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## Abstract

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# X-Ray $K_{\alpha_{1,2}}$- and $K_{\beta_1}$-Emission Lines of Titanium in Oxides

*(Presented by Academician A. P. Vinogradov, 17 XII 1964)*

Previously ($^1$, $^2$), an experimental investigation was carried out of the fine structure of the $K_{\beta_5}$-emission bands of titanium in lower oxides of hexagonal (Ti—$TiO_{0.48}$) and cubic ($TiO_{0.85}$—$TiO_{1.2}$) structure in the homogeneity regions of these phases. In the present work these data are supplemented by information on the energy position and shape (width and asymmetry index) of the $K_{\alpha_{1,2}}$- and $K_{\beta_1}$-emission lines of the metal in the same phases of variable composition, and also in other oxides existing in the region $TiO_{1.5}$—$TiO_2$. Methods for preparing the lower oxides have already been described ($^1$, $^2$). Titanium sesquioxide $TiO_{1.5}$ was obtained, as in ($^3$), by sintering a pressed mixture of titanium iodide with pure dioxide in high vacuum at a temperature of 1400—1500° for 6 hr. A compound of composition $TiO_{1.67}$* was obtained by reducing titanium dioxide in a stream of purified hydrogen at a temperature of 1100° for 30 hr. It was subsequently used to obtain oxides with a higher oxygen content ($TiO_{1.735}$, $TiO_{1.874}$), belonging to the homologous series of compounds with the general formula $Ti_nO_{2n-1}$, where $n = 4, 5, \ldots, 10$, discovered** by Andersson ($^4$). For this purpose the oxide $TiO_{1.67}$ obtained was mixed in the required proportion with dioxide and calcined at 1100—1150° in high vacuum with continuous pumping for 30–40 hr. Every 10 hr the calcination was interrupted and the specimens were ground. The composition of the specimens obtained in this way was determined by the gravimetric method, by oxidizing them to dioxide in a stream of moist oxygen at 1100°. The discrepancy between the results of analysis for different samples did not exceed ±0.002 in the oxygen index. Phase analysis of the specimens obtained was carried out by measuring their magnetic susceptibility. This method, as was shown in ($^{13}$), makes it possible to judge the phase relations in the system under investigation quite reliably, since in compounds lying in the interval $TiO_{1.67}$—$TiO_{1.856}$, with increasing temperature, phase transformations are observed, accompanied by jumps in susceptibility, which for different compounds differ both in temperature and in magnitude.

Figure 1 gives the dependence of magnetic susceptibility on temperature for specimens subjected to the x-ray spectral investigation in the present work. The magnetic susceptibility of titanium sesquioxide (curve 1) changes smoothly over the entire temperature interval, which indicates the absence in this specimen of admixtures of more oxygen-rich compounds (for example, $TiO_{1.67}$ or $TiO_{1.75}$), characterized by the presence of jumps in magnetic susceptibility at temperatures of about 460° and 170°K, respectively. Comparison

* The existence of this compound was proved by x-ray structural investigations ($^{5}$).

** Andersson' s results were subsequently confirmed independently in investigations of the electrical conductivity and magnetic properties of higher titanium oxides ($^{6}$, $^{13}$).

curves 2 and 3, pertaining to the preparations $TiO_{1.672}$ and $TiO_{1.735}$, show that the first of them is a practically pure compound containing no more than 1-2% $TiO_{1.75}$ (Andersson compound with $n = 4$), whereas the second is a mixture of the same compounds in which the amount of $TiO_{1.75}$ is about 80%. An analogous consideration of curves 4 and 5, pertaining respectively to the preparations $TiO_{1.856}$ and $TiO_{1.874}$, leads to the conclusion that the preparation of composition $TiO_{1.874}$ investigated in the present work contains practically no admixture of a neighboring compound in composition—

**Fig. 1.** Dependence of the magnetic susceptibility of various titanium oxides on temperature.
1 —for $TiO_{1.500}$; 2 —for $TiO_{1.672}$; 3 —for $TiO_{1.735}$; 4 —for $TiO_{1.856}$; 5 —for $TiO_{1.874}$

**Fig. 2.** Dependence of the half-width $\Delta E$ of various emission lines of titanium in $TiO_n$ oxides on $n$

**Table 1**

Relative energy position, half-width $\Delta E$, and asymmetry index $a$ of the $K_{\alpha_{1,2}}$- and $K_{\beta_1}$-emission lines of Ti in oxides of different composition*

