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## Abstract

## Full Text

## Chemistry

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# X-ray Spectroscopic Study of Titanium Beryllides with a High Beryllium Content

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Recently (1), the first results were published of an X-ray spectroscopic study of a number of alloys of the Ti—Be system. Intermetallic compounds close in composition to TiBe and $TiBe_2$ were studied, and—in good agreement with the physical properties of these alloys—the presence in them of a metallic character of bonding and of delocalization of the valence electrons of both components was shown. It was of interest to extend these investigations and subject to analogous study phases with still higher beryllium content, which form, as could be judged from (2), an interesting and relatively little-studied group of intermetallic compounds with structures having high coordination numbers (3). At the same time it seemed advisable to check and refine the data of the previous study (1) by increasing the resolving power of the spectral apparatus used and by correcting the spectra for instrumental distortions with the aid of one of the methods now developed.

For carrying out the study, alloys* containing 88, 90, and 93 at.% Be were prepared by melting titanium and beryllium in corundum crucibles in a Tammann furnace (in an argon atmosphere). X-ray structural study of the first two samples made it possible to establish their complete identity and showed that the corresponding X-ray diffraction patterns are indexed on the basis of a trigonal lattice: $a = 7.40$ Å, $c = 10.84$ Å, and $c/a = 1.465$, characteristic of a $Th_2Zn_{17}$-type structure (space group $R\bar{3}m$, $Z = 3$). Consequently, in the alloys mentioned the compound $Ti_2Be_{17}$ is formed. This conclusion agrees well with the results of work (4), published at the time the investigations described here were being completed. The X-ray diffraction pattern of the alloy containing 93 at.% Be closely resembles those for alloys with a lower Be content (88-90%). However, at present it is not possible to decide unambiguously whether this alloy is a solid solution based on $Ti_2Be_{17}$ or a compound with the formula $TiBe_{12}$ (2). Both structures are very close to one another and are formed on the basis of a $CaZn_5$ ($RX_5$) type structure, in which a pair of smaller atoms ($X_2$) replaces, respectively, one third or one half of the larger atoms (R). Both structures, like the $TiBe_2$ structure, belong to the class of closest packings of atoms of unequal size (3) with high coordination numbers for atoms of both kinds—16(Ti) and 12(Be) in the $TiBe_2$ structure, and 20(Ti), 14, 13, and 12(Be) in $Ti_2Be_{17}$ and $TiBe_{12}$.

Figure 1

Figure 1: Figure 1

The X-ray emission and absorption spectra of titanium in the compounds under study were obtained using a vacuum long-wavelength DRS spectrograph, manufactured in the experimental workshops of Rostov State University. The reflecting crystal was quartz, planes $(10\bar{1}0)$. Bending of the crystal was carried out on four supports. To increase the resolving power of the instrument, the spectra were recorded by the method of oblique planes (⌒5). The spectra were recorded photographically in the second order of reflection. The dispersion in the region of the $K$-absorption edge and the $K\beta_5$-emission band of titanium was $\sim 7$ X/mm. The resolving power was 10,000. As reference lines in making the measurements, the $L\alpha_1$ lines of Ce and Pr in the second order of reflection were used. The emission spectra were obtained by the primary method using an aluminum anode to reduce the background. The operating conditions were 12 mA and 24 kV. The exposure was $\sim 2$ hours. The absorption spectra were obtained using a tantalum anode and an absorber density of $\sim 5$ mg/cm$^2$ (in terms of titanium). The operating conditions were 25 mA and 12 kV. The exposure time was 3–4 hours. The spectrograms were photometered in three different cross sections of the photographic film and, after averaging, were presented graphically as curves of quantities proportional to the absorption coefficient versus the energy of the X-ray quanta (in electronvolts). The accuracy of the energy determination was $\sim 0.2$ eV.

**Fig. 1.** X-ray $K$-absorption spectra and the last emission lines of titanium in $TiBe_2$ and $Ti_2Be_{17}$

To check the dispersion character of the instrumental-distortion function and to determine its half-width, the experimental shape and width of the $K\alpha_1$ line of Ge was investigated; in the fourth order of reflection it lies in the region of the spectrum of interest to us. In the region of the titanium $K$-absorption edge the desired half-width of the distortion function proved to be 0.39 eV and amounted to $\sim 28\%$ of the natural half-width of the line. Correction of the shape of the experimental spectra for the distortion introduced by the apparatus, and for the width of the initial level of the transition, was carried out by Nikiforov’ s method (⌒6).

