

Localized spin fluctuations and singularities of the electric resistance of Ti_x-V_{1-x} alloys

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The temperature dependences of the electric resistance in Ti_x-V_{1-x} alloys are studied over a broad range of concentrations and temperatures. Anomalies which are ordinarily observed in alloys are detected as well as the Kondo saturation of the resistance at low temperatures and a negative linear course of the $\rho(T)$ curves at $T > 20^\circ K$ and $0.6 < x < 0.85$. The residual resistance varies almost linearly with concentration and reaches values as high as $170 \mu \Omega \text{ cm}$. The anomalies are regarded as confirming the hypothesis of the presence in the Ti-V system of virtual coupled states of localized spin fluctuations. In this connection, some features of the resistive transition from the normal to the superconducting state are discussed. The $\sigma(T)$ dependence can be described by an exponential and does not satisfy the main results of Aslamazov-Larkin fluctuation theory. The introduction of an unpairing mechanism removes all restrictions on the magnitude of ΔT and thus solves the chief difficulty of the problem.

Detailed studies of the electric resistance in alloys of the Ti_x-V_{1-x} system^[1] have shown that the anomalously wide resistive transitions from the normal to the superconducting states are not random events and can be explained by simple considerations of the presence of a second phase with a very high T_C or a nonequilibrium distribution of the alloy components. Both these versions turn out to be unsatisfactory if we recognize that the broad transitions are observed over the entire range of concentrations; moreover, in the region of good solid solutions, i.e., in the case of a small Ti content, the width of the transition (ΔT) is directly proportional to the Ti concentration; any signs of stepwise transitions are entirely absent; the temperature up to which the traces of superconductivity are preserved exceeds by nearly a factor of two the maximum value of T_C in the system Ti-V. Meanwhile there can be no doubt that the wide transitions indicate a strong spatial change in the superconducting order parameter.

To explain the latter, it has been proposed^[2] to use the mechanism of localized spin fluctuations, the effect of which on the superconductivity in the Ti-V system has been estimated by Benneman and Garland.^[3] The additional conductivity at $T > T_C$ is now considered as the remnant of traces of a much higher temperature superconductivity than is determined from the resistance jump, in the presence of a pair-breaking mechanism.

It is clear that the temperature at which the normal state is completely established should be related to the parameter T_C^{BS} of the Benneman-Garland theory, and the width of the superconducting transition with the parameter ΔT_C^{Sf} . (T_C^{Sf} , by the definition of^[3], is the T_C found from the jump in the resistance and needs no identification.)

The alloys were prepared in an arc furnace with a non-wearing tungsten electrode in a helium atmosphere cleaned by a getter. Titanium iodide and vanadium brand VEL-1 were used as initial materials, previously subjected to recrystallization in an electron-beam furnace. For homogenization purposes, the ingots were remelted and overturned six times, subjected to cold deformation by ~50% and annealed in a vacuum of 10^{-6} mm Hg

(1500°C, 2 hr). Samples ($1 \times 1 \times 15$ mm) were then cut by an electric spark cutter for measurement of the resistance. To preserve the solid solution of β phase at room temperature, the samples were quenched from 1100°C in water.

Figure 1 gives data on the temperature dependence of the electric resistance near the superconducting transition temperature for almost all the alloys studied. It is seen that the resistance begins to decrease long before the onset of the completely superconducting state. The results of the determination of the quantities T_C^{BS} , T_C^{Sf} and ΔT_C^{Sf} were published previously^[2] and are included in the table.

A number of authors^[4,5] have explained the pre-mature decrease in the resistance as due to thermodynamic fluctuations of the order parameter, drawing on the theory of Aslamazov and Larkin.^[6] It is of interest to analyze the problem of the legitimacy of such an approach. In the Aslamazov-Larkin theory, an estimate is given of the temperature interval ΔT in which the additional conductivity becomes equal to the conductivity of the normal state. In the three-dimensional case, this quantity can be $\Delta T \sim 10^{-3}^\circ K$.

Making use of the data of Fig. 1, it is not difficult to establish the fact that the analogous experimental quantity is practically equal to ΔT_C^{Sf} , i.e., several degrees, and exceeds the theoretical value by more than 1000 times! Further, the temperature dependence of the additional conductivity in the theory of^[6] has a steplike character and is described by a formula of the form

$$\sigma - \sigma_0 = \sigma_0 \left(\frac{T_C}{T - T_C} \right)^{1/2}, \quad (1)$$

where σ_0 is the conductivity of the normal state. We

TABLE I.