| Oxide composition | Energy of maximum, eV $K_{\alpha_1}$ | Energy of maximum, eV $K_{\alpha_2}$ | Energy of maximum, eV $\Delta(K_{\alpha_1}-K_{\alpha_2})$ | Energy of maximum, eV $K_{\beta_1}$ | $K_{\alpha_1}$ $\Delta E$, eV | $K_{\alpha_1}$ $a$ | $K_{\alpha_2}$ $\Delta E$, eV | $K_{\alpha_2}$ $a$ | $K_{\beta_1}$ $\Delta E$, eV | $K_{\beta_1}$ $a$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Ti metal | 0 | 0 | 0 | 0 | 1.4 | 1.2 | 1.8 | 0.9 | 2.8 | 1.7 |
| $TiO_{0.102}$ | +0.02 | −0.03 | +0.05 | +0.04 | 1.5 | 1.2 | 1.8 | 0.9 | 3.0 | 1.5 |
| $TiO_{0.337}$ | −0.04 | +0.02 | −0.06 | +0.01 | 1.5 | 1.1 | 1.82 | 0.9 | 3.2 | 1.5 |
| $TiO_{0.451}$ | +0.07 | +0.06 | +0.01 | −0.08 | 1.5 | 1.2 | 1.7 | 0.8 | 3.3 | 1.6 |
| $TiO_{0.850}$ | −0.06 | −0.04 | −0.03 | −0.27 | 1.6 | 1.3 | 1.80 | 0.8 | 3.6 | 1.7 |
| $TiO_{0.912}$ | −0.02 | −0.02 | −0.00 | −0.48 | 1.6 | 1.3 | 1.82 | 0.9 | 3.8 | 1.6 |
| $TiO_{1.026}$ | +0.05 | +0.08 | −0.03 | −0.5 | 1.7 | 1.2 | 1.85 | 0.95 | 3.83 | 1.5 |

Fig. 3 and Fig. 4 plots

Figure 1: Fig. 3 and Fig. 4 plots

| Oxide composition | Energy of maximum, eV $K_{\alpha_1}$ | Energy of maximum, eV $K_{\alpha_2}$ | Energy of maximum, eV $\Delta(K_{\alpha_1}-K_{\alpha_2})$ | Energy of maximum, eV $K_{\beta_1}$ | $K_{\alpha_1}$ $\Delta E$, eV | $K_{\alpha_1}$ $a$ | $K_{\alpha_2}$ $\Delta E$, eV | $K_{\alpha_2}$ $a$ | $K_{\beta_1}$ $\Delta E$, eV | $K_{\beta_1}$ $a$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $TiO_{1.072}$ | +0.09 | +0.13 | −0.14 | −0.54 | 1.6 | 1.3 | 1.88 | 0.94 | 3.8 | 1.5 |
| $TiO_{1.178}$ | −0.06 | +0.04 | −0.10 | −0.54 | 1.82 | 1.3 | 1.87 | 0.94 | 4.13 | 1.6 |
| $TiO_{1.191}$ | −0.07 | −0.02 | −0.05 | −0.54 | 1.85 | 1.3 | 1.88 | 0.97 | 4.08 | 1.61 |
| $TiO_{1.50}$ | −0.32 | −0.12 | −0.20 | −0.98 | 2.0 | 1.20 | 1.95 | 1.0 | 4.32 | 1.2 |
| $TiO_{1.672}$ | −0.46 | −0.14 | −0.32 | −1.0 | 1.8 | 1.02 | 2.03 | 1.0 | 4.22 | 1.2 |
| $TiO_{1.735}$ | −0.45 | −0.16 | −0.22 | −0.8 | 2.0 | 1.03 | 2.22 | 1.05 | 4.24 | 1.25 |
| $TiO_{1.874}$ | −0.54 | −0.14 | −0.40 | −0.8 | 1.9 | 0.95 | 2.32 | 0.9 | 3.92 | 1.3 |
| $TiO_2$ (rutile) | −0.67 | −0.19 | −0.48 | −0.5 | 1.5 | 0.8 | 2.2 | 1.0 | 3.3 | 1.4 |
| Error | $±$0.1 | $±$0.1 | $±$0.2 | $±$0.1 | $±$0.05 | $±$0.05 | $±$0.05 | $±$0.05 | $±$0.05 | $±$0.05 |

* The half-width and asymmetry index of the $K_{\alpha_{1,2}}$ lines of metallic titanium and of the oxides, in contrast to [1], were measured from spectra recorded in the third order of reflection and, consequently, were obtained with greater accuracy.

⋯tion (it thus corresponds to the Andersson compound with $n = 8$). The X-ray fluorescence spectra of titanium in the oxides were obtained on a DRS-2 spectrograph under conditions analogous to those described in ([1,2]).

The experimental results obtained are given in Table 1 and in Figs. 2 and 3. Examination of them makes it possible to draw the following conclusions.

1. The energy position of the maxima of the titanium $K_{\alpha_1}$- and $K_{\alpha_2}$-emission lines in the lower oxides (in the regions $0 < n < 0.45$ and $0.85 < n < 1.20$) remains, within the accuracy of the energy determination (±0.1 eV), unchanged and practically coincides with that in the spectrum of metallic titanium. Therefore, for these compounds the value $\Delta(K_{\alpha_1} - K_{\alpha_2})$ is also unchanged (within the accuracy of the experiment). The behavior of the $K_{\beta_1}$ line in this respect is more complicated. The position of its maximum for the lower oxides with a hexagonal

