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Abstract

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PHYSICS

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THE K_β GROUP OF LINES IN THE X-RAY FLUORESCENCE SPECTRUM OF SCANDIUM IN THE METAL AND IN SOME REFRACTORY COMPOUNDS

(Presented by Academician G. V. Kurdyumov, November 24, 1965)

The recently carried out study of the fine structure of the X-ray K-absorption edges of scandium in the pure metal, diboride, carbide, nitride, and oxide (^{1}), associated with the free electron states of the valence band, is part of a series of works performed for analogous series of refractory metal-like compounds of titanium, vanadium, and chromium (^{2},^{3}). In them it was possible to show that the class of compounds under consideration is characterized by a quite definite type of chemical bonding (metallic-covalent-ionic) and by a specific structure of the electron energy spectrum, which correlates well with the data of quantum-mechanical calculations (^{4}). According to (^{5}), the only "free" $3d$ electron of scandium (as also the $5d$ electron in the lanthanides) in the pure metal and carbide becomes collectivized and goes into the formation of the conduction band, determining the metallic nature and the comparatively high electrical conductivity of these phases*. Data on the emission spectra of Sc are absent from the literature.

In order to judge the structure of the valence band as a whole, it was of interest to study the fine structure of the K_β series of the emission X-ray spectrum of scandium in the pure metal, carbide, boride, nitride, and oxide. In view of the chemical instability of metallic scandium, and also, though to a lesser degree, of its compounds, the method of secondary excitation of spectra was used, in which the substance under study was brought outside the X-ray tube into a vacuum and was practically not subjected to heating. The same preparations as in (^{1}) were studied. The spectra were obtained on a DRS spectrograph with a fluorescent attachment in the second order of reflection from the $(10\bar{1}0)$ plane of a quartz crystal bent to a radius of 500 mm, with a linear dispersion of 3.0 X/mm. Fluorescence was excited by radiation from a copper anode at a voltage of 30 kV and a current of 30–35 mA. No reabsorption phenomena were observed. The resolving power was 10,000. The spectra were photometered on an MF-2. After conversion of blackenings into intensities, the spectrum was averaged over

2–3 parallel spectrograms. Figure 1 gives the curves, and Table 1 the results of the measurements.

In the figure only the short-wavelength slope of the K_{β_1} line of scandium in the metal and compounds is shown (transition $3p \rightarrow 1s$). Its shape proved unchanged in all spectra, while its position, with the exception of the carbide spectrum, was constant (accuracy of determinations 0.2 eV). This made it possible to take it conventionally as the origin of the energy scale. The shift of K_{β_1} in the carbide spectrum by 1 eV to the long-wavelength side is apparently the result of a strong perturbation of the ψ-functions of the carbide valence band owing to the sharp change in chemical interaction and the resulting shift of the potential of the outer and adjacent electron shells of the scandium atom. In ([6]) it is proposed to explain such a displacement of the $3p$ shell in the spectra of atoms with $Z = 15 \div 24$ by a decrease in the density of $3d$ electrons in the atomic volume. Comparing this shift with the significant short-wavelength displacement observed in ([1]) of the initial portion

* In checking the data of ([5]), which indicate the constancy of the energy position of the Sc K edge in the metal, carbide, and oxide, it turned out that the displacement of the edge of some elements upon transition to compounds is about 3.5 eV.

the scandium K-absorption edge in the carbide, which is associated with vacancies in the d-shell, one may assume, in agreement with ([5]), a greater degree of collectivization of the valence electrons in the ScC crystal than in the other compounds; this occurs through a decrease in the density of d-electrons in the atomic volume and their transition into the electron gas, which accounts for the comparatively high electrical conductivity of scandium carbide ([8]).

No less noticeable an influence of chemical bonding on the X-ray spectrum can be observed in changes in the shape, position, and intensity of the shortest-wavelength K_{β_5}-band, formed by transitions of electrons from the valence (and, apparently, hybridized) *dsp*-band of the crystal to the K-energy level closest to the nucleus. The asymmetry index and the shape of the short-wavelength slope of this band in the spectrum of metallic scandium are typical of metallic conductors and differ by a steep drop in intensity, which clearly conveys the sharp "Fermi" break of the occupied electronic states within the band. In the spectra of compounds the band shape is different. Here, first of all, a fairly pronounced double-humped form is observed, with different relative intensities of the two maxima. In those compounds where, judging by certain strength-related, physical, and chemical properties ([7],[8]), the covalent and ionic components of the bonding forces should be larger, the intensity of the short-wavelength maximum in the spectra proves to be smaller. Conversely, in cases where a predominance of metallic bonding is more probable, the intensity of the short-wavelength maximum of the K_{β_5}-band proves to be greater than that of the long-wavelength maximum. The intensity of the long-wavelength maximum changes in the opposite sense. Similar regularities were recorded in ([3]) for emission K_{β_5}-bands of chromium in a series of similar refractory compounds; later

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Figure 1. K_β-group of lines of the X-ray fluorescence spectrum of scandium in pure metallic scandium and compounds.

