Investigation of the superconducting properties of V-Al and V-Sn solid solutions

N. E. Alekseevskiĭ, A. V. Mitin, and N. M. Matveeva

Institute of Physics Problems, USSR Academy of Sciences and Metallurgy Institute, USSR Academy of Sciences

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We measured the critical superconducting transition temperatures T_c, the critical magnetic fields H_{c2}, and the resistivities of the alloys as functions of the composition. It was observed that increasing the Al and Sn contents in the solutions with V leads to an exponential decrease of T_c. The T_c of the alloys becomes much lower than the T_c of the two components. As the Al concentration in the V-Al system is increased, the sign of the temperature coefficient of the resistivity $(\partial\rho/\partial T)$ changes, and minima in the $\rho(T)$ plots are observed for certain alloys of this system. The resultant data are discussed.

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Studies of the alloys of the V—Al system were carried our previously in a number of works. The behavior of solid solutions of the V—Al system was considered in[1-4], while the possibility of the existence of the intermetallide V_3Al was considered in[5-7]. There has been interest in carrying out further detailed studies of the V—Al system in the region of existence of solid solutions from the side of V, in particular, in the measurement of the dependence of T_c on the Al concentration over a wider range of temperature.

EXPERIMENTAL METHOD

The samples were prepared from V of purity 99.9 and Al of purity 99.999. In the first series, the components were pressed into tablets in a helium atmosphere in a high-frequency furnace and then quenched. In the second series, the samples, after melting, were homogenized at 1500°K for 15 hr, after which quenching was again carried out. X-ray structure analysis, carried out for samples of both series, did not reveal any significant effect of the heat treatment on the period of the lattice, and showed the presence in both alloys of only a single phase with a bcc structure.

To determine T_c and H_c, the apparatus shown in Fig. 1 was used; it permitted a rather easy replacement of the samples. The temperature in the time of measurement could be varied in the range 0.5—10°K.

Cooling of the sample to 0.5°K was effected in the following way. The temperature in the outer helium container 1 was cooled to 1.5°K. Then the heater 2 of the carbon "pump" 3 was connected, the He^3 was described and its pressure increased. Upon increase of the pressure above the equilibrium valve for 1.5°K, the He^3 was condensed on the surface of the condenser 4. The liquid helium formed flowed down into the region 5 located near the sample 6. The thermal contact with the sample was accomplished through a small amount of superfluid He^4. Then the heater was turned on. As the carbon "pump" cooled the rate of the pumping of the He^3 increased and the temperature of the liquid He^3 decreased to 0.5°K. For operation at reduced temperatures, the He^3 was vaporized and the temperature raised by the heater.

For all the samples, we measured the critical temperature T, the critical magnetic field H_{c2}, and the dependence of the electrical resistance on the temperature in the region of temperatures both above the Debye temperature Θ_D and below it. The sample transition curves to the superconducting state were recorded by measuring their resistance, using an x-y recorder, connected through an F-116 amplifier.

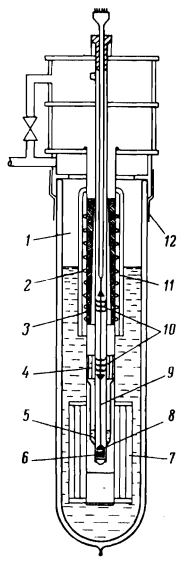

FIG. 1. Scheme of apparatus: 1—helium bath, 2—heater, 3—carbon "pump," 4—condenser, 5—liquid He^3, 6—sample, 7—solenoid, 8—carbon thermometer, 9—insert, 10—radiation screen, 11—vacuum "jacket," 12—rubber sleeve.

The magnetic field was produced by a superconducting solenoid.

RESULTS AND DISCUSSION

Figure 2 shows the concentration dependence of the critical temperatures of the V—Al sample, and Fig. 3 the concentration dependence of the values of $(\partial H_{c2}/\partial T)_{Tc}$. Figure 4 gives the dependence of $\rho(T)$ for $V_{1-x}Al_x$ alloys with different contents of Al. Table I gives the values of T_c, $(\partial H_{c2}/\partial T)_{Tc}$, ρ_{300}, $(\partial\rho/\partial T)_{2\Theta D}$.

