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Abstract

Full Text

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FINE STRUCTURE OF THE X-RAY K-ABSORPTION SPECTRA OF TITANIUM IN TITANATES

(Presented by Academician A. P. Vinogradov, May 19, 1958)

In work (^{1}), the fine structure of the X-ray K-emission spectra of titanium was studied in a series of titanates of Mg, Ca, Ba, Sr, Fe, and Zn. The present communication gives the results of a study of the K-absorption spectra of titanium in the same compounds.

The spectra were obtained with a focusing X-ray tube spectrograph (^{2}) with a quartz crystal bent to a radius of 2.5 m, under the same conditions under which (^{3}) the absorption spectra of titanium in its oxides had previously been studied. For the best detection of the details of the fine structure of different portions of the absorption edge, the work was carried out with absorbers of different thicknesses, from 3 to 14 mg/cm^2. In spectra obtained using thin absorbers, the short-wavelength structure of the edge appears better and without distortions, but the intensity is weakened and the structure of the long-wavelength group of absorption lines is indistinctly revealed; in spectra from thick absorbers the opposite is true. In a certain sense, the optimum absorber density for the substances studied by us is about 5 mg/cm^2. This can be verified by considering the series of absorption curves given as an example in Fig. 1. The absorption spectra of titanium in the investigated group of titanates and in rutile (TiO_2), obtained for each of the compounds at absorber densities of 4-5 mg/cm^2, are compared in Figs. 2–4.

Fig. 1. X-ray K-absorption spectra of titanium in barium titanate at different absorber thicknesses: 1 –3 mg/cm^2; 2 –5 mg/cm^2; 3 –8 mg/cm^2; 4 –14 mg/cm^2.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

Consideration of the experimental results obtained makes it possible to draw the following conclusions:

1. The X-ray absorption spectra of titanium in titanates are characterized by a distinct fine structure, rich in fluctuations, whose form varies depending on the type of crystal structure, the features of the chemical bond in the compound, and the state of polarization of the titanium and oxygen atoms in it. The titanium absorption edge in $ZnTiO_3$ has the simplest form. The long-wavelength absorption band, arising from transitions of the $1s$ electrons of the absorbing atom to free levels within the $3d$ energy band, in this compound is a syn-

Thus, the distance between the first two maxima of the fine structure within the main absorption edge of titanium in $ZnTiO_3$ is 13 eV.

2. In the X-ray absorption spectra of titanium in compounds having a crystal structure of the ilmenite type ($FeTiO_3$, $MgTiO_3$), the shape of the long-wavelength absorption band and the energy position of its maximum remain the same as in the spectra of $ZnTiO_3$. However, the fine structure of the short-wavelength region of the absorption edge has a more complex form.

Fig. 2. X-ray K-absorption spectra of titanium in a series of titanates with a perovskite-type structure.
1—$SrTiO_3$; 2—$BaTiO_3$; 3—$CaTiO_3$

Fig. 3. X-ray K-absorption spectra of titanium in barium metatitanate (1) and tetratitanate (2).

The positions of individual fluctuations of the absorption coefficient in the spectra of titanium in ilmenite and magnesium titanate do not depend on the nature of the cation and, within the accuracy of measurement, are the same for both compounds. The distance between the first two maxima of the fine structure in this region of the spectrum practically coincides with that observed in the Ti spectrum in $ZnTiO_3$.

Fig. 4. X-ray K-absorption spectra of titanium in the compounds $FeTiO_3$ (1);

Fig. 4

Figure 4: Fig. 4

$MgTiO_3$ (2); $ZnTiO_3$ (3) and rutile (4).

3. In the absorption spectra of titanium in rutile and in compounds with a perovskite-type structure, a double splitting of the long-wavelength absorption band is observed. In this case, the energy corresponding to the maximum of the most long-wavelength absorption line coincides with the energy of the maximum of the unsplit band in the titanium spectra of all the other compounds of this element studied in the present work.

The structure of the main absorption edge of titanium in compounds of the perovskite type changes little depending on the nature and size of the cation and depends strongly on the polarization conditions of the atoms in the compound under investigation. Thus, the sharpest change in the short-wavelength structure of the edge is observed in the transition from barium tetratitanate to barium monotitanate (Fig. 3). The special polarization conditions in which the titanium atoms find themselves in the latter compound, which, as is known, account for its phenomenal ferroelectric properties, apparently are also the cause of the splitting of the 4*p*- and 5*p*-energy bands in this compound into several levels. Thus, instead of two broad maxima in the titanium absorption spectrum in $BaO \cdot 4TiO_2$, two many-···

indistinct groups of absorption lines with an approximately constant spacing between the components within each of the multiplets. For the maxima observed on the long-wavelength side of the edge and apparently corresponding to splitting of the 4*p*-band of energy, this spacing is ~ 4.3 eV. For the lines formed as a result of the transition of 1*s*-electrons into the 5*p*-band, it is somewhat larger (~ 5 eV)*.

The position of the centers of gravity of the titanium absorption bands, which are complex in structure, in $BaTiO_3$ approximately corresponds to the position of the absorption maxima in the spectrum of titanium in barium tetratitanate. The distance between these maxima in the spectra of the transition metal in all compounds of the group under consideration is ~ 14—15 eV.

4. The interpretation set forth for the fine structure of the X-ray absorption spectrum of titanium in barium titanate differs substantially from that proposed by M. A. Blokhin (^{4}), who believed that the appearance of an additional maximum on the long-wavelength side of the titanium absorption edge in $BaTiO_3$ is explained by the presence in the lattice of this compound of trivalent titanium ions (in addition to tetravalent ones). The unfoundedness of such an assumption becomes obvious, in particular, from consideration of the fine structure of the titanium absorption spectrum in rutile (Fig. 4, 4). Here, as in $BaTiO_3$, on the long-wavelength side of the main absorption edge one can observe the appearance of additional maxima; however, from the chemical point of view, the assumption that trivalent titanium ions exist in this compound is unacceptable.

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* The values of the latter quantities are determined less accurately.

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

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