Effect of spin fluctuations on the superconducting and normal properties of alloys of Ti containing V, Nb, or Ta

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The temperature dependences of the electric resistance in Ti–Nb and Ti–Ta alloys are studied in a broad range of concentrations and temperatures. A comparative analysis of the earlier data on Ti–V alloys is carried out with the aim of ascertaining the causes and conditions of appearance of scattering with spin flip. It is shown that anomalous properties due to the negative resistance temperature coefficient and to the broad transitions to the superconducting state become weaker on going from V to Ta. This points to the decisive role played by the *d*-band width in these effects and that the general assumption of the Rivier–Zlatic model, that incomplete collectivization of *d* electrons is a necessary condition for the appearance of spin inhomogeneities, is correct. Lattice deformation may be the initiator of the electron spectrum with a narrow band of virtual states near the Fermi level. It is pointed out that the magnetic contribution to the specific heat may be considerable at low temperatures and result in deviations from the shape predicted by the microscopic theory of superconductivity.

It was shown earlier[1] that the resistivity of $Ti_x - V_{1-x}$ is characterized by a negative temperature coefficient and by anomalously broad transitions from the normal to the superconducting state. These singularities could be explained by assuming an additional scattering mechanism accompanied by spin flip. The influence of this scattering on the resistance of normal metals is widely known as the Kondo effect. For the superconducting state, it is a pair-breaking mechanism and lowers the critical temperature from the value T_c^{bs} to a value T_c^{sf}.[2] The width of the superconducting transition gives the difference between these quantities ($\Delta T_c^{sf} = T_c^{bs} - T_c^{sf}$)[3]. An analysis[1] has shown that the most acceptable model is in this case that of localized spin fluctuations (LSF), which was developed recently by Rivier and co-workers[4,5]. Allowance for the fluctuations of the spin of the resonant electrons in the Friedel-Andersen model leads to the appearance of a high-temperature minimum of the resistivity.

Naturally, the applicability of this model to concentrated alloys is far from obvious, although the methods of obtaining virtual bound states near the Fermi level are not stipulated in[4,5]. We show in the present paper that the source of the anomalous kinetic properties of the concentrated alloys, just as in the LSF model, is the incomplete collectivization of the d electrons. As a proof, it was proposed to observe a common tendency for the anomalies to become weaker in the series V – Nb – Te (when these elements are fused with Ti), because it is in this direction that the width of the D band increases and the density of the D states on the Fermi level decreases[6-8]. To this end, we measured the resistivity of the alloys Ti_x-Nb_{1-x} and Ti_x-Ta_{1-x} in the entire range of concentrations where quenching fixes a β-solid solution with bcc structure. We shall compare below all three systems of alloys.

Figures 1 and 2 show plots of $\rho(T)$ for Ti-V and Ti-Nb alloys, quenched from 1100°C in water (with the exception of the Ti-25%Nb sample). We see that in none of the Ti-Nb samples was a negative temperature coefficient of resistivity observed, whereas in Ti-V this effect is clearly pronounced and depends little on the quenching temperature. For only one sample, Ti-25%Nb, it was possible, by quenching it from 900°C, to obtain a $\rho(T)$ curve with a negative temperature coefficient of resistivity (it is shown in Fig. 2). This agrees qualitatively with the fact[9] that anomalous $\rho(T)$ dependences can be obtained in Ti-Nb only in a narrow region of concentrations and quenching temperatures. In Fig. 1 one can see quite distinctly the divergence of the $\rho(T)$ curves with decreasing temperature. It is

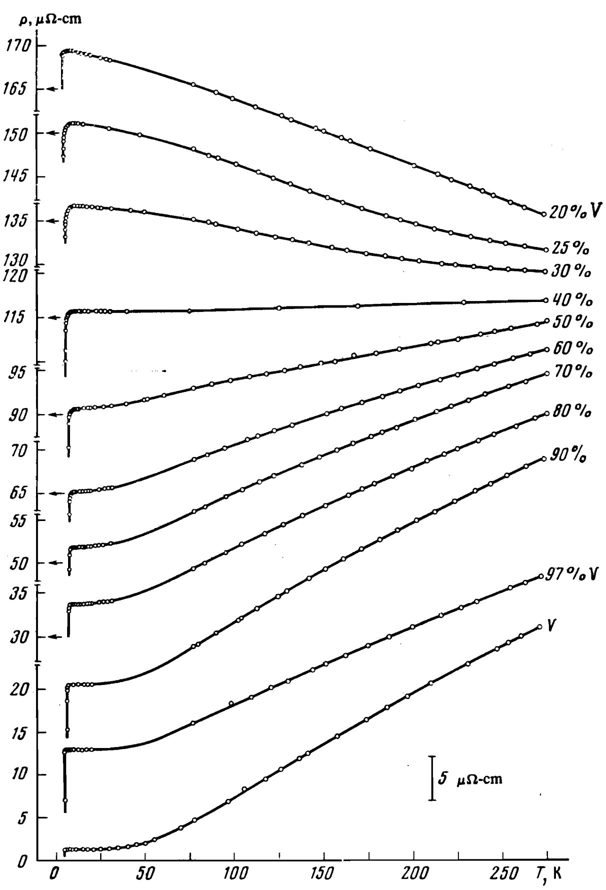

FIG. 1. Temperature dependence of the resistance of the alloys Ti_x/V_{1-x}.

