

Investigation of the electronic structure of the A 15 structure superconducting compounds V_3Ge and V_3Al and alloys based on them

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The results of an x-ray spectral investigation of alloys based on A 15-type superconducting compounds are used to obtain information about the variation of the electronic-structure parameters. The causes of the energy shifts of the lines are analyzed, and a new procedure for estimating the shift-related change in the electronic susceptibility of the compounds is proposed. As an illustration, the method is used to investigate the energy shifts of the $AlK\alpha_{1,2}$ and $AlK\alpha_{3,4}$ lines in the system $V_3(Ge-Al)$. The shapes and integrated intensities of the vanadium and aluminum K bands of these alloys are studied. This allows the effect of the substitution of the atoms of the nontransition constituent on the density of electronic states both at the Fermi level, $N(E_F)$, and in the interior of the valence band to be followed. The results are compared with the concentration dependences, obtained with the same samples, of the changes that occur in the superconducting transition temperature, the magnitude of the paramagnetic susceptibility, and the distortion of the phonon spectrum of V_3Ge when this compound is doped with aluminum atoms. The growth of $N(E_F)$ is accompanied by the growth of the electronic susceptibility and the softening of the phonon spectrum. As a result, the electron-phonon interaction constant increases, and the T_c almost doubles.

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§ 1. INTRODUCTION

The A_3B -type compounds with the A15 structure are known at present as materials possessing the highest superconducting transition temperature T_c . High- T_c compounds are characterized by unusual physical properties: anomalous temperature dependences of the magnetic susceptibility, the Knight shift, and the electrical resistance, the occurrence of structural transitions at temperatures $T \geq T_c$, the softening of the frequencies of the phonon spectrum, etc.^{1,2} Of critical importance from the point of view of the development of the theory of the superconducting state of these compounds is the existence of a close interrelationship between the degree of abnormality of the properties of the normal nonsuperconducting state and the value of the T_c . These properties are, in the final analysis, determined by the characteristics of the electronic structure of the compounds in question.

The unit cell of an A15 structure compound contains six atoms of the transition metal A and two atoms of the nontransition element B. The atoms of the transition constituent guarantee quite a high density $N(E_F)$ of electronic states at the Fermi level. On the other hand, the phonon characteristics of the crystal are determined by the form of the distribution of the density of states in the interior of the valence band, over whose formation the nontransition constituents do exert a significant influence. Therefore, the variation of the B-type atoms can lead to radical changes in the superconducting properties of the compound. Thus, for example, the T_c 's of the isoelectronic compounds V_3Si and V_3Ge differ in value by almost a factor of three.

For a long time the explanation of certain anomalous properties of the A15 compounds was based on the use of Weger's idea,³ put forward on the basis of data accumulated by 1964, concerning the applicability of the

quasi-one-dimensional model for the electronic spectrum of the linear chains of A atoms located at the edges of the unit cell. This idea gave an unexpected boost to Labbé and Friedel's simplified model,⁴ in which numerical estimates of the temperature dependence of the magnetic susceptibility and some other physical properties have been carried out under the assumption that there exists an extremely narrow (< 0.01 eV) electronic-state-density peak at the Fermi level. This model has a disadvantage, to say nothing of the fact that there do not exist at present experimental methods that allow us to identify peaks of such width. It is impossible to describe within the framework of this model and those variants of it which use the presence of extreme electronic-spectrum parameters the effects connected with the characteristics of the interference of the various states of the constituent atoms of the compound.

More fruitful in this respect have been the numerical computations, performed from first principles,⁵⁻⁷ of the density of electronic states of the A15 compounds. The results of these calculations have allowed the following conclusions to be drawn: a) the density of electronic states at the Fermi level is largely formed on account of the contributions of the d electrons of the A atoms; b) the fine structure of the d states of the A atom has a characteristic energy scale tens of times greater than the scale predicted by the Weger-Labbé-Friedel model; c) the role of the B atoms in the A15 compounds consists not only in the fact that they determine the lattice constant and, in addition to that, the A-atom spacing, but also in the fact that the A-B interaction affects the form of the local partial densities of states of the A atoms. These conclusions are in good agreement with the results of the construction of the composition-physical properties (magnetic susceptibility, NMR,⁸ specific heat,⁹ lattice dynamics,¹⁰ etc.^{1,2}) diagrams by doping the individual binary A15 compounds with different masses and electronic concentrations.^{1,8-12}

The investigation of the magnetic properties of the A15 compounds allowed the assumption to be made¹¹ that the anomalous growth of the paramagnetic susceptibility as the temperature is lowered is not connected with the narrowness of the $N(E)$ peak in the vicinity of E_F , but may reflect the variation of the strengths of the electron-phonon and exchange interactions.

