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Abstract

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FINE STRUCTURE OF X-RAY K-ABSORPTION SPECTRA AND THE HALL EFFECT IN VANADIUM SILICIDES

(Presented by Academician A. P. Vinogradov on 29 IV 1960)

Silicides of transition metals have a complex character of interatomic interaction and, in their properties, occupy an intermediate position between substances with metallic and semiconductor mechanisms of conductivity.

A study of the fine structure of the absorption spectra of metal atoms in titanium (^{1}) and chromium (^{2}) silicides revealed the complex character of the metal K-absorption edge in these compounds, reflecting the complex nature of interatomic interaction and a fairly sharply expressed dependence of the character of the absorption edge on the silicon content in the silicides. A definite correlation was also established between the character of the titanium K-absorption edge in its silicides (according to the results of work (^{1})) and the effective atomic concentration of current carriers in the corresponding phases and their magnetic susceptibility (^{3}).

In the present work, the fine structure of the x-ray K-absorption spectra of vanadium, which occupies an intermediate position in the periodic system between titanium and chromium, was investigated in its silicides V_3Si, V_5Si_3, and VSi_2. These compounds differ substantially in their crystal structure (^{4}). In V_3Si (a cubic lattice of the βW type), the silicon atoms are not bonded to one another, while the vanadium atoms form chains of mutual covalent bonds, similarly to what occurs in σ-phases (^{5}). In V_5Si_3 (a hexagonal lattice), along with chains of V—V bonds, chains of Si—Si bonds parallel to them appear. Finally, VSi_2 (a hexagonal lattice of the $CrSi_2$ type) is characterized by the absence of directed bonds between vanadium atoms. By contrast, the silicon atoms form two-dimensional hexagonal networks of covalent bonds. In all the compounds considered, one can distinguish structurally nonequivalent positions of vanadium atoms with respect to the surroundings by their neighboring atoms.

The vanadium silicides investigated in the present work were obtained by direct synthesis from the components (^{6}). The degree of agreement of the composition of the samples obtained with the chemical formulas given above was checked by chemical and phase x-ray analyses. The content of unreacted (free) silicon did

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not exceed 0.6%. The apparatus and experimental conditions for studying the fine structure of the x-ray K-absorption edge of vanadium have been described previously (^{7}). As comparison lines in determining the energies of the x-ray photons, the $K_{\alpha 1}$ line of As and the $L_{\beta 1}$ line of Pt in second order of reflection were chosen. The accuracy of determining individual points of the spectrum was 0.2 eV. The results obtained for the vanadium K-absorption edge in pure metal and in the silicides V_3Si, V_5Si_3, and VSi_2, and also, for comparison, in the oxide V_2O_5 (^{7}), are given in Fig. 1. Here the abscissa axis gives the energy of the x-ray photons, counted from an arbitrarily chosen zero, while the ordinate axis gives a quantity proportional to the absorption coefficient.

Simultaneously with the investigation of the absorption spectrum, the Hall coefficient was measured for each of the three silicides studied. All three silicides showed a negative sign of the Hall coefficient, which corresponds to predominantly electronic conductivity, in contrast to

metallic vanadium, which has predominantly hole conductivity (^{8}). The established values of the Hall coefficients R were used to calculate the effective concentration n^* of current carriers ($n^* = 1/Re$) and their Hall mobility $U_H = R/\rho$. The results obtained are given in Table 1.

As can be seen (Fig. 1), with increasing silicon content in the silicides, the vanadium K-absorption edge in them undergoes significant and regular changes. Only the edge point remains unchanged, characterizing the energy position of the initial absorption region. In going from the lower silicide to the higher one, in parallel with the increase in the relative role of the V—Si bond as compared with the bond between atoms of the transition metal, there is a regular increase in the fraction of absorption caused by photoelectron transitions into the region of the *sp* states of vanadium in the conduction band of the silicides. This may be interpreted as evidence in favor of the successive liberation of the upper part of the conduction band in the series of silicides studied, and is in good agreement with the results of measurements of the Hall coefficients in these compounds. Indeed, as can be seen from Table 1, as the silicon concentration in the silicide increases, there is a regular decrease in the value of n^* and an increase in the mobility of the current carriers. The conclusion regarding the increasing role of interaction between vanadium and silicon atoms in silicides with increasing content of the latter element, and the decisive significance that this interaction has for the character of the change in the fine structure of the principal K-absorption edge of the metal in these compounds, is also confirmed by a number of other observations.

