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Abstract

Full Text

Physical Chemistry

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Structure of the X-ray K_{β_5} Emission Bands of Titanium in Oxides ($\text{TiO}_{0.85}$ — $\text{TiO}_{1.20}$)

(Presented by Academician A. P. Vinogradov, February 20, 1964)

In continuation of the investigations begun in ⁽¹⁾, in the present work we undertook a study of the fine structure of the X-ray K_{β_5} emission band of titanium in samples corresponding to the homogeneity range of the metal monoxide. The material for these investigations was provided to us by Ya. V. Vasil' ev. The oxide preparations were synthesized by calcining thoroughly ground mixtures of hydrated titanium iodide and especially pure dioxide, pressed in a press mold made of organic glass, in high vacuum at 1400°.

The titanium monoxide samples prepared in this way were held at this temperature for 3 hr, then calcined at 1150° for 15 hr and at 1000° for 10 hr, after which they were quenched from this temperature. X-ray diffraction studies showed the single-phase character of the titanium monoxide preparations studied over a broad range of composition, from $\text{TiO}_{0.85}$ to $\text{TiO}_{1.20}$. Within this entire homogeneity range, the lattice parameter of the monoxide (which has the NaCl-type structure with a considerable fraction of vacancies in both sublattices) is a linear function of the oxygen index (TiO_n).

Six titanium monoxide samples of the following composition were subjected to X-ray spectral investigation: $\text{TiO}_{0.850}$; $\text{TiO}_{0.912}$; $\text{TiO}_{1.026}$; $\text{TiO}_{1.072}$; $\text{TiO}_{1.178}$ and $\text{TiO}_{1.191}$.

In addition, the Ti spectrum in a nitride close in composition to the stoichiometric one was studied; this nitride, like the monoxide samples, has an NaCl-type structure.

The experimental conditions were very close to those described in ⁽¹⁾. The temperature of the substance during operation of the tube was 80—100°. The experimental results obtained are presented in Figs. 1 and 2 and in Table 1. Their consideration and comparison with the data of work ⁽¹⁾ make it possible to draw the following conclusions.

Table 1

Dependence of the relative integral intensity and energy position of the components of the Ti K_{β_5} emission band on the composition of the oxide

Oxide composition	$\frac{I_{\text{int}} K_{\beta_5}^{\text{I}}}{I_{\text{int}} K_{\beta_1}}$	$\frac{I_{\text{int}} K_{\beta_5}^{\text{II}}}{I_{\text{int}} K_{\beta_1}}$	$\frac{I_{\text{int}} K_{\beta_5}^{\text{III}}}{I_{\text{int}} K_{\beta_1}}$	$K_{\beta_5}^{\text{I}}$	$K_{\beta_5}^{\text{II}}$	$K_{\beta_5}^{\text{III}}$
TiO _{0.850}	0.0054	0.0209	0.0034	30.9	25.2	21.1
TiO _{0.912}	0.0036	0.0214	0.0024	30.8	25.1	21.0
TiO _{1.026}	0.0036	0.0225	0.0033	30.9	25.3	21.1
TiO _{1.072}	0.0027	0.0233	0.0053	30.8	25.3	21.1
TiO _{1.178}	0.0019	0.0237	0.0062	30.8	25.6	21.2
TiO _{1.191}	0.0018	0.0253	0.0061	30.8	25.5	21.1
Error	±10%	±3%	±20%	±0.3	±0.2	±0.4

* The energy of the maximum of the K_{β_1} line of metallic titanium was chosen as the zero of the energy scale.

As in the titanium oxides studied earlier ⁽¹⁾, the K_{β_5} emission band of the atoms of this element in the monoxide has a complex structure, the details

which, however, differ substantially from that observed earlier. In both cases, within the complex titanium K_{β_5} emission band in the oxide one can distinguish three regions or, conventionally speaking, three emission bands, denoted in Figs. 1, 2, and 4 by the symbols $K_{\beta_5}^{\text{I}}$, $K_{\beta_5}^{\text{II}}$, and $K_{\beta_5}^{\text{III}}$. To carry out a concrete decomposition of the experimentally observed titanium K_{β_5} band in these compounds into components, use was made of the circumstance that the shape of the $K_{\beta_5}^{\text{II}}$ band of the oxides can be described fairly well by a dispersion law of the dependence of its intensity on frequency, while the half-width throughout the entire homogeneity range does not depend on the oxide composition. The results of the decomposition of the spectra performed in this way, as well as data characterizing the relative intensity of the components and the energy positions of their maxima, are presented in Fig. 2 and in Table 1 of the present work and in ⁽¹⁾.

In the emission spectra of titanium in the lower oxide, the position of the maximum of the $K_{\beta_5}^{\text{I}}$ band undergoes (in comparison with the oxides with $0 < n < 0.48$) a noticeable long-wavelength shift. Within the accuracy of measurement of this quantity it does not depend on the composition of the oxide and, practically, coincides with the position of the principal (short-wavelength) emission maximum of the K_{β_5} band in metallic titanium. Conversely, the maximum of the $K_{\beta_5}^{\text{II}}$ band in the spectrum of titanium in the lower oxide is shifted toward the shorter-wavelength side and shows a tendency for the magnitude of the shift to increase with increasing n .