Recently, authors have begun to use the so-called plasma model for the description of the electron-phonon system of metals¹³ to explain the anomalous properties of the A15 compounds. According to McMillan, the electron-phonon interaction constant λ is given by the expression

$$\lambda = N(E_F) \langle J^2 \rangle / M \langle \omega^2 \rangle, \quad (1)$$

where J is the electron-ion interaction matrix element, M is the ion mass, and $\langle \omega^2 \rangle$ is the mean square phonon frequency.

Within the framework of the plasma model for the electron-phonon interaction we have

$$\langle \omega^2 \rangle = \langle \Omega_q^2 [1 - g_q \chi_e(q, \omega)] \rangle, \quad (2)$$

where the Ω_q are the bare phonon frequencies, g_q is the bare electron-phonon interaction constant, and $\chi_e(q, \omega)$ is the electronic susceptibility (the function characterizing the linear response of the electron density to the unscreened perturbation potential).

Apparently, the use of this semiphenomenological approach, in which the interelectron interactions could be reduced to directly observable quantities, would allow the construction of a more consistent theory of the A15 compounds, but this advance is being held up by the absence of data on the form of the electronic susceptibility or the permittivity.

It was recently shown that the parameters connected with these functions can be determined by investigating the Bragg scattering of x rays by the outermost electronic shell of the atoms in the crystal lattice.¹¹ But there are no experimental data on the effect of the composition on the electronic susceptibility of the A15 compounds. It is shown below that the x-ray spectral methods allow us to estimate the changes that occur in the electronic susceptibility when the composition of the compounds or alloys is varied.

In the present article we report the results of an investigation of the binary A15 compounds V_3Al and V_3Ge and ternary alloys based on them. We present the x-ray emission K bands of vanadium and aluminum, and determine the energy shifts of the x-ray $AlK\alpha_{1,2}$ and $AlK\alpha_{3,4}$ lines in the investigated systems. To analyze the line shifts, we use for the first time a method¹⁴ that allows us to correctly estimate the magnitudes of the charges in the core region of the aluminum atom. Using a procedure proposed in the present paper, we estimate the changes that occur in the electronic susceptibility of the investigated alloys as the germanium atoms are replaced by aluminum atoms. The results are discussed together with the data, obtained with the same samples, on the T_c , the paramagnetic susceptibility, and the distortion of the phonon spectrum of V_3Ge as it is doped with aluminum in increasing amounts.

§2. THE OBJECTS OF THE INVESTIGATIONS AND THE PREPARATION OF THE SAMPLES

The compound V_3Ge ($T_c = 6$ K), which is isoelectronic to V_3Si ($T_c = 17$ K), is characterized by an anomalously high anharmonicity of its lattice vibrations and a temperature-dependent paramagnetic susceptibility $\chi_p(T)$, characteristics which are typical of the high-temperature superconductors. The replacement of the germanium atoms by other atoms leads to a sharp increase in the value of T_c and a sharp enhancement of the anomalous temperature dependences of the physical properties, the greatest effect being obtained in the case of doping with aluminum. For V_3Al Matthias has, on the basis of empirical correlations, predicted a T_c value in the range 25–30 K. But because of the difficulties encountered in the preparation of this compound, the study of its physical properties has only just begun.^{12,15,16}

For the performance of the comprehensive investigations of the parameters of the phonon spectrum, the low-temperature specific heat, the temperature dependence of the electrical resistance, and the electronic and spin susceptibilities of the $V_3(Al-Ge)$ alloys we prepared for each composition several ingots with an overall weight of 150–200 g. As before,¹² the samples were prepared from high-purity components: monocrystalline vanadium ($B = \rho_{300\text{ K}} / \rho_{6\text{ K}} = 1000$) and monocrystalline Ge and Al ($B = 10000$). This circumstance is of critical importance in connection with both the attainment of the highest possible T_c values in this system and the production of V_3Al and quasibinary alloys based on it.

