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Abstract

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PHYSICS

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THE INFLUENCE OF CHEMICAL BONDING ON THE FINE STRUCTURE OF THE LINES OF THE $K\beta$ GROUP OF THE X-RAY EMISSION SPECTRUM OF TITANIUM IN CERTAIN COMPOUNDS

(Presented by Academician A. P. Vinogradov on 25 XII 1956)

The aim of the present work is a comparative study of the fine structure of the lines of the K-series of the x-ray emission spectrum of titanium in its dioxide (rutile), in simple and complex titanium-tungsten carbide, nitride, and hydride. Obtaining these data is of interest both from the standpoint of the theory of x-ray spectra and for resolving the question of the nature of the forces of chemical bonding in these compounds.

Titanium carbide was obtained by calcining, in a stream of hydrogen, a mixture of titanium dioxide with soot in a carbon-tube furnace at a temperature of $\sim 2000°$. The amount of carbon bound in the carbide was 19.1%. The structure and lattice constant of the compound, determined by us radiographically, agreed well with the data given in (^{1}). The complex carbide $TiWC_2$ studied was an industrial sample containing 24.05% Ti and 9.5% bound carbon.*

Titanium nitride was obtained, according to (^{2}), from metallic titanium by calcining the metal in a stream of nitrogen in a porcelain tube of a furnace at a temperature of 1200°. To purify the nitrogen from oxygen, bubblers with an alkaline solution of pyrogallol and copper turnings heated to 600° were placed in the gas path. The crystal structure of the titanium nitride preparation obtained was studied radiographically. In this, the data of earlier investigations (^{3}) were confirmed, and the invariability of the structure of the substance under the conditions arising at the anode of the x-ray tube when titanium spectra are excited by the primary method was demonstrated.

Titanium hydride was prepared according to (^{4}) by calcining metallic titanium powder, degassed at high temperature, in a stream of hydrogen in a tube furnace

Figure 1

Figure 1: Figure 1

at a temperature of ~ 400°.

The structure of the preparations before and after the x-ray spectral investigation was monitored radiographically.

The x-ray spectra were obtained with a vacuum x-ray spectrograph RSD-2 (5) with a quartz crystal used as analyzer. The reflecting planes were $(10\bar{1}0)$. In the spectrograph, Johann focusing was implemented (6). To increase the resolving power of the instrument in the region of small reflection angles, the surface of the bent crystal was cut so that it formed a small (~ 10°) angle with the reflecting planes of the crystal (7). The dimensions of the surface of the bent crystal were 10×50 mm. The crystal was bent in a special crystal holder (5), in which elastic bending of the crystalline plate on four supports was carried out. The spectra were photographed in the second order of reflection on film placed perpendicular to the direction of the beam of diffracted x-rays. The dispersion of the instrument in the considered—

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* The sample was kindly placed at our disposal by E. A. Shchetilina.

of the spectral region under study was ~ 6 X/mm. The substance under investigation was placed on the anode of the x-ray tube. The anode was copper. Tube operating conditions: 55 mA and 12 kV. The spectrograms were photometered with an MF-2 photometer in three cross sections along the height of the lines; the measurement data were averaged. For each substance, three mutually well-reproducing microphotograms were obtained. The $K\beta''$- and $K\beta_5$-lines are located on the descending branch of the element' s spectrum relative to the considerably more intense $K\beta_1$-line. The method for isolating weak x-ray lines was the same as in previous works (8). It is illustrated, for metallic titanium, by the curves shown in Fig. 1*.

Fig. 1. Intensity of the $K\beta_5$-line of the x-ray spectrum of titanium in the metal (after (8)): 1—total experimental curve; 2—$K\beta_5$-line after allowance for the intensity of the $K\beta_1$-line.

The experimental results obtained, which characterize the relative position, shape, and intensity ratio of the $K\beta''$-, $K\beta_5$-, $K\beta_1''$- and $K\beta_2''$-lines in the x-ray spectra of titanium in various compounds,** are presented in Figs. 2 and 3. At the same time, the change in position and shape of the titanium $K\beta_1$-line in the same compounds was studied. When measuring the position of the titanium $K\beta_1$- and $K\beta_5$-lines in the spectra of various compounds, the lines of the vanadium $K\alpha_{1,2}$-doublet were used as reference lines. The positions of the remaining lines of the titanium spectrum were determined relative to its $K\beta_5$-line.

