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Abstract

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FINE STRUCTURE OF THE MAIN X-RAY L_{III}-ABSORPTION SPECTRUM AND OF THE LAST $L\beta_5$-EMISSION BAND OF YTTERBIUM IN THE OXIDE AND HEXABORIDE

(Presented by Academician A. P. Vinogradov on 25 IV 1964)

Alongside theoretical methods for calculating the band structure of solids, in recent years various experimental techniques for studying the structure of the energy spectrum of these substances have become widely developed; many of them possess properties important for practice. Interesting possibilities in this respect are opened, for example, by the use of methods of X-ray spectral analysis, especially in the simultaneous study of the fine structure of the emission and absorption spectra of atoms in these substances.

The aim of the present work is to use this method to study the energy structure of the valence band in crystals of ytterbium oxide and hexaboride. Ytterbium hexaboride was prepared by the method described in (^{1}), and was kindly provided to us for investigation by Yu. B. Paderno. The spectra were obtained with a DRS-3 X-ray focusing spectrograph with a bent crystal and photographic recording.

The bent crystal was quartz, with reflecting planes $(13\bar{4}0)$. The spectra were recorded in the first order of reflection. The dispersion in the region of the ytterbium L_{III}-absorption edge and of the $L\beta_5$-emission line was 3.8 X/mm. The resolving power of the instrument was ~ 6000. The comparison lines used were ZnK_{α_1} and GaK_{α_2}. In recording absorption spectra the anode of the X-ray tube was tungsten; in studying the structure of emission lines it was aluminum. The operating conditions of the tube when recording absorption spectra were 30 mA, 20 kV, exposure 4 hours; when obtaining the last $L\beta_5$-emission line of the spectrum, 12 mA, 35 kV with an exposure of 2–3 hours.

The ytterbium $L\beta_5$ line undergoes strong self-absorption, which greatly distorts its shape. Therefore the experimental results were corrected by us for self-absorption, instrumental distortions, and the width of the inner level. To correct for instrumental distortion, the form of the distortion (the degree of its correspondence to the dispersion law) and the width of the distortion function were determined from the GaK_{α_1} line, whose true form, as is known (^{2}), is close

Fig. 1

Figure 1: Fig. 1

to dispersion-like. The correction was carried out by the column method ([3]). The width of the distortion function (γ), on the basis of the experimental data, was taken equal to 1.5 eV. The correction for self-absorption was carried out separately for the self-absorption of the continuous and characteristic spectra by the method of ([4]). The density values of the investigated samples of ytterbium hexaboride and oxide required for carrying out this stage of the spectral correction were determined pycnometrically and proved to be, respectively, 5.5 and 8.5 g/cm^3. At the last stage of correction of the experimental curves, a correction was made for the width of the inner L_{III}-level of ytterbium. The latter value was taken as 4 eV. It represented the mean of two values. One of them (3.85 eV) was obtained by linear interpolation between the values of the widths of the inner L_{III}-levels of 47 Ag (2.3 eV) and 79 Au (4.4 eV), which were borrowed from ([2]) and ([5]). The second (4.1 eV) was calculated from the semiempirical formula of Maisel and Nefedov ([6]).

The experimental data we obtained and the results of the successive correction are presented graphically in Fig. 1. Consideration of these data makes it possible to draw the following conclusions.

The energy position and fine structure of the x-ray L_{III} absorption spectra of ytterbium and of its last emission $L\beta_5$ band in the oxide and hexaboride differ substantially and evidently reflect differences in the structure of the energy spectrum of the valence r.e.e. electrons in these compounds. In going from the oxide to the hexaboride, a considerable long-wavelength shift occurs both for the main absorption edge and for the position of the maximum of the last emission band. After correction of the spectra, the magnitudes of these shifts proved to be, respectively, 4 and 6 eV. As is known (1), this is accompanied by a change in the valence of the r.e.e. metal from the trivalent state in the oxide to the divalent state in the hexaboride. In accordance with this, and also in connection with the change in the character of the interatomic interaction in the compounds considered, there is a significant change in the half-widths of the last emission bands of ytterbium from 3.5 eV in the hexaboride to 2.2 eV in the oxide.

Fig. 1. Comparison of the x-ray L_{III}-absorption edge and $L\beta_5$-emission line (hatched) of ytterbium in the hexaboride (1) and oxide (2). *a* –experimental curves, *b* –after correction for instrumental distortion and self-absorption, *v* –after correction for the width of the L_{III} level.

As far as can be judged from the shape of these bands in the corrected spectra, the asymmetry index of the lines does not undergo noticeable changes and in both cases is close to unity. However, in the oxide, apparently as a result of the reduced symmetry of the crystalline field acting on the energy levels of the metal in the compound, there is a noticeable splitting of the valence band, manifested in the appearance of an additional, weaker emission band (Fig. 1, 2), located at a distance of 4.2 eV from the main maximum (Fig. 1, 1). On the contrary, the fine structure of the ytterbium absorption spectrum in the oxide proves to be simpler and contains only one maximum. In the hexaboride, however, within the limits of the main edge, after correction of the spectrum it is possible to record three maxima—A', A, and B, the distances between which are, respectively, 7.2 and 8.6 eV.

A remarkable feature of the x-ray absorption and emission spectra of ytterbium in the hexaboride is the large degree of their mutual overlap, manifested, in particular, in the presence of a weak absorption maximum (A') on the long-wavelength side of the emission band. This indicates the complex character of the filling and the peculiar nature of the hybridization law of the wave functions of the electrons forming the valence band of the compound and, apparently, is generally typical—if not for all, then at least for some rare-earth and certain other elements with defects in the nf- and nd-shells. An analogous phenomenon, for example, has already been observed-

was made earlier in the study of the $M_{\mathrm{IV,V}}$ absorption spectra and the $M_{\alpha,\beta}$ emission bands of erbium in work (^{7}), and was noted in (^{8}) when comparing the position of the L_{III} absorption edge and the last emission band of molybdenum in certain compounds.

It should be noted, however, that at present there is no well-developed theory of this phenomenon. Therefore, for example, in the case of ytterbium hexaboride we intend to approach a more detailed discussion of it after completing work on a theoretical calculation of the band structure of the energy spectrum of the valence electrons in this compound, which is currently under way. Nevertheless, certain preliminary judgments about the features of the band structure of the compounds studied, closely connected with the presumed mechanism of conduction in them, follow directly from consideration of the data presented in Fig. 1. This concerns the magnitude of the width of the forbidden band (ΔE) in the oxide and in the hexaboride; a judgment about its magnitude can be obtained from measurements of the energy gap between the short-wavelength emission edge and the beginning of absorption of the element in the compounds, which in our case was taken to coincide with the point of inflection of the absorption curve at half the height of the main maximum. As can be seen, in ytterbium oxide the magnitude of the energy gap under consideration reaches an appreciable value, of the order of 1 eV, whereas in the hexaboride it is close to zero and in any case (allowing for a number of corrections) does not exceed values of the order of 0.1 eV. In agreement with this conclusion are the results of studies of the electrophysical properties of ytterbium hexaboride and, in particular, the temperature dependence of its electrical resistance, which, as established by Yu. B. Paderno (private communication), increases with temperature according to a law typical of substances with a metallic character of conduction.

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