noticeable also in Fig. 2, but already quite weakly. We do not show the analogous plots for Ti-Ta. They have no pronounced singularities and it appears that in their case it is impossible to obtain curves with a negative temperature coefficient of resistivity. There is also practically no divergence.

Another feature of the properties of the normal state is the unusually large residual resistivity. It is seen from Fig. 3 that it reaches the largest values in the case of Ti-V and decreases in alloys with Nb and Ta (see also[10]. A very sharp peak is observed in the concentration dependences of the residual resistivity at $x \approx 0.8$.

We proceed now to analyze the singularities of the superconducting transition. The parameters T_s^{bs}, T_c^{sf}, and ΔT_c^{sf} for the systems with V and Nb have already been published[1,11]. In Fig. 4 we show data for the system with Ta. Since the parameter ΔT_c^{sf} reflects the effect of the spin suppression of the superconductivity, it is reasonable to compare the three systems relative to this parameter. It is easily seen from Fig. 5 that the largest suppression occurs in the case of Ti-V, and is smallest in the case of Ti-Ta.

As already reported[11], a region with a sharp transition up to $x \lesssim 0.07$, coinciding with the minimum of the $T_c(x)$ curve, was observed,in the Ti-Nb system. As seen from Fig. 5, this singularity is repeated also in the Ti-Ta system, but in a wider range of concentrations $x > 0.1$. In Ti-V alloys, no such singularity could be observed because alloys with less than 3 at.% Ti were not investigated, although according to the data of Muller[12] at 1.5 at.% Ti the temperature T_c is increased by $\sim 0.1°$K in comparison with pure V. It appears that the alloys $Ti_{0.07}$-$Nb_{0.93}$ and $Ti_{0.1}$-$Ta_{0.9}$ in systems with Nb and Ta play respectively the role of the same matrix in the appearance of the spin inhomogeneities as played by V in the Ti-V system.

From an analysis of the experimental data, with the possibility of obtaining a negative behavior of the $\rho(T)$ curves, the value of the residual resistivity, the maximum effective suppression of superconductivity, and the concentration shift of the instant of appearance of spin fluctuations as examples, it follows that all the anomalies of in the properties become weaker in the alloys of Ti with V, Nb, and Ta in succession. We propose that this is the result of the broadening of the d band in the direction from V to Ta. The addition of Ti probably leads to an overall narrowing of the d-band, as a requirement for the appearance of quasistationary states with LSF. Since these phenomena occur in concentrated alloys, a natural difficulty arises in explaining the structure of the electron spectrum with virtual states, which is suggested by the LSF model[5].

Our data indicate that an important role can be played here by the deformation of the lattice. Additional investigations were carried out in the Ti-V with an aim at obtaining the complete picture of the variation of the parameters T_c^{bs} and T_c^{sf} with changing Ti concentration. Figure 6 shows both previously obtained data and new data. It was observed that the $T_c^{bs}(x)$ curve has a sharp dip in the same concentration region ($x = 0.8$) as

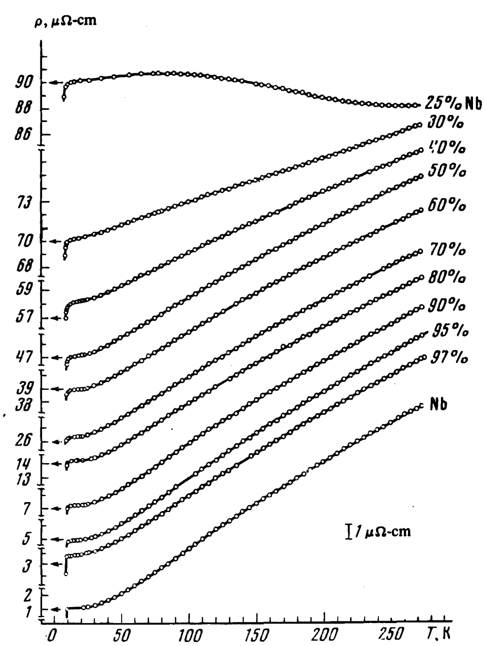

FIG. 2. Temperature dependence of the resistivity of the alloys Ti_x-Nb_{1-x}.