The experimental data thus obtained enable us to calculate the value of the Sommerfeld constant γ, similar to what was down in[8]. The values of γ calculated by us are given in Table II. In the same table are given for comparison the values of γ obtained by Pessal et al.[4] from calorimetric measurements. It is seen that they are in excellent agreement.

If we determine the density of states on the Fermi surface, N_0, from the values of γ, it then turns out that N_0 falls off approximately exponentially with concentra-

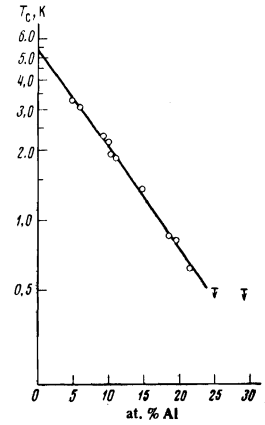

FIG. 2

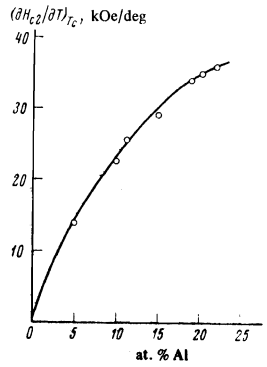

FIG. 3

FIG. 2. Concentration dependence of the critical transition temperature of samples (to the superconducting state) for the system V-Al (arrows indicate the temperature above which no superconductivity was observed).

FIG. 3. Dependence of the derivative of the critical magnetic field of the samples on the Al concentration.

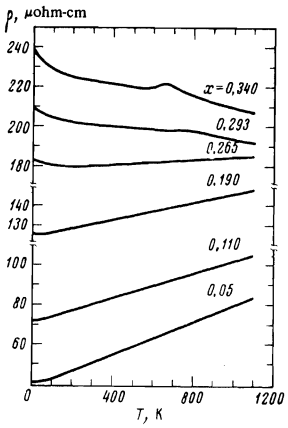

FIG. 4

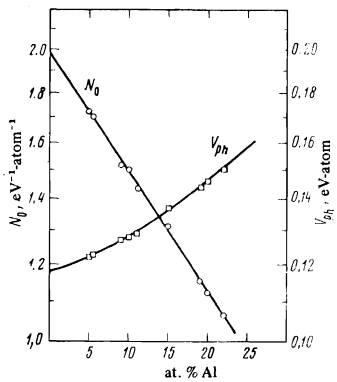

FIG. 5

FIG. 4. Temperature dependence of the electrical resistance for a number of $V_{1-x}Al_x$ samples.

FIG. 5. Change in the parameter of electron-phonon interaction V_{ph} and density of states on the Fermi surface N_0 in the V-Al system as a function of Al content.

tion in the region of 0–25 at. % Al, and ranges from 2 to 1 states per 1 eV-atom (see Fig. 5).

Making use of the BCS formula

$$T_c=1.14\Theta_D \exp(-1/N_0V_{ph}), \quad (1)$$

obtained, as is well known, under the approximation of weak interaction of electrons with phonons, i.e., $N_0V_{ph} \ll 1$, we can estimate the parameter of electron-phonon interaction V_{ph}. (Use of the McMillan formula does not bring about any appreciable correction in the calculations of the investigated alloys, which are superconductors with weak coupling.) On the other end, the estimate of the parameter V_{ph} for the investigated system, which consists essentially of the transition metal V, can be carried out on the basis of the model of[9] for the resistivity of the transition metals. In the high temperature limit ($T > \Theta_D$), the temperature-dependent part of the resistivity is of the form

$$\rho=\text{const}\cdot\left[1+C^*\frac{N_{0d}}{N_{0s}}\right]TV_{ph}, \quad (2)$$

TABLE I. V-Al System.

Content at. % Al	T_c, °K	$\left(\frac{\partial H_{c2}}{\partial T}\right)_{T_c}$, kOe/deg	ρ_{300}, μohm-cm	$\left(\frac{\partial\rho}{\partial T}\right)_{2\Theta_D}$, 10^{-8} ohm-cm/deg	Content Al	T_c, °K	$\left(\frac{\partial H_{c2}}{\partial T}\right)_{T_c}$, kOe/deg	ρ_{300}, μohm-cm	$\left(\frac{\partial\rho}{\partial T}\right)_{2\Theta_D}$, 10^{-8} ohm-cm/deg
0	5.43	0.57	23	55	20	0.86	35	137	22
5	3.30	14	50	48	22	0.63	37	150	17
5.5	3.10	15	53	47	26,5	<0.5		180	7.1
9	2.30	20	71	43	29,3	<0.5		200	−9.1
10	2.20	22	74	42	34,0	<0.5		225	−17.3
11	1.75	24	80	41	25	<0.5		175	
15	1.37	29	103	32	30	<0.5		205	
19	0.87	34	131	24	40	<0.5		230	