All the alloys were prepared by the crucibleless method through levitation fusion by a high-frequency electromagnetic field,¹⁶ which ensured a high degree of homogeneity of the ingots (the T_c values for different parts of the ingots did not differ by more than 0.2 K). The pressure of the inert gas in the chamber was not lower than 1 atm, which guaranteed a component waste of not more than 0.1% of the weight of the stock, and allowed the determination of the composition with an accuracy higher than the accuracy attainable in the usual chemical analysis. A spot analysis of the distribution of the components with the aid of an x-ray microprobe confirmed the high degree of homogeneity of the prepared ingots. The magnetic susceptibility was determined by the standard Faraday method. The highest sensitivity of the balances used is 10^{-8} g. The largest error made in the measurement of the absolute values of the susceptibility was 5%.

X-ray and metallographic phase analyses confirmed the results of our earlier investigations. The values obtained for the crystal-lattice constants, the T_c , and the paramagnetic susceptibility also coincided within the limits of the experimental error ($\pm 0.001 \text{ \AA}$, ± 0.2 K, and ± 0.2 emu/g respectively) with the results obtained in earlier investigations.¹² The x-ray and metallographic phase analyses showed that samples with up to 30% V_3Al content in V_3Ge are practically single-phase alloys (with the A15 structure), while samples with up to 40 and 60% V_3Al contents respectively contain 5 and 7% phases with the bcc structure.

For the investigation of the binary compound V_3Al we used the sample investigated in the work reported in Ref. 12, in which it was established that the greatest amount of the A15 phase is contained in a sample whose composition deviates slightly from the stoichiometric composition: $V_{3.04}Al_{0.96}$. As was demonstrated,¹² the compound V_3Al , like the isoelectronic V_3Ga , is produced as a result of the decay of the solid solution. Therefore, to increase the content of the A15 phase, we deformed an initial V_3Al -alloy cast sample with the bcc structure. A subsequent annealing (375 h at 950 °C) enabled us to bring the A15 phase content up to 90%.

§3. ANALYSIS OF THE CONNECTION OF THE X-RAY SPECTRAL LINE SHIFTS WITH THE ELECTRONIC SUSCEPTIBILITY AND THE CHANGE IN THE LOCAL CHARGES ON THE ATOMS

A procedure for determining the charge of atoms in compounds has been developed in x-ray spectroscopy (see, for example, Ref. 17). It is based on the use of the dependence of the location in energy terms of the x-ray spectral lines on the density of the valence electrons in the region of the atomic core. It has recently been shown^{14,18} that another cause of the line shift is the difference in the degrees of relaxation of the valence electrons of the various compounds in the field of the electron vacancy that arises upon the x-ray excitation of the atom.

In Ref. 14 the Green-functions method is used to analyze the influence of the relaxation effects on the shifts of the $K\alpha_{1,2}$ line (in the initial state of the vacancy in the 1s shell) and its satellite—the $K\alpha_{3,4}$ line (in the initial state of the vacancy in the 1s and 2p shells respectively). It follows from that paper that the magnitude of the $K\alpha_{1,2}$ -line shift $\Delta E\alpha_{1,2}$ can be represented in the form of the sum

$$\Delta E\alpha_{1,2} = \Delta\varepsilon\alpha + \Delta R,$$

where $\Delta\varepsilon\alpha$ is the contribution to the line shift of the effects connected with the reconstruction of the electron density upon the introduction of an atom into the various compounds and ΔR is the change in the energy of the lines, that stems from the difference in the degrees of relaxation of the valence electrons of the various compounds in the field of the vacancy. The quantity ΔR depends linearly on the number of vacancies (at least if this number is less than three); therefore, the following relations are valid with a sufficiently high degree of accuracy¹⁴:

$$\Delta\varepsilon\alpha = 2\Delta E\alpha_{1,2} - \Delta E\alpha_{3,4}, \quad \Delta R = \Delta E\alpha_{3,4} - \Delta E\alpha_{1,2}, \quad (3)$$

where $\Delta E\alpha_{3,4}$ is the shift of the $K\alpha_{3,4}$ satellite line.

Let us introduce the following quantities: Q , the charge of the valence electrons in the region of the core of the unexcited atom in the crystal,

$$Q = \int_{\Omega_c} \rho(r) dr, \quad (4)$$

where $\rho(r)$ is the valence-electron density of the unperturbed system; Ω_c , the region in which the 1s and 2p functions of the atom have finite values; Q' , the electronic charge induced in the region Ω_c in the course of

the relaxation in the field of the vacancy that arises when the atom undergoes an x-ray transition; ΔQ and $\Delta Q'$, the changes found in these charges on going from one compound to another.

As follows from Ref. 19,

$$\Delta Q = -c\Delta\varepsilon\alpha,$$

where c is a positive constant.