Figure 1: Figure 1. K_β-group of lines of the X-ray fluorescence spectrum of scandium in pure metallic scandium and compounds.

they were noted in (2) for K_{β_5}-fluorescence of vanadium. In scandium diboride covalent bonds predominate. This is due to the tendency of boron to form rigid structural elements (chains, nets, frameworks) from boron atoms. The metallic bonds in the diboride are considerably inferior in strength to the covalent Me—B and B—B bonds. Therefore the short-wavelength maximum of the K_{β_5}-band in the diboride spectrum should be weaker. As can be seen from Fig. 1, this is confirmed experimentally.

Fig. 1. K_β-group of lines of the X-ray fluorescence spectrum of scandium in pure metallic scandium and compounds

The coincidence of the position of the short-wavelength maximum of the K_{β_5}-band in the spectrum of ScB_2 with its single maximum in the spectrum of metallic scandium also supports the assumption that the short-wavelength peak in K_{β_5} corresponds to metallic Me—Me interaction, while the long-wavelength peak corresponds to covalent Me—B interaction.

In the spectrum of scandium in the carbide, both maxima are approximately equal in intensity and are shifted by 2 eV toward the long-wavelength side in comparison with their position in the spectrum of metallic scandium, which agrees

with the hypothesis proposed above concerning a decrease in the density of 3*d*-electrons in the atomic volume.

This also correlates satisfactorily with the concept developed in (2) that the high cohesion forces in refractory compounds of transition metals owe their origin to the practically equivalent participation in bonding of electrons of covalent (quasiatomic) and metallic (collectivized) states. Some features of the spectrum of scandium carbide are characteristic of carbides of rare-earth metals.

Table 1

Relative position and intensity of the K_{β_5}- and K''_β-emission bands of the X-ray fluorescence spectrum of scandium in the metal and in compounds

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Compound	Relative position of the K_{β_5}-band* — long-wavelength maximum	Relative position of the K_{β_5}-band* —center of gravity	Relative position of the K_{β_5}-band* — short-wavelength maximum	Distance between the centers of gravity of the K_{β_5}-band and K''_{β}-bands	Relative position of the satellite K''_{β} — long-wavelength max.	Relative position of the satellite K''_{β} — short-wavelength max.	Ratio of integral intensities $\frac{I_{K''_{\beta}}}{I_{K_{\beta_5}}}$, %	Width of K_{β_5}, eV	Asymmetry index of K_{β_5}
Sc_{met}	–	26.45 (0)	–	–	–	–	–	5	2.5
ScB_2	25.25(−1.2)	25.50(−0.95)	25.75(−0.7)	11.75	8.6	13.3	33	4	1.3
ScC	23.9(−2.55)	24.3(−2.15)	24.9(−1.55)	10.6	11.6	15.8	39	4.8	1.35
ScN	24.0(−2.45)	24.9(−1.55)	25.1(1.35)	9.7	12.6	15.2	41	6.7	1.8
Sc_2O_3	24.65(−1.8)	25.0(−1.45)	25.5(−0.95)	14.5	10.6		40	4	1.1

* The first numbers refer to the position of the K_{β_5}-band relative to K_{β_1}. The numbers in parentheses refer to the shift of the K_{β_5}-band in the spectra of the compounds. The position of the K_{β_5}-band in the spectrum of the metal is conventionally taken as zero. The minus sign denotes a shift toward the long-wavelength side.

This includes the large energy gap, characteristic of ionic compounds, between the "end of emission" and the "onset of absorption," amounting, according to the data of Table 1 and (1), to about 4.5 eV, of which 3.5 eV is due solely to the short-wavelength shift of the edge onset, not observed by Vickeri (5). The shift in the spectra of rare-earth carbides is likewise short-wavelength. In the spectrum of TiC there is no energy gap.