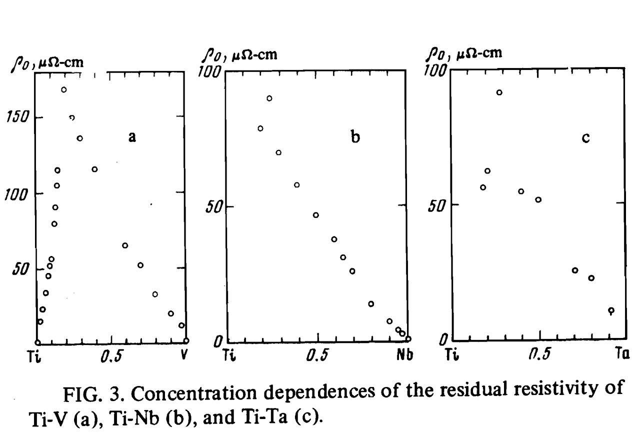

FIG. 3. Concentration dependences of the residual resistivity of Ti-V (a), Ti-Nb (b), and Ti-Ta (c).

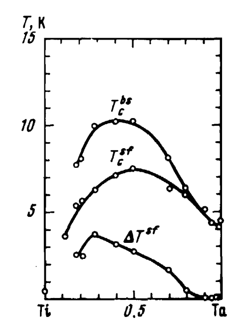

FIG. 4

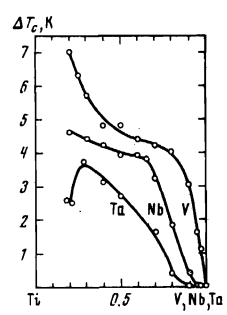

FIG. 5

FIG. 4. Concentration dependences of the parameter T_c^{bs}, T_c^{sf}, and T_c^{sf} for the alloys Ti_x-Ta_{1-x}.

FIG. 5. Concentration dependences of the parameter ΔT_c^{sf} for three systems of alloys: Ti-V, Ti-Nb, and Ti-Ta.

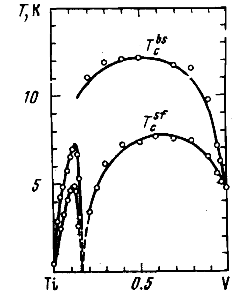

FIG. 6. Complete picture of variation of the parameters T_c^{bs} and T_c^{sf} in the alloy system Ti-V with the sharp dip in the region of existence of the metastable ω phase.

the $T_c^{sf}(x)$ curve. This is the region of the existence of the intermediate ω phase. Since the ω phase is produced with practically zero energy loss[13], it can be assumed that the lattice becomes unstable at concentrations located to the right and to the left of x_ω. Then the instant of the appearance of the LSF determines automatically the instant of the appearance of the lattice instability. Direct attempts to observe instability here are unknown to us, but an indirect confirmation may be provided by the singularities of the structural state, which leads to diffuse x-ray scattering. Diffuse scattering effects have recently been theoretically interpreted in terms of fluctuating displacement waves[14].

A very interesting fact is the initial decrease of T_c when small amounts of Ti are added to Nb and Ta, and the simultaneous absence of anomalies of the superconducting transition in this concentration region. This permits an analysis of the cause of the deviation of the temperature dependence of the specific heat at $T \ll T_c$[15,16] from the form predicted by the microscopic theory of superconductivity. This property was interpreted as an attribute of the superconducting state, characterized by two energy gaps of the s and d type, and by two critical temperatures.

Our experiments also offer evidence of two critical temperatures, T_c^{sf} and T_c^{bs}. We can accordingly postulate two groups of electrons capable of superconducting condensation. But the presence of concentration regions with sharp transitions automatically excludes "two-band behavior" in Nb and Ta, which contradicted the experimental data available until recently[16].

Another explanation may be the following: in addition to the usual contributions, the experimentally measured specific heat contains a magnetic contribution due to inhomogeneities of the spin structure. But in this case there must of necessity follow the existence of spin fluctuations in pure Nb and Ta, a fact that contradicts the above-described concentration shift in the appearance of the LSF.

Recent papers have resolved these difficulties. It was shown that pure Nb does not have a second energy gap[17], and the previously observed anomalies are due to impurities[18]. These facts cast doubts on the validity of the assumption of the two-band origin of the anomalous specific heat and, conversely, corroborate the point of view that it is of magnetic origin. A strong argument is also the phenomenon of the turn-up of the temperature dependence of the specific heat in titanium-rich Ti-V alloys[19]. This phenomenon was observed in a number of nonsuperconducting alloys and was explained by Benneman[20] as being a paramagnetic contribution.

Thus, the proposed approach using the spin-fluctuation mechanism makes it possible to explain, in a unified scheme, a large number of properties of the normal and superconducting states of binary alloys of transition elements of groups IV and V of the periodic system.

Naturally, further experimental research is necessary to confirm the spin-fluctuation mechanism and to reveal its causes.

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