The error made when the charges are determined from these relations ~2–5% if the changes affect mainly valence electrons of the same symmetry¹⁹ (e.g., in the case of the compounds being investigated by us) and ~20% if the contributions of the valence s and p electrons to ΔQ are comparable.

The authors of the present paper have drawn attention to the fact that, on the basis of Ref. 14, the quantities $\Delta Q'$ and ΔR are connected by a linear relation:

$$\Delta Q' = -c'\Delta R, \quad (5)$$

where c' is a positive constant. The quantities Q and $\Delta Q'$, on the other hand, can be expressed in terms of the electronic susceptibility of the crystal of which the radiating atom is a constituent.

Let $V_h(q, \omega)$ be the Fourier transform of the unscreened potential of a core vacancy; $\rho'(q, \omega)$, the Fourier transform, corresponding to this perturbation, of the electron-density fluctuation. Then we can define the electronic susceptibility in the linear-response approximation in the linear-response approximation as follows:

$$\chi_e(q, \omega) = \rho'(q, \omega) / V_h(q, \omega). \quad (6)$$

Since the electronic susceptibility in the present case is of interest in connection with the relaxation of the valence electrons in the field of the 1s and 2p vacancies, we should take into account the fact that the lifetime of these vacancies in atoms of the first half of the periodic system is 10–1000 times longer than the relaxation time for the valence electrons. Therefore, we can assume

$$V_h(q, \omega) = V_h(q, 0) = V_h(q)$$

and represent the perturbation of the electron density in the form

$$\rho'(r) = \frac{1}{8\pi} \int \chi_e(q) V_h(q) e^{iqr} dq. \quad (7)$$

The potential $V_h(q)$ is formed by a vacancy in the atomic core; therefore, its form practically does not depend on the surroundings of the excited atom. Consequently, the change $\delta\rho'(r)$ resulting from a change in the composition of the compounds is given by

$$\delta\rho'(r) = \frac{1}{8\pi} \int \delta\chi_e(q) V_h(q) e^{iqr} dq. \quad (8)$$

Using (3), (5), (8), and the definition of the quantity $\Delta Q'$, we obtain

$$\Delta E\alpha_{1,2} - \Delta E\alpha_{3,4} = \frac{c'}{8\pi} \int_{\Omega_c} dr \int \delta\chi_e(q) V_h(q) e^{iqr} dq. \quad (9)$$

Thus, the quantities $\Delta E\alpha_{1,2}$ and $\Delta E\alpha_{3,4}$, which can be determined from an x-ray experiment, are connected

with the change that occurs in the electronic susceptibility upon the variation of the composition of the compounds and alloys. But the expression (9) is an integral relation, and we are interested in the variation $\delta\chi_e(q)$ proper. Therefore, we have performed an analysis of the integral in (9), using for $\chi_e(q)$ an expression derived in the random-phase approximation with allowance made for the correlations and the exchange in accordance with the Hubbard prescription.

It was found in the analysis that the quantities $\Delta E\alpha_{3,4} - \Delta E\alpha_{1,2} = -\Delta Q'/c'$ and $\delta\chi_e(q)$ have the same sign for all values of q . Consequently, we can estimate the change that occurs in the electronic susceptibility upon the variation of the composition of the compounds or alloys from the energy shifts of the $K\alpha_{1,2}$ and $K\alpha_{3,4}$ x-ray lines.

It also follows from the analysis that the quantity $\Delta Q'$ is determined largely by the values of $\delta\chi_e(q)$ in the region $0.5k_F \leq q \leq 3k_F$. The wave numbers of the phonons participating in the formation of the Cooper pairs are contained in the same range. Therefore, the electronic-susceptibility data obtained from the x-ray line shifts may be useful in the interpretation of the superconducting properties of the compounds and alloys.

§4. EXPERIMENTAL PROCEDURE

All the x-ray spectra were obtained in the present work on a double-crystal vacuum x-ray spectrometer by the primary method. The pressure in the x-ray tube was 10^{-5} Torr. The test specimen in the form of powder was smeared on the target plate of the x-ray tube. The experimental conditions (the power of the x-ray tube, the size of the focal spot on the target) were chosen such that the sample temperature did not exceed 200°C .

