PHYSICS

1957

SovietRxiv

Abstract

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PHYSICS

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ON CERTAIN REGULARITIES IN THE STRUCTURE OF THE X-RAY K-EMISSION SPECTRA OF TITANIUM IN TITANATES

(Presented by Academician A. P. Vinogradov, 27 VI 1957)

Recently, in the study of the x-ray K-emission spectra of titanium in certain compounds (^{1}), it was suggested that the appearance in the spectrum of the element in compounds of the satellite $K_{\beta'}$ is connected with a "cross" transition to the metal K level of the corresponding electrons of the anion. Later (^{2}) the validity of this conclusion was again confirmed in a series of specially designed experiments.

This assumption makes it possible (^{1}) to explain very simply many properties of this line and, in particular, its absence in the spectra of the metal and the sharp dependence of its relative intensity on the valence of the atoms in the compound.

A number of phenomena observed in x-ray (^{3,4}) and optical (^{5}) absorption spectra are apparently also connected with "cross" transitions of electrons of atoms in compounds. Since the relative intensity of selective lines in x-ray absorption spectra, due to "direct" and "cross" transitions of electrons of the absorbing atom, depends strongly on the state of polarization of the atoms of this element in the compound (^{6}), it could be thought that the same factor also influences the relative intensity of the corresponding emission lines.

The purpose of the present work was to test this conclusion experimentally. The lines of the K_β group of titanium were investigated in the x-ray emission spectra of this element in brookite, anatase, and a number of titanates—Mg, Ca, Sr, Ba, Fe, and Zn.* Among the barium titanates, mono- and tetratitanates were studied ($BaO \cdot TiO_2$ and $BaO \cdot 4TiO_2$). In all these compounds, the titanium atoms are located at the center of regular or deformed octahedra, joined to one another in different ways, of TiO_6. In brookite and anatase each octahedron is joined to others along several edges, while zigzag chains of titanium-occupied polyhedra alternate with similar chains of empty octahedra. In structures of the perovskite type ($CaTiO_3$, $SrTiO_3$, and $BaTiO_3$), the octahedra (TiO_6) are connected to one another by vertices and form an infinite three-dimensional anion, in the interstices of which the ions of the alkaline-earth metal are located. The connection of TiO_6 octahedra at opposite vertices apparently also occurs

Fig. 1. Lines $K_{\beta''}$ and K_{β_5} of the X-ray spectrum of titanium in various compounds: 1—$CaTiO_3$; 2—$SrTiO_3$; 3—$BaTiO_3$; 4—$BaO \cdot 4TiO_2$; 5—TiO_2 (anatase); 6—$FeTiO_3$; 7—$ZnTiO_3$; 8—$MgTiO_3$; 9—TiO_2 (brookite)

Figure 1: Fig. 1. Lines $K_{\beta''}$ and K_{β_5} of the X-ray spectrum of titanium in various compounds: 1—$CaTiO_3$; 2—$SrTiO_3$; 3—$BaTiO_3$; 4—$BaO \cdot 4TiO_2$; 5—TiO_2 (anatase); 6—$FeTiO_3$; 7—$ZnTiO_3$; 8—$MgTiO_3$; 9—TiO_2 (brookite)

in the structure of barium tetratitanate (^{7}). Thus, in all these compounds the nearest environment of the titanium ions consists of six oxygen ions arranged octahedrally around it, and direct interaction between with atoms of unlike metals in a compound is impossible. In contrast to this, in the structure of ilmenite ($FeTiO_3$, $MgTiO_3$) both metals are in approximately equivalent positions. The occupied hexagons of octahedra are each divided into a pair of triangles, in which Fe or Ti ions are arranged alternately. In the vertical columns of the structure, octahedra occupied by Fe and Ti ions alternate with empty ones. It is evident that the polarization conditions and the character of the interaction of titanium ions with other atoms in these compounds differ from what occurs in compounds with a perovskite-type structure.

Fig. 1. Lines $K_{\beta''}$ and K_{β_5} of the X-ray spectrum of titanium in various compounds: 1—$CaTiO_3$; 2—$SrTiO_3$; 3—$BaTiO_3$; 4—$BaO \cdot 4TiO_2$; 5—TiO_2 (anatase); 6—$FeTiO_3$; 7—$ZnTiO_3$; 8—$MgTiO_3$; 9—TiO_2 (brookite).

