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X-RAY K-EMISSION SPECTRA OF TITANIUM IN LOWER OXIDES ($Ti—TiO_{0.48}$)

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In recent years the titanium–oxygen system has repeatedly been subjected to comprehensive and thorough physicochemical investigation (^{1}). This is connected chiefly with the broad and varied practical use of titanium and its oxides in modern technology. At the same time, this system represents a very convenient object for studying a number of theoretical questions and, in particular, questions associated with elucidating and investigating the character of interatomic interaction in phases of variable composition, which are widely represented in it and are usually characterized by fairly extended concentration regions of homogeneity.

In the present article the first results are given of an X-ray spectral investigation of the lower titanium oxides, whose homogeneity region lies in the concentration interval $Ti—TiO_{0.48}$ (^{2}). According to X-ray structural studies ($^{2-5}$), these oxides are solid solutions of oxygen in the hexagonal α-lattice of titanium, in which the metalloid atoms statistically fill part of the octahedral voids of the structure. With increasing oxygen content, the number of atoms in the elementary cell of the oxide increases monotonically and, at the boundary of the homogeneity region of the phase, approaches three. The number of titanium atoms in the cell in the metal and in the oxides, however, remains unchanged.

Oxides of composition $TiO_{0.102}$, $TiO_{0.248}$, $TiO_{0.337}$, $TiO_{0.401}$, $TiO_{0.451}$ and the initial iodide titanium, kindly placed at our disposal by E. S. Makarov and L. M. Kuznetsov, were subjected to X-ray spectral investigation. The oxides were prepared by saturating titanium with a prescribed amount of gaseous oxygen at a temperature of 500-550° by the procedure described in (^{6}). Earlier they had also served as material for the X-ray structural investigation mentioned above (^{2}). The obtained oxide specimens were homogenized by annealing at a temperature of $\sim 1000^\circ$ for 15 hours, after which they were rapidly cooled in a vacuum system to room temperature. Direct determination of the oxygen content in the samples was checked by the method of vacuum melting. Attempts to use the primary method of exciting X-ray spectra did not lead to positive results, since even under a very mild operating regime of the X-ray tube it was not possible to obtain sufficiently reproducible results. It is not excluded that, in addition to the interferences usual for the primary method, in the study of lower oxides the matter is further complicated by the sharp dependence of their electrical resistivity on temperature (^{7}). Therefore the work was carried out by the fluorescence method on a DRS-2 spectrograph in the second order of reflection. The analyzer crystal was quartz, plane $(10\bar{1}0)$. The resolving power of the spectrograph in the region of the titanium $K\beta_5$ emission band was 8000-10000, and in the region of the $K\alpha_{1,2}$ lines, 18000-20000. The operating regime of the X-ray tube was 25 kV, 25 mA. Exposure time was 20-25 hours. Recording of the spectra was photographic. As comparison lines, Ni$K\alpha_1$ III; V$K\alpha_1$ II; Cr$K\beta_1$ IV; Co$K\alpha_1$ III* were used. Accuracy in de-

* Roman numerals denote the order of reflection.

···of the energy determination was ±0.2 eV. The reproducibility error in measurements of the relative intensity of the lines was 3-4%.

The shape and energy position of the $K\beta_1$ and $K\alpha_{1,2}$ emission lines of titanium in the metal and in all the oxides studied proved to be identical within the limits of experimental accuracy. The ratio $IK\alpha_2/IK\alpha_1 = 0.46 \pm 0.005$. In accordance with the ideas developed in (^{8}), this may be regarded as an indication that the degree of involvement of the $3d$ electrons of titanium in bonding in the metal and in solid solutions with oxygen remains practically unchanged and does not depend on the composition of the oxide. In contrast to the lines of the x-ray spectrum that arise owing to electronic transitions between deep-lying atomic energy levels, the structure of the latter emission bands of titanium, associated with valence energy levels in the oxides, undergoes substantial changes in comparison with the spectrum of the metal (Figs. 1, 2 and Table 1). In the spectra of titanium in oxides a new weak line appears—the satellite $K\beta^{\mathrm{II}}$, whose intensity increases as the relative oxygen content in the compounds increases (Fig. 1). This fact is not surprising and agrees well with the hypothesis on the origin of this line (^{9}) and with the results of its subsequent verification ($^{10-14}$). More interesting are the changes occurring in the structure of the $K\beta_5$ band. On going from the metal to the oxides (Fig. 2) this band is clearly split into two components ($K\beta_5^{\mathrm{I}}$ and $K\beta_5^{\mathrm{II}}$). The $K\beta_5^{\mathrm{I}}$ line in many respects resembles the initial $K\beta_5$ band in the spectrum of the metal. It has an asymmetric shape and the same asymmetry index

Microphotometric recording of the latter x-ray lines of the $K\beta$-group of titanium in the metal and in some oxides