In the investigation of the K spectra of vanadium we used as the radiation monochromators quartz crystals cut parallel to the (1120) plane, which guaranteed a 0.2-eV resolution for the spectrometer. The operating conditions of the x-ray tube ($u = 25$ kV; $i = 5$ mA) allowed us to obtain peak intensities of 10–12 and 500–600 pulses/sec for the $VK\beta_5$ and $VK\beta_1$ lines respectively. The spectrum for each compound or alloy was measured five times; the $VK\beta_5$ bands were matched with respect to the energy position of the $VK\beta_1$ lines and integrated. The x-ray photographs of the $VK\beta_5$ bands were taken in an energy interval where the peaks corresponding to the vanadium oxides could be detected in the spectrum when these oxides appeared on the target (the locations of the $VK\beta_5$ -band peaks for samples with different degrees of oxidation of the vanadium were taken from Ref. 20). The fairly low target temperature maintained in the experiment made the appearance of vanadium carbides and nitrides on the test-sample surface impossible.

The integrated intensity of the $VK\beta_5$ bands was normalized to the value of the integrated intensity of the $VK\beta_1$ line. In this case the $VK\beta_1$ -line intensity was integrated in the energy range $E_0 - 14$ eV $\leq E \leq E_0 + 6$ eV, where E_0 is the energy of the line peak. The background line was approximated by a straight line intersecting

the "tails" of the $VK\beta_1$ line at the limits of this range. This procedure allowed us to determine the normalized integrated intensity of the bands to within 5–6%.

To obtain the $K\alpha$ lines and $K\beta$ bands of aluminum, we used cesium biphthalate crystals. In this case the resolution of the spectrometer was 0.9 eV. The x-ray tube operated at $u = 10$ kV and $i = 4$ –10 mA (the spectra of the samples with low aluminum content were obtained with the highest plate-current values). The peak intensity of the spectral lines as a function of the composition varied in the ranges: 500–2000 pulses/sec for the $AlK\alpha_{1,2}$ line, 40–200 pulses/sec for the $AlK\alpha_{3,4}$ lines, and 20–50 pulses/sec for the $AlK\beta$ band.

To determine the energy shifts ($\Delta E\alpha_{1,2}$ and $\Delta E\alpha_{3,4}$) of the "centers of gravity" of the aluminum lines, we used a datum: the $L\alpha_{1,2}$ line of bromine contained in the compound KBr. Located in the energy region of the $AlK\alpha_{1,2}$ line are weak $BrL\alpha'$ satellite lines. Therefore, we separated the entire group of $BrL\alpha$ lines from the total spectrum, and only then did we determine the $\Delta E\alpha_{1,2}$ values. Each spectrum was measured five times; the root-mean-square deviation of the shift values were: 0.01 eV for $\Delta E\alpha_{1,2}$ and 0.02 eV for $\Delta E\alpha_{3,4}$. The integrated $AlK\beta$ -band intensity was normalized to the integrated $AlK\alpha_{1,2}$ -line intensity. The procedures for normalizing the integrated $AlK\beta$ - and $VK\beta_5$ -band intensities differed only in the choice of the energy range in which the line intensities were integrated. For the $AlK\alpha_{1,2}$ line this range corresponded to the energy region $E_0 - 5$ eV $\leq E \leq E_0 + 5$ eV.

§5. THE X-RAY SPECTRAL INVESTIGATIONS AND THEIR DISCUSSION

1. Figure 1 shows the $K\beta_5$ emission bands of vanadium in the $V_3(Al_x-Ge_{1-x})$ alloys, matched at the location of the Fermi energy (the point of inflection of the short-wave branch of the spectrum). As the concentra-

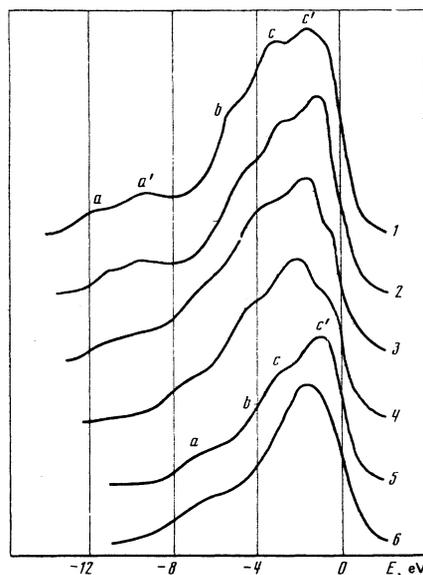


FIG. 1. The $K\beta_5$ x-ray emission bands of vanadium in the alloys $V_3(Al_x-Ge_{1-x})$: 1) $x=0$; 2) $x=0.2$; 3) $x=0.4$; 4) $x=0.6$; 5) $x=1$; 6) $x=1$ (bcc).