In going from metallic vanadium to silicides with increasing silicon content and further to the oxide V_2O_5, there is a noticeable

Fig. 1. Fine structure of the principal K-absorption edge of vanadium in silicides, the metal, and the oxide: 1 —metal; 2 —V_3Si; 3 —V_5Si_3; 4 —VSi_2; 5 —V_2O_5

shift of the principal absorption maximum (as well as of the less intense long-

Fig. 1. Fine structure of the principal vanadium K-absorption edge in silicides, the metal, and the oxide: 1 –metal; 2 –V3Si; 3 –V5Si3; 4 –VSi2; 5 –V2O5

Figure 1: Fig. 1. Fine structure of the principal vanadium K-absorption edge in silicides, the metal, and the oxide: 1 –metal; 2 –V3Si; 3 –V5Si3; 4 –VSi2; 5 –V2O5

wavelength maxima) toward higher energies. With the position of the initial absorption region unchanged, this is manifested in total as an increase in the width of the principal edge and a short-wavelength shift of the "mean point" of the K edge. As can be seen from Table 1, this width in the silicide V_3Si, as in vanadium hydrides, carbides, nitrides, and borides ([7]), differs comparatively little from that for the metal. In going to silicides with a higher silicon content, V_5Si_3 and VSi_2, the width of the principal edge increases noticeably and approaches the value typical of an oxide–a compound with a significant fraction of ionic bonding. This, apparently, indicates polarization of the metal atoms in silicon-rich silicides and the presence of a heteropolar component in the Me–Si bond, which agrees well···

compared with the results of a quantum-mechanical calculation of the electron energy spectrum, carried out for molybdenum disilicide ([9]).

Of known interest is the behavior of the longest-wavelength absorption maximum (A), corresponding to the transition of K-electrons into the region of hybridized $3d$ states of the transition-metal atoms ([10]). This maximum is well expressed in the spectrum of metallic vanadium and, with its position on the energy scale unchanged in V_3Si, has the character of a shoulder. If no substantial change is assumed in the degree of overlap of the dsp functions of the atoms in these compounds, this indicates a decrease in the number of vacant $3d$ states of vanadium in V_3Si, which may be caused either by the involvement of vanadium $3d$ states in the valence bonds Me–Me ([5]) and Me–Si, or by the transfer of part of the valence electrons of silicon into the metal $3d$ shell, as occurs in hydrides. The latter seems less probable in view of the high ionization potential of silicon.

Table 1

Effective concentration of current carriers and width of the main x-ray absorption edge in vanadium silicides

Phase	$R \cdot 10^5$, cm^3/C	ρ, $\mu\Omega\cdot$cm	U_H, cm/(V · sec)	n^* per V atom	n^* per Si atom	Width of the main absorption edge, eV
V (metal)	+8.2	26.6	3.1	1.1	–	21 ± 1

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Phase	$R \cdot 10^5$, cm^3/C	ρ, $\mu\Omega$·cm	U_H, cm/(V · sec)	n^* per V atom	n^* per Si atom	Width of the main absorption edge, eV
V_3Si	−1.7 ($±$30%)	203.5	0.1	6.4	19.2	24 ± 1
V_5Si_3	−10.0 ($±$6%)	114.5	0.9	1.3	2.2	32 ± 1
VSi_2	−19.5 ($±$1%)	66.5	2.9	1.2	0.6	31 ± 1
V_2O_5	–	–	–	–	–	30 ± 1

In V_5Si_3 the maximum (A) is strongly shifted toward short wavelengths and can be isolated only tentatively. Finally, in the disilicide VSi_2 the maximum (A) again appears almost as sharply as in metallic vanadium, but is located in a considerably shorter-wavelength region of the main edge. It is possible that the sharper manifestation of the maximum (A) in VSi_2 in comparison with V_3Si and V_5Si_3 is connected with the absence in the former of directed Me–Me bonds and with the involvement of a sufficiently large number of vanadium electrons in bonding with silicon. The short-wavelength shift of the maximum (A) may be associated with perturbation of the vanadium d states by the surrounding silicon atoms. The main absorption edge in VSi_2 has a complex structure, which accordingly reflects the complex multiband structure of the electron energy spectrum in this compound, probably close to that established for $MoSi_2$ (^{9}).

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REFERENCES

1. E. E. Vainshtein, E. A. Zhurakovskii, *Izv. AN SSSR, OKhN*, 1959, No. 8, 1493.

2. S. A. Nemnonov, V. Z. Menshikov, *Collected Proceedings of the Seminar on Heat-Resistant Materials*, Bull. No. 5, Kiev, 1960.

3. D. Robins, *Phil. Mag.*, **3**, 313 (1958).
4. G. V. Samsonov, *Silicides and Their Use in Technology*, Kiev, 1959.
5. T. Millner, *Zs. anorg. Chem.*, **292**, 25 (1957).
6. G. V. Samsonov, M. S. Kovalchenko, T. S. Verkhoglyadova, *ZhNKh*, **4**, 2759 (1959).
7. E. A. Zhurakovskii, E. E. Vainshtein, *DAN*, **127**, 534 (1959).
8. S. Fouer, *Phys. Rev.*, **107**, 1513 (1958).
9. H. Schenk, U. Dehlinger, *Acta Met.*, **4**, 7 (1956).
10. E. E. Vainshtein, *X-ray Spectra of Atoms in Molecules of Chemical Compounds and Alloys*, Publishing House of the Academy of Sciences of the USSR, 1950, p. 188.

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