**Fig. 3.** Dependence of the asymmetry index $a$ of various emission lines of titanium in the oxides $TiO_n$ on $n$

**Fig. 4.** Comparison of the course of the dependence of some characteristics of the oxides $TiO_{1\pm x}$ in the homogeneity region of this phase. *a*—asymmetry indices of the $K_{\alpha_1}$- and $K_{\beta_1}$-lines of the X-ray spectrum of titanium; *b*—magnetic susceptibility, referred to the gram-formula of the oxide according to ([12]); *c*—gram-formula volume $V = M/d$, where $M$ is the molecular weight of the oxide, and $d$ is its density according to ([10])

structure remains unchanged, as it does for the $K_{\alpha_{1,2}}$-line. In the region $0.85 < n < 1.2$ a long-wavelength shift of the maximum of the $K_{\beta_1}$-line is observed in comparison with the spectrum of the metal. The magnitude of the shift gradually increases as $n$ increases from 0.85 to 1 and then, at $n > 1$, remains constant.

The shape of the $K_{\alpha_{1,2}}$-lines (half-width and asymmetry index) in the region $0 < n < 0.45$ practically does not change. By contrast, for the $K_{\beta_1}$ lines in these oxides there is a linear increase in the half-width and a more complex law of variation of the asymmetry index (Figs. 2 and 3). In the spectra of titanium in oxides with cubic structure ($0.85 < n < 1.2$), the shape parameters of the $K_{\alpha_{1,2}}$- and $K_{\beta_1}$-lines change in a completely analogous way. The widths of the $K_{\alpha_1}$- and $K_{\beta_1}$-lines increase with $n$ according to a linear law, the shape of the $K_{\alpha_2}$-lines remains practically unchanged, and the asymmetry index of the $K_{\alpha_1}$- and $K_{\beta_1}$-lines exhibits a nonmonotonic course of variation with a minimum at the point corresponding to the oxide of stoichiometric composition ($n = 1$). It is curious that an analogous point of inflection at $n = 1$ is observed for these same compounds on the curves of the dependence on $n$ of the magnetic susceptibility of the oxides and their gram-formula volume (Fig. 4)*.

The angular coefficient of the straight lines describing the change in the width of the titanium $K_{\alpha_1}$- and $K_{\beta_1}$-lines in oxides with $n$, varying within the limits from 0.85 to 1.2, is the same. In accordance with the conclusions of the theory ([8]), the asymmetry index of the titanium $K_{\alpha_2}$-emission lines in all oxides proves to be smaller (the region of lower oxides) or equal (for oxides with $1.5 < n < 2$) to unity and relatively less sensitive to changes in the oxide composition and to the features of interatomic interaction in it than for the $K_{\alpha_1}$ line.

On the other hand, the theory ([7–9]) makes it possible to regard the observations made by us, relating to the shape and position of the titanium $K_{\alpha_{1,2}}$- and $K_{\beta_1}$-emission lines in lower oxides, as an indication of the constancy, within the entire homogeneity range of the phases studied, of the degree of participation in bonding and of the number of unpaired $3d$-electrons of titanium. This conclusion is in good agreement with our previous observations ([1],[2]). At the same time, the regular increase in the width of the $K_{\beta_1}$- and $K_{\alpha_1}$-emission lines in oxides as a function of $n$ and in the region $0.85 < n < 1.2$ may, according to ([7],[8]), indicate a gradual increase in the degree of ionicity of the bonds in these compounds.

2. In the interval $1.5 < n < 2$ in the Ti–O system, no oxides with any appreciable homogeneity range are observed. Most of the compounds in-

> vestigated by us belong to the Andersson homologous series. With increasing $n$ here, a regular long-wavelength shift of the $K_{\alpha_{1,2}}$- and $K_{\beta_1}$-lines is observed, together with a noticeable change in the parameters of their shape**. In the spectrum of titanium in the higher oxides the interdoublet $K_{\alpha_{1,2}}$-distance also changes substantially, decreasing regularly as the relative oxygen content in the oxide increases.

The width of the titanium $K_{\alpha_1}$- and $K_{\beta_1}$-lines in oxides of different composition changes in an analogous manner and, in the Ti spectrum in rutile, becomes minimal, close in value to the width of the corresponding lines in metallic titanium. The asymmetry indices of the $K_{\alpha_1}$- and $K_{\beta_1}$-lines change in opposite directions with increasing $n$.

Attention is drawn to the opposite character of the change in the magnitudes of the shift of the maxima of the titanium $K_{\alpha_1}$- and $K_{\beta_1}$-lines in the higher oxides with increasing $n$. In accordance with ([8],[9]), this apparently indicates that, in addition to the increase in the degree of involvement of the $3d$-electrons in bonding that occurs in this series of compounds, the number of unpaired electrons or the effective charge concentrated on the metal atom may also increase in the oxides.

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* A special point corresponding to the composition $n = 1$ was also observed on the curve of enthalpy of formation—composition ($^{11}$).

** As should have been expected, the $K_{\alpha_2}$-line proved to be least sensitive to changes in the oxide composition; for this line, minimal shifts of the maximum and a certain change in the half-width are observed (with an almost unchanged asymmetry index).

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

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