Composition at % Ti	T_C^{Sf} , °K	T_C^{BS} , °K	ΔT_C^{Sf} , °K	$10^6 A$	Composition at % Ti	T_C^{Sf} , °K	T_C^{BS} , °K	ΔT_C^{Sf} , °K	$10^6 A$
10	6.5	9.5	3.0	185.9	60	7.3	12.0	4.7	1620
20	7.4	10.5	4.1	420.0	70	5.7	10.5	4.8	2190
30	7.6	11.8	3.2	816.4	75	4.75	10.9	5.25	1192
40	7.6	12.0	4.4	1315	80	3.35	7.0	3.65	1236
50	7.5	12.0	4.5	1414					

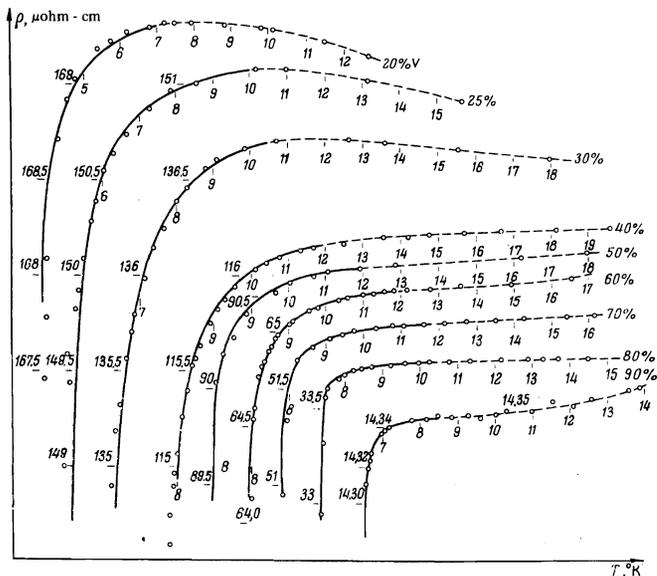


FIG. 1. Temperature dependence of the resistance near the superconducting transition, \circ - results of experiment, solid curves - calculation from Eq. (2).

carry out the treatment of our data in accord with (1) and establish the complete inapplicability of this expression for the description of the curves of Fig. 1. We therefore assume that there is no basis for explaining the phenomenon of wide resistance transitions as due to thermodynamic fluctuations at $T > T_c$.

The curves of Fig. 1 are well described by an exponential of the form

$$\sigma = \sigma_0 e^{A\tau}, \quad \tau = (T_c^{b_1} - T) / (T - T_c^{b_2}), \quad (2)$$

where σ is the total conductivity at the given temperature, A is a constant factor, τ is the reduced temperature parameter, and σ_0 is the conductivity of the normal state. The solid lines in Fig. 1 indicate the results of the calculation according to (2), carried out on the machine "Promin"-2M." The values of the coefficient A are given in the last column of the table.

At the present time, too little is known of the effect of localized spin fluctuations on superconductivity to make clear the physical meaning of the empirical formula (2). Somewhat more is known about the effect of localized spin fluctuations on scattering processes generally.^[7,8] Therefore, signs of the appearance of spin fluctuations should be sought in the singularities of the electric resistance at $T \gg T_c$. With such a goal, we carried out measurements of the resistance right up to room temperature. The results are shown in Fig. 2. We note the following basic singularities: 1) a very large value of the residual resistance; 2) a negative temperature coefficient of the resistance α in the range of concentrations $0.6 < x < 0.85$. This is clearly seen in Fig. 3, where the concentration dependence of α is shown in the linear portion of the curves $\rho(T)$. The quantity α twice passes through zero, taking on positive values for $x < 0.6$ and $x > 0.85$ and negative for the intermediate values of x ; 3) the curves $\rho(T)$ with negative α have a tendency toward saturation at low temperatures; 4) the negative course of the curves $\rho(T)$ is preserved right up to room temperature; 5) the alloys with $x > 0.5$ have a practically linear dependence of $\rho(T)$ for $T > 50^\circ\text{K}$.

The concentration dependence of the residual resis-

tance $\rho_0(x)$ is also unusual for binary solid solutions. It is seen from Fig. 4 that ρ_0 increases almost linearly with the Ti concentration, up to the limit of existence of the body-centered cubic lattice of the solid solution.^[9] Precipitation of the α phase leads to a rapid decrease of ρ_0 to ordinary values and a change of sign of the temperature coefficient (curve 11 in Fig. 2).