A focusing X-ray tube spectrograph (^{8}) with a quartz crystal as analyzer was used to carry out the work. The reflecting planes were the planes of the prism ($d = 3.33$ Å). The radius of curvature of the crystal was 2.5 m; the length of the working section of the crystal was 15 mm; the linear dispersion of the spectrograph in the investigated spectral region was ~ 2.5 X/mm. To investigate fluorescence spectra, the substance was placed outside the X-ray tube at a distance of 26 mm from its anode. The anode was copper, chromium-plated. The operating conditions of the X-ray tube were: 35 kV, 50 mA; exposure 15-25 h; registration of spectra was photographic. The positions, shapes, and relative intensities of the lines K_{β_1}, K_{β_5}, $K_{\beta'}$, and $K_{\beta''}$ of ti-

in the aforementioned compounds. The maxima of the titanium K_{β_1} and K_{β_5} lines in all compounds proved to be slightly shifted toward the long-wavelength side in comparison with their position in the spectrum of the metal (1). For the first of these lines the magnitude of the shift is very small and lies within the limits of measurement accuracy (±0.2 eV) (Table 1). The maximum of the K_{β_5} line is shifted by a larger amount, ~ 0.6 eV. The energy position and shape (width and asymmetry index) of the diagram emission lines of titanium (K_{β_1}

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* Some of the titanates studied in the present work were kindly provided to us by Prof. G. I. Skanavi, to whom the authors express their deep gratitude.

Fig. 2. Titanium $K_{\beta'}$ line in some titanates: 1—$CaTiO_3$, 2—$SrTi_3O$

Figure 2: Fig. 2. Titanium $K_{\beta'}$ line in some titanates: 1—$CaTiO_3$, 2—$SrTi_3O$

and K_{β_5}) in various compounds do not undergo noticeable changes (exceeding the limits of measurement error). The same also applies to the satellites—$K_{\beta'}$ and $K_{\beta''}$ (Figs. 1 and 2). At the same time, the relative intensity of the $K_{\beta''}$ line in the emission spectrum of the element in various

Table 1

Position of the titanium K_{β_1} line in compounds

Substance	Energy, eV	Substance	Energy, eV
Ti (metal)	4931.5	$SrTiO_3$	4931.1
$MgTiO_3$	4931.2	$BaTiO_3$	4931.2
$CaTiO_3$*	4931.3	$BaO \cdot 4TiO_2$	4931.3
$ZnTiO_3$	4931.3	TiO_2 (anatase)	4931.3

* In work (1), the energy position of the titanium K_{β_1} line in this compound was determined incorrectly.

Fig. 2. Titanium $K_{\beta'}$ line in some titanates: 1—$CaTiO_3$, 2—$SrTi_3O$

compounds, even allowing for the comparatively low accuracy of determining this quantity, does not remain constant (Table 2) and, evidently, depends on the polarization state of the absorbing atom and of the entire complex anion TiO_6 in the compound. The experimentally observed course of the change in the relative intensity of the $K_{\beta''}$ line, as compared with the intensity of the K_{β_5} line, is in qualitative agreement with what may be expected

Table 2

Relative intensity of the titanium $K_{\beta''}$ and K_{β_5} lines in compounds

Substance	$IK_{\beta''}/IK_{\beta_5}$	Substance	$IK_{\beta''}/IK_{\beta_5}$	Substance	$IK_{\beta''}/IK_{\beta_5}$
$FeTiO_3$	0.24	$BaO \cdot 4TiO_2$	0.48	$CaTiO_3$*	0.56
$ZnTiO_3$	0.40	TiO_2 (rutile)	0.49	$SrTiO_3$	0.58
TiO_2 (brookite, anatase)	0.41	$MgTiO_3$*	0.51	$BaTiO_3$	0.56

* In the course of the work several different samples of these compounds were studied, differing in degree of chemical purity and in their dielectric characteris-

tics. The x-ray spectra of titanium in these compounds practically did not differ from one another. Table 2 gives the average values of the ratio $IK_{\beta''}/IK_{\beta_5}$ in the x-ray spectrum of titanium in each of these substances.

(6), proceeding from the previously advanced (1) assumption about the mechanism of the origin of these lines.

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Received
11 VI 1957

CITED LITERATURE

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