The position of the maximum of the $K_{\beta_5}^{\text{III}}$ emission band in the spectrum of titanium in the lower oxide remains practically unchanged throughout the entire homogeneity range of the compound in oxides of different composition.

Fig. 1. Structure of the last emission K_{β} bands of titanium in lower oxides (experimental curves)

Figure 1: Fig. 1. Structure of the last emission K_{β} bands of titanium in lower oxides (experimental curves)

Fig. 2

Figure 2: Fig. 2

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The most striking differences in the structure of the titanium K_{β_5} band in the lower oxides, corresponding to different intervals of variation of the index n , are associated with the difference in the relative intensity of the band components. Qualitatively this appears as a relative increase in the intensity of the long-wavelength region of the emission band (the $K_{\beta_5}^{\text{II}}$ and $K_{\beta_5}^{\text{III}}$ components) and a decrease in the emission intensity in the region of the $K_{\beta_5}^{\text{I}}$ component. The latter band is weakened in the spectrum of the lower oxide so strongly that (in contrast to ⁽¹⁾) it becomes much weaker than the $K_{\beta_5}^{\text{II}}$ band. An idea of the quantitative relationships revealed in processing the experimental data can be obtained from consideration of the data presented in Figs. 3, 4 and in Table 1. As is seen (Fig. 3), the relative intensity of the $K_{\beta_5}^{\text{II}}$ titanium emission band in oxides of both types is a linear function of the index n , which characterizes their composition*. However

* The large scatter of points at the boundaries of the homogeneity regions of the oxides is evidently connected with possible changes in their state during the quenching of the specimens studied (⁽⁷⁾).

the slope of these straight lines in the region $0 < n < 0.48$ and $0.85 < n < 1.2$ is different. It may be thought that this is a consequence of a decrease in the probability of a radiative transition to the $1s$ -levels of the emitting atom for the valence electrons of titanium in oxides with cubic symmetry of the ligand field (the region $0.85 < n < 1.2$), as compared with the lower oxides having a hexagonal structure.

Fig. 2. Fine structure of the titanium K_{β_5} -emission band in oxides after subtraction of the background from the K_{β_1} -line and reduction to a single scale (with respect to the integral intensity of the K_{β_1} -line). The components of the band are indicated by dashed lines.

Fig. 3

Figure 3: Fig. 3

Fig. 3. Dependence of the relative integral intensity of the titanium $K_{\beta_5}^{II}$ -emission band on the composition of the oxides Ti–TiO_{0.48} (hexagonal lattice) and TiO_{0.85}–TiO_{1.20} (cubic lattice), n being the oxygen index.

To an even greater extent the aforementioned decrease in the probability of a radiative transition, evidently associated with a decrease in the share of participation of p -symmetry orbitals in the formation of molecular orbitals* in oxides having a structure of the NaCl type, is manifested when considering the shortest-wavelength component of the titanium K_{β_5} -band in these compounds—the $K_{\beta_5}^I$ band. This leads to a sharp weakening of the intensity of this band in the spectra of Ti in monoxide as compared with the lower oxides with a hexagonal structure. That this phenomenon is of a sufficiently general character, and is not a property inherent only in titanium oxides, but rather is connected with the symmetry of the crystal lattice of the compound and with the features of hybridization of the wave functions of the central ion and of the atoms forming its nearest environment, can be seen from consideration of the data presented in Fig. 4. At the same time, the experimental results obtained by us, relating to the proposed structure of the energy spectrum

* This, on the basis of the conclusions of the modern ligand theory, can be expected theoretically ⁽⁴⁾.

electrons in these compounds are qualitatively compared in this figure with the data of Bilz' s theoretical calculation ⁽³⁾!

In the homogeneity region of titanium monoxide, with increasing n , the intensity of the $K_{\beta_5}^I$ band decreases almost rectilinearly. This is accompanied by a change in the intensity of the third $K_{\beta_5}^{III}$ component of the K_{β_5} band in the opposite direction. The law of this change, however, is difficult to establish, because of the lower accuracy with which the magnitude of the integral intensity of the $K_{\beta_5}^{III}$ band can be determined experimentally.

In paper ⁽¹⁾ we already touched upon the question of the possible origin of the $K_{\beta_5}^I$ and $K_{\beta_5}^{II}$ emission bands in the spectra of titanium in the lower oxides. In particular, it was noted that one of the most probable causes capable of explaining their appearance may be the assumption of two types of valence electrons effecting the chemical bond in these compounds—delocalized and localized $3d$ electrons.

According to the concepts developed in ^(5,6,8), in titanium monoxide, along with a relatively broad p band, one should also expect a special $3d$ band, whose width should decrease rather rapidly on passing to compounds of other transition elements of the iron group that are analogous in composition and structure and have larger atomic numbers. Unfortunately, the calculations ⁽⁸⁾ were carried out on the basis of rather crude ideas and require refinement in the future. This makes a scrupulous comparison of the conclusions of the theory with the experimental results premature at present. It should be noted, however, that between the main conclusions of the calculation and the results obtained by us

there is, in general, already good agreement.

Fig. 4. Comparison of the fine structure of the K_{β_5} emission bands and the scheme of the energy bands of valence electrons in titanium compounds with cubic (NaCl type) and hexagonal lattices. For comparison, the theoretical scheme of the electron density of states in compounds with an NaCl-type lattice according to Bilz⁽³⁾ is given.

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