It is also seen from Figs. 3 and 4 that there are no isolated values of x for the appearance of anomalies. The effect has a cumulative property and the anomaly becomes significant only in concentrated alloys. By virtue of this fact, not only are separations of any of the characteristics difficult, but so is also the treatment of the phenomenon itself. Actually, models of spin-compensated states^[10] and localized spin fluctuations^[8] which describe the anomalies of electric resistance, similar to those described above for Ti-V, are connected in one way or another with problems of the formation of localized magnetic moment and assume dilute solid solutions with magnetic or almost magnetic impurity atoms. Therefore we can at the present time make only a qualitative comparison, comparing the characteristic features of the experimental and theoretical results. In this case, the localized spin fluctuations model appears^[8] to be preferable, since it allows us to explain simultaneously both the negative course of the curves $\rho(T)$ and also the large value of the residual resistance. In this model, the electrons that are scattered directly by the localized spin fluctuations are resonance electrons, i.e., they already have a formed virtual bound state. The resistance is equal to its unitary limit at $T = 0$ and fall off with increase in temperature as T^2 , T , $\ln T$ and T^{-1} .

It is seen from a comparison with our data that the term T^2 corresponds to the effect of saturation, noted in singularity 3). The linear term T describes the transition region between T^2 and $\ln T$. Thanks to the large value of the Kondo temperature (the singularity 4)) it should be observed over a wide temperature range. This is found in complete correspondence with the singularity 5) of our conclusions

For alloys with a small amount of Ti, the situation is considerably more complicated. The curves $\rho(T)$ at high temperature generally do not have a linear part, but have a convexity for all temperatures above 100°K . Probably this effect arises from V. It must be noted: our data

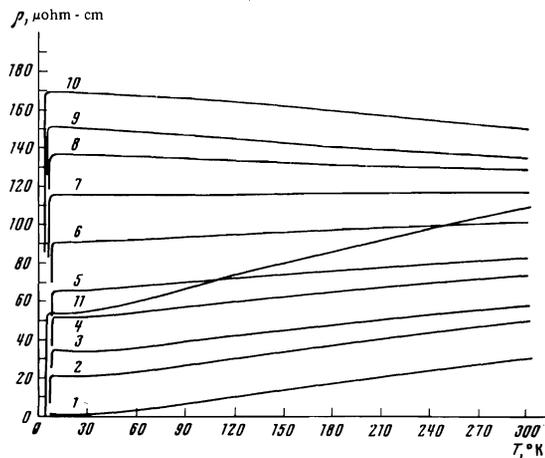


FIG. 2. Temperature dependence of the resistance of $\text{Ti}_x - \text{V}_{1-x}$ alloys. 1 - 100, 2 - 90, 3 - 80, 4 - 70, 5 - 60, 6 - 50, 7 - 40, 8 - 30, 9 - 25, 10 - 20, 11 - 10% V

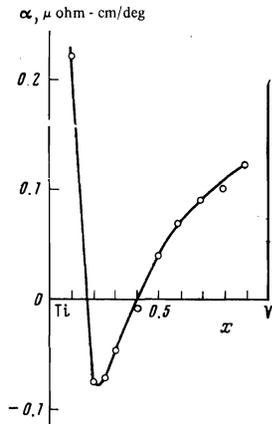


FIG. 3

FIG. 3. Concentration dependence of the temperature coefficient of the resistance.

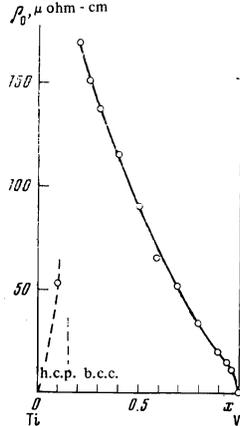


FIG. 4

FIG. 4. Concentration dependence of the residual resistance.

do not agree with the work of Taylor,^[11] where it is confirmed that the curves $\rho(T)$ have a break at some temperature which is itself a function of the composition. We have carried out careful construction of curves on a large scale and have not observed breaks in any of the alloys. So far as the large values of the residual resistance are concerned, then, in accord with Friedel,^[12] they are the consequence of resonance scattering of the electrons by the virtual bound states.

Thus the singularities of behavior of the electric resistance of Ti_x-V_{1-x} alloys near the temperature of the superconducting transition and for high temperatures can be explained from a single point of view under the assumption that there are localized spin fluctuations in the Ti_x-V_{1-x} alloys of the type considered by Rivier and Zlatic.^[13] The fundamental result of our research can probably be formulated in the following fashion: the band structure allows the Ti_x-V_{1-x} alloys to have critical superconducting temperatures equal to the values

T_c^{bs} ($T_{max} \approx 12^\circ K$) but not the values T_c^{sf} ($T_{max} \approx 7.6^\circ K$) as T_c^{sf} was considered previously. It is necessary to take this into account in the calculation of T_c from parameters of the normal state.

¹⁾We are grateful to E. G. Maksimov for acquainting us with this research.

Note added in proof (November 25, 1973). The values of the quantities T_c^{bs} and ΔT_c^{sf} given in table were obtained from the condition of the best description of the experimental curves by Eq. (2) and differ somewhat from the values previously published. [2]

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