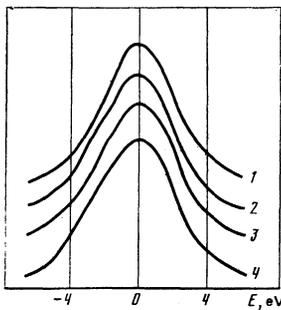


FIG. 2. The $K\beta$ x-ray emission bands of aluminum in the alloys $V_3(Ge_{1-x}Al_x)$: 1) $x=0.2$; 2) $x=0.4$; 3) $x=0.6$; 4) $x=1$.

tion in the ternary alloys is varied, the shape of the long-wave part of the band changes noticeably. There arises in the short-wave part of the spectrum at the concentration $x=0.4$ an additional swelling that increases in intensity on going over to the alloy with $x=0.6$. Furthermore, the integrated intensity of the $VK\beta_5$ band ($IV\beta$) undergoes a jump in the concentration region $0.4 \leq x \leq 0.6$.

The shape of the spectrum for V_3Al given in Ref. 15 differs from the shape obtained by us, which may be due to the use by Kurmaev *et al.*¹⁵ of a V-25% Al alloy sample with the bcc structure. This is confirmed, in particular, by the fact that the shapes of the spectra obtained in our investigation for V_3Al (A15) and V-25% Al (bcc) also differ significantly from each other: in the case of the compound V_3Al (A15) there occur additional swellings at the middle of the long-wave part of the band.

Figure 2 shows the $K\beta$ emission bands of aluminum. The spectra are matched at the locations of their intensity peaks. They do not significantly differ in their shapes. But as the concentration x is decreased, the $AlK\beta$ bands narrow, and their integrated intensities assume the maximum value for the medium Al concentrations. In Table I we give for different values of x the $AlK\beta$ -band widths (δE) at half-height, as well as the integrated-intensity (I) values for these bands, normalized to the integrated intensities of the $AlK\alpha_{1,2}$ lines in the respective alloys. Also given in Table I are the shifts of the centers of gravity of the $AlK\alpha_{1,2}$ and $AlK\alpha_{3,4}$ lines ($\Delta E\alpha_{1,2}$ and $\Delta E\alpha_{3,4}$ respectively) in the investigated alloys relative to their energy locations in metallic aluminum.

2. The emission bands of vanadium and aluminum. According to the selection rules, the $VK\beta_5$ emission band arises as a result of the transition to the 1s level of valence electrons possessing the p symmetry with respect to the vanadium atom. In the compounds and alloys the

TABLE I.

Concentration x	0.1	0.15	0.2	0.3	0.4	0.6	1.0	1.0 bcc
δE , eV	—	—	5.0 ± 0.05	—	5.3 ± 0.05	5.5 ± 0.05	5.7 ± 0.05	—
I , rel. units	—	—	0.085	—	0.102	0.096	0.075	—
$\Delta E\alpha_{1,2}$, eV	0.23	0.11	0.00	-0.05	-0.10	-0.13	0.25	0.46
$\Delta E\alpha_{3,4}$, eV	0.97	0.62	0.30	0.15	0.09	0.03	0.30	0.97
$\Delta \alpha$, eV	-0.51	-0.40	-0.30	-0.25	-0.29	-0.29	0.2	-0.05
ΔR , eV	0.74	0.51	0.30	0.20	0.19	0.16	0.05	0.51

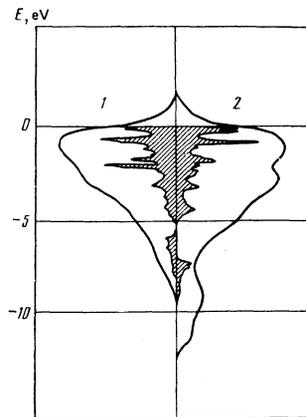


FIG. 3. Total density of electronic states (the hatched region, which shows the results of the calculations performed in Ref. 7) and the emission bands of the A15 compounds: 1) V_3Al ; 2) V_3Ge .

p states of vanadium are filled as a result of the spd hybridization, and also as a result of the redistribution of the electron densities of the other constituents of the compounds. In view of this, the shape of the $VK\beta_5$ band reflects the structure of the entire valence band of the crystal.