In the spectrum of ScN, on the contrary, the nonequivalence of the two maxima of the K_{β_5}-band is expressed most clearly: both the intensity and the width are greater for the short-wavelength maximum. As is known (2, 5), the degree of overlap of the $2p$-orbitals of the metalloid with the $3d$-orbitals of the metal should increase in nitrides simultaneously with an increase in the degree of polarization of the packet of bonding hybrid orbitals in the Me—N direction. An increase in the admixture of nitrogen $2p$-states in the $3d$-band promotes an increase in the probability of the radiative transition. Apparently, all these factors must be taken into account simultaneously. The increased metallization of the bond in the nitride is supported by the disappearance of the long-wavelength maximum of absorption in the K-edge, which was interpreted as the filling of vacancies in the d-band (1), and by the closest, among the scandium phases studied, energetic convergence of the K_{β_5}-band ($2p + 3d$-states) with the satellite K'_β ($2s$-states of the metalloid, according to (4)). The same is indicated by the smooth course of the temperature dependence of the electrical resistivity of scandium nitride (8).

According to the ideas developed in (9), confirmed in (2, 3) and refined by theoretical calculation (4), the appearance of the satellite K'_β is explained by "cross" transitions of electrons from the $2s$-levels of the metalloid atom, where there is a small admixture of p-states, to vacancies formed in the process of excitation of X-ray spectra in

the $1s(K)$-shell of the metal atom. It follows from this that the distance between the K_{β_5}- and K_β-bands may, to a certain extent, characterize the energetic proximity of the interacting valence bands of the metal and the metalloid. Their convergence evidently leads to a predominance of metallic exchange interaction over covalent interaction. It has recently been shown that such convergence is maximal in the spectra of intermetallic compounds and hydrides ([2,3]). Conversely, when ionic interaction predominates, the spectral bands diverge, while the intensity of the satellite increases. Intermediate positions in this respect are occupied by ScB_2 and ScC. The maximum convergence of the bands among the refractory compounds of transition metals of the first period investigated by this criterion is observed in ScN, TiC and VC, CrB, i.e., in cases where the sum of the valence electrons of the interacting atoms approaches the "stable" octet. This is accompanied by the greatest refractoriness and suggests the existence of general regularities in the structure of the electron energy spectrum which also determine bond strength. It is curious that the melting temperatures of scandium phases decrease in the same sequence ($ScN \rightarrow ScC \rightarrow ScB_2 \rightarrow Sc_2O_3$) in which the separation of the $2s$- and $2p + 3d$-bands increases.

The weak background and high resolution made it possible to reveal a double fine structure of the K''_β satellite, which, as in the spectra of the analogous series of vanadium compounds ([1,2]), can be explained by the special role of d-electrons in the formation of hybrid bonding orbitals. Its meaning is that on the part of the hybridized bonding electron cloud gravitating toward the metalloid atom there is superimposed, dominating in the sphere of the metal atom, according to the ideas of ([10]), a reduction in the expression of the wave d-functions from fivefold (as in the free atom of a transition metal) to twofold; this leads to the splitting of the d-states of the metal into two groups of different symmetry, $d_\gamma(e_g)$ and $d_\varepsilon(t_{2g})$, and evidently determines the "double" fine structure of the K_{β_5}-band. In a cruder form this could be regarded as "collectivization," according to ([5]), of the scandium d-electron. In confirmation of this hypothesis it should be noted that the doubleness of the satellite is observed in metallic-like compounds with different types of crystal lattice and, consequently, does not depend on the distribution of the intracrystalline field. In compounds of a predominantly ionic type (Sc_2O_3), where hybridization is less probable, the satellite has a regular dispersion form.

The study of X-ray K-absorption spectra and of the K_β-group of emission lines of scandium in compounds with light elements, as well as their strength and physicochemical properties (^{7,8}), leads to the conclusion that the series of scandium compounds considered here gravitates, in its physical nature, more toward interstitial phases formed by transition metals with a high degree of incompleteness of the d-shell than toward the analogous series of compounds of rare-earth elements. The peculiarity of the electronic structure of scandium is manifested, however, in the absence of the direct linear dependence that was found between the difference in electronegativities of the metal and metalloid atoms (for Ti, V and Cr) and the distance between the valence $3d+2p$ (K_{β_5})- and $2s$ (K''_β)-bands in the spectra of refractory compounds, according to (^{2,3}).

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