Consideration of the data obtained permits the following conclusions to be drawn:

1. The shape and position of some of the emission lines of the titanium $K\beta$-group ($K\beta_1$ and $K\beta''$) in the compounds studied remain practically unchanged; their relative intensity also does not change. For example, the intensity of the titanium $K\beta_2''$-line in all compounds is about 1/3 of the intensity of the element' s $K\beta_5$-line.***
2. In contrast to the $K\beta_1$- and $K\beta''$-lines of the x-ray spectrum of titanium, the $K\beta_5$-line is subject to a noticeable influence of the chemical bond. In the oxide and both carbides (Fig. 2) its position remains unchanged. In the nitride a long-wavelength shift of the maximum of the titanium $K\beta_5$-line is observed ($\sim$ 1.6 eV), indicating a decrease in the degree of filling by electrons of the corresponding energy bands in the compounds. Still larger changes in the position of the maximum of the titanium $K\beta_5$-emission band are observed in its hydride. As verification has shown, this conclusion remains valid despite the preliminary nature of the data on hydrides presented in the present work, which were obtained by means of the primary method of spectrum excitation and therefore bear traces of distortions,

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* Data taken from (^{8}).

** The titanium $K\beta_1''$- and $K\beta_2''$-lines in $TiWC_2$ were not measured, since a more intense tungsten emission line is superposed on them.

*** The appearance of a satellite of $K\beta''$ in the emission x-ray spectrum of elements is sometimes explained by electron transitions in atoms that have undergone multiple ionization. In this connection, attention is drawn to the fact that the relative intensity and mutual energy position of the two lines $K\beta_2''$ and $K\beta_1''$ that we have detected, on the one hand, and of the lines $K\beta_5$ and $K\beta''$, on the other, are very close. Therefore the possibility is not excluded that each of these pairs of lines arises as a result of analogous transitions in titanium atoms that are in different excited states. Such an assumption would also make it possible to understand the practical invariability of the position of the K_1''- and K_2''-lines relative to the first group of lines in different compounds, and makes probable a dependence of the relative intensity of these lines on the method of excitation of the x-ray spectra.

caused by chemical decomposition of the initial product and accumulation* in the course of the investigation of a phase with a lower hydrogen content. The titanium $K\beta_5$ band observed under these conditions in the hydride has a complex structure. It is characterized by two clearly pronounced maxima,

Fig. 2. Relative position and shape of the lines of the $K\beta$-group of the X-ray spectrum of titanium in the compounds $TiWC_2$, TiC, and TiO_2

Fig. 2 and Fig. 3: relative position and shape of the lines of the $K\beta$-group of the titanium X-ray spectrum in compounds

Figure 2: Fig. 2 and Fig. 3: relative position and shape of the lines of the $K\beta$-group of the titanium X-ray spectrum in compounds

Fig. 3. Relative position and shape of the lines of the $K\beta$-group of the X-ray spectrum of titanium in compounds (from top to bottom): simple carbide, nitride, and hydride

the relative intensity of which changes depending on the exposure time and the experimental conditions, i.e., it depends on the degree of decomposition of the initial product and on the relative content in the resulting mixture of components with different hydrogen contents. The energy position of both of these maxima remains unchanged. In comparison with the position of the maximum of the titanium $K\beta_1$ band in the carbide, the short-wavelength maximum of the $K\beta_5$ band in the hydride is shifted toward shorter wavelengths by 1.6 eV, while the long-wavelength maximum is shifted in the opposite direction by 3.9 eV.

3. The effect of the chemical bond in the compounds studied on the metal $K\beta''$ line is especially significant. A change of the anion leads to a considerable displacement of the position of these lines, to a change in their shape, and has a marked effect on their relative intensity. In the series of compounds TiO_2; TiC; $TiWC_2$; TiN and TiH, a gradual decrease in the relative intensity of the $K\beta''$ line is observed, down to its practically complete disappearance in the hydride. The ratio of the integral intensities of the $K\beta''$ and $K\beta_5$ lines in the spectra of titanium in the compounds is 0.52 for rutile; 0.4 for the simple and complex carbides; and 0.18 for the nitride. This is in good qualitative agreement with the assumption, previously advanced by us ([8]), concerning the mechanism of formation of this satellite, the verification of which was one of the most important tasks of the present investigation.

The relatively higher resolving power of the instrument made it possible to resolve, even more clearly than in (8), two components of the $K\beta''$ line in the titanium emission spectrum in rutile. Attention is drawn to the fact that, among the compounds we studied, the distance between the $K\beta''$ and $K\beta_5$ lines in the titanium spectrum is minimal in the carbides, in which these two lines essentially constitute a single emission band with two characteristic maxima. Titanium dioxide (especially if one takes into account the titanium spectra in brookite and anatase (8)) and the nitride differ qualitatively from the carbide in this respect.

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* This is indicated by the X-ray structural data for the initial preparation and for the hydride extracted from the X-ray tube after the investigation of the titanium spectra.

investigation of the specimens used in the present work.

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