In Fig. 3 we compare the results of the investigation of the emission bands with the results of self-consistent band-structure calculations.⁷ The comparison allows us to establish the nature of the various characteristics of the $VK\beta_5$ band for the compounds V_3Al and V_3Ge . Thus, the peaks a and a' (see Fig. 1) are connected with the s electrons of Al and Ge respectively. The swelling b is largely determined by the peak of the p states of the same atoms. The peaks c and c' arise as a result of the pd hybridization, and therefore reflect the characteristics of the d -electron structure of vanadium. The shape of the $AlK\beta$ emission band (Fig. 2) also imparts the characteristics of the energy distribution of the occupied p states of aluminum, but the hybridization plays a lesser role in the formation of the structure of the spectrum in this case than in the case of the $VK\beta_5$ bands, so that the atom has an intrinsic valence p electron.

If the crystal structure does not change on going from one compound to the other, then the changes in the integrated intensities of the $VK\beta_5$ and $AlK\beta$ bands are respectively proportional to the valence- p -electron-density changes occurring in the regions of the atomic cores of vanadium and aluminum respectively.

Let us analyze the shapes and intensities of the emission bands in the ternary alloys $V_3(Ge_{1-x}Al_x)$. The shape of the long-wave part of the $VK\beta_5$ band for the intermediate values of the concentration x corresponds to a simple superposition of the spectra of the original binary compounds, which reflects the additivity of the contributions of the weakly interacting s electrons of aluminum and germanium to the density of states of the alloy.

The presence of an additional short-wave swelling for $x=0.4-0.6$ indicates a substantial reconstruction of the

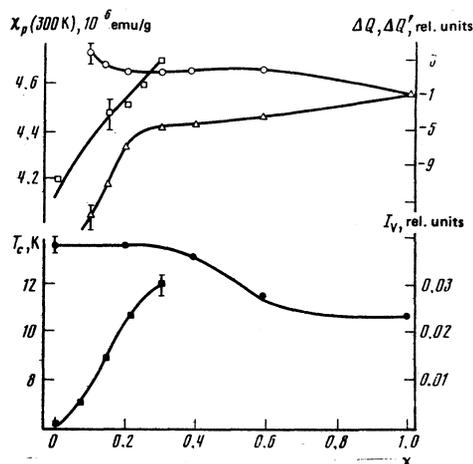


FIG. 4. Dependence of the physical parameters of the alloys $V_3(Ge_{1-x}Al_x)$ on x : ● I_{V_1} ; ○ ΔQ ; △ $\Delta Q'$; □ X_p ; ■ T_c .

band at these concentration values. Since the p -electron states near the Fermi level in vanadium arise as a result of the pd hybridization, the appearance of the short-wave swelling may be due to the presence of an additional peak in the density of occupied d states of the vanadium in these alloys.

The sharp jump in the integrated $VK\beta_5$ -band intensity in the concentration region $0.4 \leq x \leq 0.6$ (Fig. 4), which indicates the nonlinear dependence of the number of p electrons of vanadium on the concentration x , is noteworthy. This fact also indicates the reconstruction of the valence band for $x = 0.4 - 0.6$.

It follows from the analysis of the shapes of the $VK\beta_5$ bands of the compound V_3Al (A15) and the disordered alloy $V-25\%Al$ (bcc) that the density-of-occupied- d -states distributions for the vanadium components in these systems differ significantly in their shapes. The self-consistent band-structure calculations for the A15 compounds⁷ are, as can be seen from Fig. 3, in good agreement with the indicated results of the x-ray spectral investigations.

3. *The shifts $\Delta E\alpha_{1,2}$ and $\Delta E\alpha_{3,4}$.* In Table I we give the values of the shifts $\Delta E\alpha_{1,2}$ and $\Delta E\alpha_{3,4}$ for different concentrations x , as well as $\Delta\varepsilon$ and ΔR values computed from the formulas (3). In Fig. 4 we show the dependence on x of the quantities ΔQ and $\Delta Q'$ as given by the formulas (5) and (4). As a unit of ΔQ and $\Delta Q'$, we took the changes that occur in the charges Q and Q' on the aluminum atoms when we go over from metallic aluminum to the compound V_3Al under investigation.

The charge distributions in the systems $V-25\%Al$ (bcc) and V_3Al (A15) are different. The valence electrons in the alloy with the bcc structure are more strongly localized on the aluminum atoms than the valence electrons in the pure metal (the charge Q is greater). The value of the charge Q in the compound V_3Al (A15) is smaller than the value in metallic aluminum. The doping of the compound V_3Al with germanium leads to the increase of the charge Q . The valence electrons are especially strongly localized on the aluminum atoms at low concentrations x . As we go from $x=0.6$ to $x=0.4$,

the growth of the charge on the aluminum atoms slows down. But then the number of p electrons on the vanadium atom increases sharply (see above).

