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Abstract

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PHYSICS

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FINE STRUCTURE OF THE X-RAY K-ABSORPTION SPECTRA OF SCANDIUM IN THE METAL AND IN HARD REFRACTORY COMPOUNDS

(Presented by Academician G. V. Kurdyumov, January 23, 1963)

In a series of works devoted to investigations of the energy spectrum of hard refractory substances ([1–4]), the fine structure of the x-ray K-absorption and emission spectra of titanium and vanadium in the compounds formed by them with hydrogen, boron, carbon, and nitrogen was studied. In works ([1–4]) a number of assumptions were made concerning the nature of the forces of chemical interaction in these phases and the relation of the spectral features to the crystal chemistry and properties of the compounds under consideration. In particular, it was pointed out that the d-electrons are only weakly involved in the chemical bond, and that there is no such "metallization" of the bond, by which some investigators understand partial filling of the d-energy sublevels of transition-metal atoms by electrons detached from the metalloid.

It was of theoretical interest to check whether these conclusions could be extended to a series of compounds similar in crystal-chemical structure, hardness, and refractoriness, of the neighboring element—scandium—which, being a transition metal, at the same time opens the series of rare-earth and dispersed metals. In D. I. Mendeleev' s periodic system, scandium, as is known, is the first element in which not an outer level is being completed, but the inner d-electron level following it; it thus has one d-electron. Recently, the indicated scandium compounds have also acquired independent practical interest. For example, there are data on the use of scandium carbide and nitride, which at high electrical conductivity have melting temperatures near 3000°, in electrical engineering and for obtaining refractory alloys.

In the present work the fine structure of the K-absorption spectra of scandium in the pure metal, diboride, monocarbide, and mononitride has been studied. For comparison, scandium oxide Sc_2O_3 was also investigated. The boride, carbide,

and nitride were synthesized at the Institute of Metal Ceramics and Special Alloys of the Academy of Sciences of the Ukrainian SSR by O. E. Andreichenko* (according to an already known ([5,6,9]) procedure). X-ray phase analysis confirmed ([5,8]) the presence in scandium carbide and nitride of a face-centered cubic lattice of the NaCl type with parameters 4.5 and 4.44 Å, respectively, and of a hexagonal lattice of the AlB_2 type with periods $a = 3.14$, $c = 3.52$ Å and $c/a = 1.056$ in the diboride ([6,7]).

The work was carried out on a focusing x-ray tube spectrograph of a design now generally accepted. The radius of curvature of the bent quartz crystal was 150 cm. The reflecting planes were $(10\bar{1}1)$. The linear dispersion of the spectrograph was 3.5 X/mm. The spectra were recorded photographically. In determining the wavelengths of individual points of the scandium absorption edge in compounds, the titanium K_{α_1} line was used as the comparison line. The accuracy of determining photon energies was ~ 0.2 eV. The optimum absorber density was 6 mg/cm^2.

The scandium K-absorption spectra in the metal, oxide, and synthesized compounds, averaged over 3–5 independent measurements, are presented

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in Fig. 1. The vertical straight lines in the figure characterize the energy positions of the three most clearly fixed points in the spectrum of the pure metal: the onset of the edge, the long-wavelength maximum, and the main absorption maximum.

The fine structure of the K-absorption edge in metallic scandium is typical of transition metals. The long-wavelength maximum in its spectrum is commonly associated with the capture of the photoelectron predominantly by vacant d-states of the transition-metal atom. In the absorption edge of scandium in the sesquioxide, the long-wavelength maximum is expressed still more sharply, which can be explained by the transfer of the single scandium d-electron to oxygen.

The course of the absorption coefficient in the spectra of scandium in the diboride, carbide, and nitride, while possessing common features by which these spectra may be assigned an intermediate position between the two mentioned above (the metal and the oxide), has in each case a number of individual features characteristic only of the given compound. Thus, the fine structure of the K-edge in the diboride differs from the others by its greater complexity—the presence in the edge of 2–3 additional fluctuations of the absorption coefficient in the initial region. This may be connected, first of all, with the increased complexity of the crystal structure of scandium diboride and with another type of hybridization of the outer electron orbits. A distinctive feature of the K-absorption edge of scandium in the diboride is also the increased absorption in the $4s$ region, indicating the presence of vacancies in the $4s$-band of its atom

Fig. 1. X-ray K-absorption spectra of scandium in the metal and compounds

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and the possible participation of the scandium 4s-electrons in covalent scandium –boron and boron–boron bonds. This is in good agreement with the crystal-chemical features of the diborides–the presence in their structure of separate structural elements made up of boron atoms (chains, nets).

Fig. 1. X-ray K-absorption spectra of scandium in the metal and compounds

In the spectrum of scandium in the carbide, the long-wavelength maximum is expressed less sharply than in the metal and oxide and is shifted toward shorter wavelengths. It is considerably less intense than in the carbides of titanium and vanadium structurally isomorphous with this carbide ($^{1-4}$), although, it would seem, taking into account the larger number of vacancies in the d-band of scandium and the identical type of hybridization of the outer electron orbits in all the carbides mentioned, the opposite picture should be observed here. It is not unknown, however, that the probability of absorption of a 1s-electron by the 3d-band in K-spectra depends to a large extent on the degree of overlap of the d- and p-bands in the crystal, since the direct s—d transition is quadrupole. Such overlap in scandium carbides and nitrides should be smaller in connection with the larger (in comparison with Ti and V) atomic radius of scandium. It may be that the influence of precisely this factor can explain the complete disappearance of the long-wavelength maximum in the spectrum of scandium in the nitride, where, as is seen from Fig. 1, the course of the absorption coefficient is close to arctangent-like.

A feature common to the group of structurally isomorphous nitrides and carbides of scandium, titanium, and vanadium in the K-absorption edge is the far-reaching similarity of their "distant" fine structure, which, undoubtedly,

is due to the identical octahedral symmetry of the field of the crystal lattice and to the identical parameters of the nearest atomic coordination.

Common to all the spectra in Fig. 1 is a shift of the edge-structure elements toward shorter wavelengths (especially the principal absorption maximum, whose origin is customarily explained by the capture of the photoelectron by that region of the hybridized dsp energy band which has predominantly P-symmetry) as the atomic number of the metalloid increases. This is apparently connected with the energetic conditions for deformation of the levels of the scandium atom upon introduction into the lattice of metalloid atoms with an ever increasing radius (boron, with its anomalously large radius, as might be expected, falls out of this sequence).

Thus, in the spectra of scandium in the series of compounds studied, constancy of the energy position of the long-wavelength maximum is not observed, as was

the case for titanium and vanadium ([1–4]). Its shift toward shorter wavelengths is especially noticeable in the carbide, while in the nitride this maximum disappears. This indicates a substantially different character of the interatomic interaction in the interstitial phases formed by scandium, despite the isomorphism of the lattices. At the same time, comparison of the spectra of scandium in the metal, the boride, and the oxide makes it possible to establish the invariance of the photon energy corresponding to this maximum (within the limits of experimental error). The chemical interaction in refractory scandium compounds is apparently based on covalent–metallic interaction of the outer *s*- and *p*-orbitals of the metal and the metalloid.

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