makes it possible to draw the following conclusions.

1. The position of the absorption-edge boundary and of the principal maximum in the spectra of each of the rare-earth elements in the compounds studied remains unchanged within the accuracy of the experiment. This indicates the absence of a noticeable change in the valence state of the rare-earth atoms in these compounds and, as applied to the peroxides of La, Pr, Nd, and Sm, confirms the assumptions about their valence made in (4).
2. The fine structure of the X-ray absorption spectra of La, Nd, and Sm in the compounds studied is analogous, and in passing from compounds of one type to another it changes in the same way. The absorption spectrum of the metal in the peroxides usually has the simplest structure. In the oxides, oxyfluorides, and fluorides of these elements, as well as in the spectrum of Sm in the peroxide, an additional relatively weak band appears on the short-wavelength side of the principal absorption maximum; its origin as yet does not admit of an unambiguous explanation. In passing from the spectrum of the oxide, in which the above-mentioned band usually has low intensity, to the oxyfluoride, a shift of its maximum toward shorter wavelengths and a noticeable increase in intensity are observed. Further replacement of oxygen by fluorine atoms affects the structure of the spectrum much more weakly.

As is seen (Fig. 1b, curve 2), the absorption spectrum of praseodymium in the oxide differs sharply from all the others obtained in the present work. It was assumed that this is explained by the presence in the substance under study of atoms of tetravalent praseodymium, the absorption edge for which should be shifted (relative to the spectrum of atoms in the trivalent state) toward shorter wavelengths. In this connection, the dependence of the fine structure of the X-ray absorption spectrum of praseodymium in the oxide on the conditions of its preparation and, in particular, on the calcination temperature was studied. As was to be expected, the relative intensity of the second absorption maximum in the spectrum proved sensitive to the conditions of preparation of the oxide and increased appreciably in the spectra obtained from samples calcined at high temperatures. This supports the assumption made.

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Note: Figure translations are in progress. See original paper for figures.