Table 1.

n	$K\beta_5^{\mathrm{I}}$ half-width, eV	$K\beta_5^{\mathrm{I}}$ energy of maximum*, eV	$\frac{I_{\mathrm{M}} K\beta_5^{\mathrm{I}}}{I_{\mathrm{M}} K\beta_1}$	$\frac{I_{\mathrm{in}} K\beta_5^{\mathrm{I}}}{I_{\mathrm{in}} K\beta_1}$	$K\beta_5^{\mathrm{II}}$ half-width, eV	$K\beta_5^{\mathrm{II}}$ energy of max., eV	$\frac{I_{\mathrm{in}} K\beta_5^{\mathrm{II}}}{I_{\mathrm{in}} K\beta_1}$
0	4.5	30.7	0.0160	0.0157	–	24.8	0.0048
0.102	3.9	31.0	0.0176	0.0154	–	24.7	0.0083
0.248	3.8	31.1	0.0185	0.0155	–	24.8	0.0110
0.337	3.4	31.3	0.0191	0.0145	3.5	25.0	0.0130
0.401	3.5	31.3	0.0182	0.0139	3.5	24.9	0.0152
0.451	3.5	31.1	0.0159	0.0118	3.6	24.9	0.0144

* The energy of the maximum of the $K\beta_1$ line of metallic titanium was chosen as the origin for the energy scale.

(independent of the oxide composition) and differs from the $K\beta_5$ band in the metal only by a smaller width and by a shift of its maximum and short-wavelength edge toward higher energies (Table 1). The $K\beta_5^{\mathrm{II}}$ band is located in the longer-wavelength region of the spectrum at a distance of 5.9–6.4 eV from the max-

of the maximum of the $K\beta_5^{\mathrm{I}}$ line. The position of its maximum on the energy scale (within the accuracy of determining this quantity) remains unchanged in the metal and in oxides of various compositions, while the intensity increases in direct proportion to the relative oxygen content in the oxides (Fig. 4).

Fig. 2. The titanium $K\beta_5$ emission band in the metal and in oxides after subtraction of the background from the $K\beta_1$ line and reduction to a common scale (with respect to the integral intensity of the $K\beta_1$ line). The results of decomposing the band into components are indicated by dashed lines.

As experience shows, this band has a symmetric shape and can be approximated by a dispersion curve with a half-width of 3.5 eV, independent of the oxide composition. This was checked directly in analyzing the spectra of the three oxides with the highest oxygen content and was extended to all the other spectra. Isolation of this band makes it possible to decompose approximately the titanium $K\beta_5$ emission band in the metal and in various solid solutions into two components (Fig. 2) and to study each of them separately. Figures 3 and 4 give the dependence of the integral (I_{int}) intensity of the titanium $K\beta_5^{\mathrm{I}}$ and $K\beta_5^{\mathrm{II}}$ emission bands on the composition of the solid solution. For the first of these bands the dependence of the band intensity at the maximum (I_{M}), located near the Fermi boundary, is also shown. The latter curve is compared with the curve of the change in the electrical resistivity of the oxides (^{7}).

Fig. 3. Dependence of the intensity of the titanium $K\beta_5^{\mathrm{I}}$ emission band on the composition (n) and its comparison with the electrical resistivity (ρ) of the

oxides according to (7) (8). a—integral intensity of the band (I_{int}), b—intensity of the band at the maximum (I_{M}).

The nature of the splitting of the x-ray titanium $K\beta_5$ emission band in its solid solutions with oxygen is at present insufficiently clear. It might be connected, for example, with submicroinhomogeneous structure of the oxides studied and with the coexistence in them of titanium atoms in two different valence states. Such ideas about the structure of these compounds are arrived at on the basis of thermodynamic and magnetochemical studies of the lower oxides of a series of metals by Aria and his coworkers (15–17). On the other hand, it is possible that the complex structure of the titanium $K\beta_5$ band observed experimentally in the oxides is a manifestation in the spectra of the presence, in transition metals and their compounds, of two types of $3d$ electrons (collectivized and localized), in accordance with the ideas developed in (18–23). The possibility of such an interpretation of the complex structure of the latter emission bands in the K- and L-spectra of transition elements had already been noted earlier in the study of Mo, Nb, and Cr in the metallic state and in compounds (24,25,14).

Fig. 4. Dependence of the intensity of the titanium $K\beta_5^{\text{II}}$ emission band in oxides on oxygen content η

In our case, such an assumption would make it possible to explain the characteristic difference in the shape of the components of the split band and to understand the experimentally observed (Fig. 3) correlation between the concentration dependence of the maximum of the short-wavelength band and the electrical resistivity of oxides possessing electronic conductivity in this region (7,26). At the same time, the experimentally determined magnitude of the splitting (~ 6 eV) seems very large in comparison with that which might have been expected theoretically.

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