4. Let us consider the $AlK\beta$ emission bands. The intensity of the short-wave branches of the bands do not undergo a sharp jump at the point corresponding to the Fermi limit. Consequently, the occupied p states of aluminum are largely located in the interior of the valence band. The narrowing of the $AlK\beta$ spectra as the concentration x is decreased indicates the localization in energy terms of the p electrons of aluminum, which is characteristic of impurity atoms in a crystal.

In Table I we give the values of the integrated intensity I of the $AlK\beta$ bands for different values of x . A comparison of the I values and the $AlK\alpha_{1,2}$ -line shifts given in the same table shows that the relation

$$\Delta I = b \Delta E\alpha_{1,2}, \quad (10)$$

where ΔI is the change that occurs in the value of I when we go over from one alloy to another and b is a positive constant, is approximately valid. The quantity ΔI is proportional to the change in the number of p electrons on the aluminum atom and the shift $\Delta E\alpha_{1,2}$ is proportional to the change in the total charge of the valence electrons in the region of the core of the aluminum atom ($-\Delta E\alpha_{1,2} \propto \Delta Q + \Delta Q'$). Therefore, it follows from the relation (10) that only the p states of aluminum undergo a reconstruction when the composition of the alloys under investigation is changed.

5. Let us compare the result obtained with the magnetic and superconducting properties of the compounds.¹⁶ Of greatest interest is the concentration region $0 \leq x \leq 0.3$, since the value of T_c increases by a factor of two when we go over from the compound V_3Al to the alloy $V_3(Al_{0.3}Ge_{0.7})$ (Fig. 4). In the process the paramagnetic susceptibility increases sharply in absolute value and its temperature dependence undergoes a strong enhancement (Fig. 4). To explain these facts we use the results of Ref. 7.

Calculations⁷ show that in the case of the binary compounds V_3Al and V_3Ge the density of electronic states in the energy region $E_F - 2 \text{ eV} \leq E \leq E_F$ is determined largely by the d electrons of vanadium, which interact weakly with the p electrons of aluminum. This circumstance allows us to assume that the distribution $N(E)$ in the region of the Fermi level does not change when we go over from the compound V_3Ge to the alloy $V_3(Ge_{1-x}Al_x)$, at least in the case of low concentrations x . At the same time, as shown in the present paper, some of the valence electrons in the ternary alloys are localized on the aluminum atoms. Furthermore, the doping of the compound V_3Ge with aluminum is accompanied by a decrease in the total number of valence electrons. Both of these phenomena should lead to a shift of the Fermi level toward the bottom of the band, i. e., toward the region of higher values of the density of electronic states, which is confirmed by the results of the paramagnetic susceptibility measurements (Fig. 4).

Figure 4 shows a plot of the function $\Delta Q'(x)$. The sharp increase that occurs in the quantity Q' as we go from $x=0.1$ to $x=0.3$, an increase which, as follows

from the results discussed in §3, should be a consequence of an increase in χ_g , is noteworthy. The growth of the electronic susceptibility should lead to the softening of the phonon spectrum of the system [see the formula (2)], which is observed in experiment. The quantity $\langle\omega^2\rangle$ decreases when we go over from the compound V_3Ge to the alloy $V_3(Al_{0.3}-Ge_{0.7})$,¹⁰ despite the appearance in the density of phonon states of a high-frequency peak due to the vibrations of the aluminum atoms. At low concentrations x the transfer of charge to the aluminum atoms cannot guarantee a significant increase in the value of the electron-ion matrix element on the V and Ge atoms. Thus, the increase in T_c observed when the compound V_3Ge is doped with small amounts of aluminum is due to an increase in $N(E_F)$, as well as to a decrease in the mean-square values of the phonon frequencies, which occurs as a result of a sharp increase in the electronic susceptibility.

As shown above, in the concentration region $0.4 \leq x \leq 0.6$ the presence of aluminum atoms in the alloys leads to a significant change in the shape of the valence band, and therefore the assumption that the shape of $N(E_F)$ in the vicinity of E_F remains unchanged may not be justified. It should be noted that the function $\Delta Q'(x) \propto \Delta\chi_g(x)$ in this concentration region, as for all other values of x , is found to correlate unambiguously with the quantity T_c . Finally, the transition from the superconductor V_3Al (A15) to the nonsuperconducting V_3Al (bcc) is also accompanied by a decrease in the quantity $\Delta\chi_g$.

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