The shape and mutual position of the $K$-absorption edges and the last emission lines in the X-ray spectra of titanium in the three investigated phases with different beryllium contents proved to be almost identical.

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* The authors are grateful to E. I. Gladyshevskii for preparing the alloys and for assistance in the study of their structure.

Figure 2

Figure 2: Figure 2

**Fig. 2.** X-ray $K$-absorption spectra of titanium in $TiBe_2$ and $Ti_2Be_{17}$ after their correction for instrumental distortions and for the width of the titanium $K$-level, which according to (⁀10) was taken to be 0.74 eV

This is in good agreement with the results of the X-ray structural studies described above and makes it possible to assert that, in addition to the similarity of their structures, the alloys studied are also very close to one another in the character of the interatomic interaction; however, as follows from the analysis of the X-ray spectral data, they differ noticeably in this respect from beryllides with a lower beryllium content. It is not difficult to verify the latter by considering the X-ray spectral data presented in Figs. 1 and 2. In Fig. 1 the X-ray $K$-absorption spectra obtained under identical experimental conditions and the last emission bands of titanium in $TiBe_2$ and in one of the beryllium-rich phases containing 90 at.% Be are compared. Figure 2 shows the same spectra after their correction for the width of the internal level and allowance for the influence of instrumental distortions. As can be seen, greater than in

in the previous work[1] the resolving power of the spectral instrument made it possible to detect additional details of the fine structure in the titanium absorption spectrum with $TiBe_2$. At the same time it was found that, in contrast to what had previously been observed in titanium mono- and diberyllide, on going over to compounds with a higher beryllium content, the x-ray absorption and emission spectra of the transition metal undergo substantial and characteristic changes.

In the absorption spectra this is expressed in a sharp change in the long-wavelength structure of the edge, which owes its origin to transitions of the $K$ electron into that part of the hybridized energy band of the alloy which lies close in position to the $3d$ energy levels of the transition metal. The changes observed in other regions of the main absorption edge are, in general, insignificant and can be explained by differences in the structure of the compounds under consideration. Special mention should be made of the fact that the energy position of the principal absorption maximum in the spectrum of titanium in $Ti_2Be_{17}$ remains practically the same as in all the other beryllides investigated by us.

In the emission spectra the transition from diberyllide to $Ti_2Be_{17}$ leads, first, to a sharp symmetrization of the titanium $K\beta_5$ emission band (with the position of its short-wavelength boundary unchanged) and to the associated redistribution of intensity over its width, manifested in a long-wavelength shift of its maximum

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[1] E. E. Vainshtein, E. A. Zhurakovskii, I. B. Staryi, DAN, **135**, 642 (1960).

($\sim 1.4$ eV). The second characteristic difference of the spectra under consideration is the appearance, in the latter case, of the satellite $K\beta''$, which is usually absent from the spectra of pure metals or alloy components where complete collectivization of the valence electrons of the atoms occurs.[2]

Thus, the x-ray absorption and emission spectra of titanium in $\mathrm{Ti_2Be_{17}}$ indicate a sharp weakening of the degree of overlap of the energy bands of the valence electrons of the alloy components observed in this compound, a weakening of the degree of hybridization of the wave functions within the $3d\,4s\,p$ band of the transition metal, and a substantial strengthening of the role of the Be—Be interaction. The latter evidently leads to a noticeable change in the effective difference of electronegativities between the unlike components of the alloy in the compound under consideration. This quantity can be estimated from x-ray spectral data if one uses the relation, previously established by one of us [3], between the magnitude of the difference in electronegativities of the components of a binary compound ($\Delta x$) and the energy separation ($K\beta'' - K\beta_5$) in the x-ray spectrum of the transition metal ($\Delta E$). Since the latter quantity in our case is equal to 4.8 eV, the effective electronegativity of beryllium in the intermetallic compound studied should differ from the electronegativity of titanium by a value close to 0.6 (instead of the practical equality of these quantities for free atoms).

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

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[2] As was shown earlier by one of us [^7]-[^9], the appearance of this satellite is associated with the cross transition of electrons of the second component to the $1s$ levels of the absorbing atom that are vacated in the process of $K$ ionization.

[3] E. A. Zhurakovskii, E. E. Vainshtein, DAN, **129**, 66 (1959).