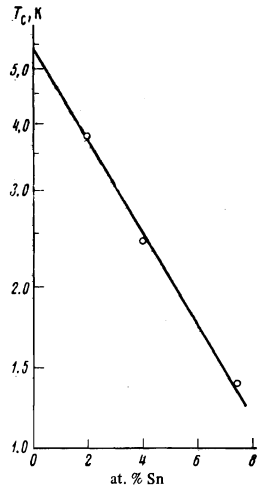

FIG. 6

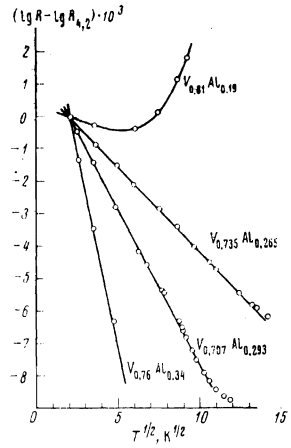

FIG. 7

FIG. 6. Concentration dependence of the critical temperature of transition to the superconducting state for the V-Sn system.

FIG. 7. Dependence of the difference log R–log $R_{4.2}$, where R is the electrical resistance, on $T^{1/2}$ for alloys of the V-Al system.

where C* is a coefficient of the order of unity, N_{0s} and N_{0d} are the values of N_0 of the corresponding bands. From (2) we obtain

$$V_{ph}\approx\text{const}\cdot\frac{\partial\rho}{\partial T}\left[\frac{N_{0s}+N_{0d}}{N_{0s}}\right]^{-1}. \quad (3)$$

According to[3], N_{0s} can be assumed to be constant and equal to 0.19 states per eV-atom, $N_{0s} + N_{0d} = N_0$.

The values of $V_{ph}(1)$ and $V_{ph}(3)$ calculated from (1) and (3), are given in Table II. As seen from the table the difference $V_{ph}(1)-V_{ph}(3)$ increases with concentration, remaining linear up to a concentration 10 at. % Al. At higher Al concentrations the values of $\partial\rho/\partial T$ decrease and change sign, which can be ascribed, as will be considered below, to the effect of paramagnons on the scattering of the conduction electrons.

In addition to the V–Al alloys, measurements were carried out on V–Sn alloys. The dependence of T_c on concentration for alloys of the V–Sn system in the region of solid solutions (0–8 at. % Sn) is shown in Fig. 6. It agrees qualitatively with the similar dependence for the V–Al system. For higher concentrations of Sn, a change is observed in the shape of the curve and is evidently due to the appearance of the intermetallide V_3Sn with the structure β-W.

It follows from our results that for alloys of the V–Al system, in the region of solid solutions, the critical temperature falls off exponentially with the Al concentration. A similar dependence is also obtained

TABLE II. V-Al System.

Al content	a, Å	γ	γ[4]	N_0,	$V_{ph}(1)$	$V_{ph}(3)$	$\lvert V_{ph}(1)-V_{ph}(3)\rvert$
		mcal/mole-deg		$eV^{-1}atom^{-1}$	eV-atom		
0	3,028	2.27	2,2	1.97	0,118	0.118	0
5	3,033	1,95		1,72	0.122	0,118	0.004
5.5	3,034	1.91		1,70	0.123	0.118	0.005
9	3,039	1.80		1,52	0.127	0.119	0.008
10	3,040	1.77		1,50	0.128	0.118	0.008
11	3.041	1.78	1.73	1,43	0.129	0.120	0.009
15	3.044	1.58		1,32	0.137	0.102	0.035
19	3,048	1.40	1,31	1,15	0.144	0,088	0.056
20	3,049	1.37		1,12	0.146	0.083	0.063
22	3.051	1.30		1.06	0.150	0,067	0.083
26.5	3.055	1.20*		0,95*	0.160*	0.031*	0.129*
30	—	—	1,00				
40	—	—	0.82				

*Results of nearest extrapolation.

for the V—Sn solid solutions. The decrease in the critical temperature is brought about by the exponential drop in the density of states on the Fermi surface, which is not compensated by the very weak increase in the electron phonon interaction parameter (see Fig. 5). An important circumstance is the fact that T_c of the binary alloy falls much lower than the T_c of both components. Such a sharp drop in T_c to values below 0.5°K for alloys with a content of 25 at.% Al and above, can be due to the increasing effect of the paramagnons (which evidently modify the scattering of the conduction electrons; see Fig. 4).

It is seen from Table II that the relation (3), which is obtained, as noted above, under the assumption of the phonon scattering mechanism, is satisfactorily fulfilled only in the range of low Al concentrations (up to 10 at.%) and ceases to be satisfied at higher Al concentrations. In the investigation, the electrical resistance[1)] of the solid V—Al solutions, it was observed that, for concentrations of Al ≥19 at.%, along with the change of sign of $\partial\rho/\partial T$, minima were observed in the temperature dependence of the resistance. The dependences of $\rho(T)$ over a wide range of temperatures for a number of alloys of the V—Al system are shown in Fig. 4. Alloys with 19 and 26.5 at.% Al have minima in the electrical resistance at temperatures ≈30 and ≈300°K, respectively. A similar dependence of $\rho(T)$ is typical of the systems of Kondo[10] with this difference, however, that in Kondo systems the impurities are magnetic and their concentration is significantly less. Correspondingly, the resistivity of Kondo systems is also significantly less. For alloys with concentrations 29.3 and 34 at.% the derivative $\partial\rho/\partial T$ becomes negative everywhere, with the exception of small regions near 600°K. It must also be noted that the $\rho(T)$ dependence does not exhibit hysteresis and is excellently reproduced both when heating and in cooling the sample. In the temperature range 250°K < T < 550°K, the $\rho(T)$ dependence is linear (the departure from a linear law does not exceed 0.1%).

A linear decrease in the resistance with increase in temperature in the range 135°K < T < 310°K in alloys of the Al-Mn system was observed in 1971 by Babic and coworkers.[11] In 1974, Rassokhin et al.[12] observed the negative linear variation of $\rho(T)$ for T > 20°K and 0.6 < x < 0.85, for alloys of Ti_xV_{1-x}. At the present time, the linear decrease in the resistance with increase in temperature has been explained by a number of authors[11,13,14] by the presence of localized spin fluctuations (LSF) or paramagnons.

In several papers, systems with LSF are divided[14] into two classes: 1) the basic component—the simple metal (for example, Al), and the impurity—the transition metal. Such systems are discussed within the framework of the Anderson model;[15] 2) alloys, where the transition metal is the impurity and the basic component. They are considered within the framework of the Wolf model.[16]

In 1972, Rivier and Zlatic[13] calculated the resistance ρ due to LSF for alloys of the first class over a wide range of temperatures, and obtained a universal dependence $\rho(T)$. The calculations were found in excellent agreement with the experimental data for alloys of the system Al-Mn. (At low temperatures (60°K for Al-Mn) the resistance follows the law $\rho_f = 1 - (T/\Theta_1^f)^2$, where Θ_1^f is a constant;[2)] for the alloy Al–Mn, it is equal to $\Theta_1^f = 530 \pm 30$°K. In the region of higher temperatures 135°K < T < 310°K, the $\rho(T)$ dependence becomes linear and takes the form $\rho_f = \alpha(1 - T/\Theta_2^f)$, where $\Theta_2^f = 2.931\,\Theta_1^f$. Upon further increase in the temperature, the theory predicts a decrease in the resistance according to the law ln T, and finally, like T^{-1}.)

Figure 7 shows the dependence of the electrical resistance on the temperature for a number of alloys of the V—Al system under study, in the temperature range from 4° to 1200°K. The results for alloys with a Al content greater than 25 at.% in the range of low temperatures can be described by the following empirical formula: $\rho = A\exp(-\beta\sqrt{T})$ or

$$\rho = A\exp[-\Delta(T)/T], \tag{4}$$

where A is a constant and $\rho(T) = \beta T^{3/2}$. In the high temperature region (above 170°K for $V_{0.735}Al_{0.265}$ and above 120°K for $V_{0.707}Al_{0.293}$), the temperature dependence ceases to be described by Eq. (4) and in the temperature range 250—500°K, ρ decreases linearly with the temperature.

In 1974, K. Fischer[14] considered the behavior of $\rho(T)$ for alloys of the second class on the basis of the generalized Wolf model.[16] If we compare the dependence of $\rho(T)$ calculated by Fischer for various values of $|V|$ and Δ (Δ is the width of the localized state and V is the shift of this state relative to the Fermi level) and that shown in Fig. 1 in[14], it is then seen that for large values of $|V|$, the $\rho(T)$ dependence obtained in[14] qualitatively recalls our data for the V—Al alloys with a content of Al of more than 25 at.%. However, as was pointed out above, in our case an exponential dependence exists for $\rho(T)$, which does not follow from[14]. If we take it into account that the results obtained in[14] refer to alloys of two transition metals, which can not include the V—Al system, then, from a comparison of the dependences $\rho(T)$ obtained by us with the data of Fischer, and also with the results of experiments carried out, for example, in[12], we can draw the conclusion that the localized spin fluctuations can be one of the probable reasons producing the singularities of $\rho(T)$.

As was noted above, the sharp decrease in T_c in the range of aluminum concentrations exceeding 25 at.%, down to values considerably less than T_c of the initial components, can also be attributed to the effect of LSF, especially if we consider the data of Benneman and Garland.[17] Such an assumption was offered in[12] in the study of the system V—Ti. Further investigations will probably enable us to establish the real reason for the features of the behavior of the V—Al system and to explain what role the local spin fluctuations play in the appearance of these singularities.[3)]

[1)]The thermal emf was eliminated in the measurements of $\rho(T)$, as usual, by alternately reversing the measurement current. It was also reduced to a minimum by use of U-shaped samples.

[2)]ρ_C and Θ^C according to the terminology of ref. 13.

[3)]The scattering of conduction electrons by microscopic inclusions of the ω phase could lead to the growth of the resistance in the case of a temperature decrease [18].

[1] N. E. Alekseevskiĭ, N. N. Kornilov, and N. M. Matveeva, Dokl. Akad. Nauk SSSR **195**, No. 2 (1970).

[2] B. A. Hatt, J. K. R. Page and V. G. Rivlin, J. Low Temp. Phys. **10**, 271 (1973).

[3] D. O. Van Ostenburg, D. J. Lam, H. D. Trapp, D. W. Pracht, and T. J. Rowland, Phys. Rev. **135**, A455 (1964).

[4] N. Pessal, N. Gupta, C. H. Cheng, and P. Beck, J. Phys. Chem. Solids **25**, 993 (1964).

[5] H. Hollek, N. Nowotny, and F. Benesovsky, Monath. Chem. **94**, 359 (1963).

[6] L. D. Hartsongh and R. H. Hammond, Solid. St. Comm. **9**, 885 (1970).

[7] L. R. Testardy, J. H. Wernick, W. A. Royer, R. D. Bacon, and A. R. Strom, Appl. Phys. **45**, 446 (1974).

[8] N. E. Alekseevskiĭ, V. I. Pizhankosvskiĭ, V. G. Shamraĭ, Ch. Bazan, and E. Troĭnar, Fiz. Met. Metallov. **34**, 972 (1972).

[9] M. Cohen, G. Gladstone, M. Jensen, and J. Schrieffer, Superconductivity of Semiconductors and Transition Metals (Russian translation, Mir, 1972, p. 145).

[10] A. Khekshus and W. B. Pearson, Can. J. Phys. **40**, 98 (1962).

[11] E. Babić, R. Krsnik, B. Leontić, Z. Yučić, I. Zoric, and C. Rizzuto, Phys. Rev. Lett. **27**, 805 (1971).

[12] V. A. Rassokhin, N. V. Volkenshteĭn, E. P. Romanov, and A. F. Prekul, Zh. Eksp. Teor. Fiz. **66**, 348 (1974) [Sov. Phys.-JETP **39**, 166 (1974)].

[13] N. Rivier and L. Zlarić, J. Phys. F: Metal. Phys. **2** L87 (619), 1972.

[14] K. Fischer, J. Low Temp. Phys. **17**, 87 (1974).

[15] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[16] P. A. Wolf, Phys. Rev. **124**, 1030 (1961).

[17] K. H. Benneman and J. W. Garland, Int. J. Magnet. **1**, 97 (1971).

[18] E. W. Collings, Phys. Rev. **B9**, 3989 (1974).

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