INVESTIGATION OF THE SUPERCONDUCTING STATE OF SOLID SOLUTIONS OF THE NIOBIUM-TITANIUM SYSTEM

B. Ya. SUKHAREVSKIĬ, I. S. SHCHETKIN, and I. I. FAL'KO

Physico-technical Institute of Low Temperatures, Ukrainian Academy of Sciences

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Results are presented of investigations of the superconducting transition of solid solutions of the niobium-titanium system, carried out by the specific-heat method. Relations are obtained between the superconducting parameters (temperature of the transition to the superconducting state, energy gaps, and pre-exponential factors) as functions of the titanium concentration in the solid solution. Good correlation is observed between the ratio of the energy gaps, the transition temperature, and the pre-exponential factors.

MUCH attention is being paid presently to the study of singularities of the superconducting state of crystals containing a noticeable amount of impurities. Interest in impurity superconductors and alloys is due, on the one hand, to further development of the concepts concerning the nature of such superconductors and, on the other, to the fact that such objects make the attainment of high critical parameters realistic, making it possible to use superconductivity in practice.

Impurity superconductors and alloys are, as a rule, superconductors of the second kind with strong coupling. Recently, a number of theoretical and experimental papers have been published devoted to the study of these objects. But significant progress was noted only in the case of superconductors with low impurity concentrations.

We present here the results of investigations of the superconducting transition of solid solutions of the niobium-titanium system, carried out by the specific-heat method. The results of direct measurements of the specific heat in the interval 2.5–20°K, with accuracy 3–0.5%, on samples of homogeneous solid solutions with titanium concentrations 10, 25, 50, 75, and 80 at.%, are described in[1]. The same reference gives data on the procedure used to investigate the specific heat, the methods of obtaining the samples, the heat treatment, and the control of their homogeneity.

The electronic component of the specific heat is separated by plotting the dependence of C/T on T^2 in the normal state. The validity of such an operation in our case is discussed in[2]. The analytic continuation of the temperature dependence of the lattice specific heat from the normal state to the superconducting region is based on the assumption that the phonon spectrum is not altered by the superconducting transition. This assumption was confirmed by a number of investigators[3,4] in the case of superconductors with weak coupling. Shen[5], using the tunnel-spectroscopy method, confirmed the absence of changes in the photon spectrum on going over to the superconducting state for tantalum which, like the isomeric niobium, is a superconductor with strong coupling.

The values of the electronic specific heat calculated in the indicated manner for the superconducting region were used to construct plots of $\ln C_{es}(T)/\gamma T_c$ against T_c/T, in order to determine the energy gaps of samples with different titanium concentrations in the solid solution ($C_{es}(T)$ is the temperature dependence of the electronic specific heat, γ is the coefficient of the specific heat in the normal state, and T_c is the transition temperature).

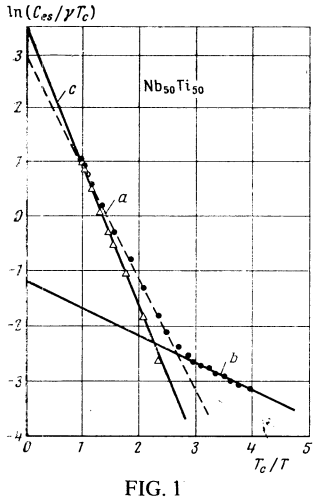

FIG. 1

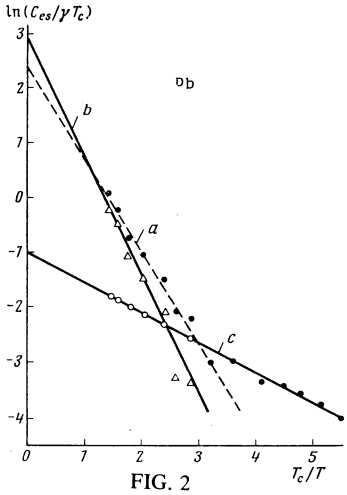

FIG. 2

FIG. 1. Behavior of the specific heat of a sample 50% Nb + 50% Ti as a function of $\ln C_{es}(T)/\gamma T_c$ vs. T_c/T. ●–experimental values; Δ–specific heat from the d-band (the specific heat of the s-band is subtracted); a–the slope of the dashed line determines the gap of the d-band, if no account is taken of the specific heat of the s-band; b–the slope of this straight line determines the gap of the s-band; c–the slope of the solid line gives a more accurate value of the d-band gap.

FIG. 2. Behavior of the specific heat of lead in the dependence of $\ln C_{es}/\gamma T_c$ on T_c/T. ●–experimental values; Δ–specific heat of p-band (the specific heat of the s-band is subtracted); a–dashed line, determining the parameters of the p-band without allowance for the s-band; b–line determining the parameters of the p-band (Δ^p and a^p) more accurately (the specific heat of the s-band is subtracted); c–line determining the parameters of the s-band.

Figure 1 shows by way of an example such a dependence for a sample 50% Nb + 50% Ti. The plots for the other compositions are of similar form. Attention is called to the positive deviation from the experimental points (black circles in Fig. 1) from the straight line at low temperatures. According to the general microscopic theory of superconductors[6,7], the dependence

$$C_{es}(T) / \gamma T_c = a \exp(-\Delta / T) \quad (1)$$

should hold at sufficiently low temperatures, where the gap remains practically constant $\Delta(T) \approx \Delta(0)$. One could expect a weak negative deviation from the linear dependence of $\ln C_{es}(T)/\gamma T_c$ on T_c/T, due to a certain increase of the gap with decreasing temperature. The behavior of the electronic specific heat, similar to that shown in Fig. 1, is interpreted for the case of pure superconductors (Nb, Ta, V[8,9], Pb[10,11], and others) by using the model of two overlapping bands proposed in[12,13].

In recent publications, the presence of two-gap superconductivity in niobium and in tantalum is confirmed to a definite degree by tunnel-spectroscopy data[14,15]. The singularity produced on the current-voltage curve by the second gap is negligible, this being fully explained by an analysis[16] of the capabilities of the tunnel method. For Pb, in particular, the two-gap character of whose superconductivity is universally conceded, no second gap has been noted so far on the current-voltage characteristic. At the same time, the presence of two energy gaps has a very strong influence on the electronic specific heat.

Figure 2 shows the temperature dependence of the electronic specific heat of lead, constructed from the experimental data[10]. This dependence can be described by the relation

$$C_{es} / \gamma T_c = a^p \exp(-\Delta^p / T) + a^s \exp(-\Delta^s / T). \quad (2)$$

The second term in (2) describes the contribution made to the electronic specific heat by the band with the smaller energy gap Δ^s. At sufficiently low temperatures (for Pb we have $T_c/T > 3$), the contribution from the s-band becomes predominant, so that the slope of the line c (Fig. 2) determines directly the value of Δ^s, and the intercept of this line with the ordinate axis gives the pre-exponential factor a^s, which is proportional to the density of states of the s-band.

With lead as an example, we see that the contribution from the s-band to the electronic specific heat can be appreciable at relatively high temperatures. In this case, to separate the contribution from the ground band (the p-band for lead) it is necessary to subtract the specific heat determined by the band with the smaller gap from the experimentally obtained values of the electronic specific heat.

The contribution made to the specific heat by the ground band is described by the linear dependence of $\ln C_{es}(T)/\gamma T_c$ on T_c/T (line b in Fig. 2). The pre-exponential factor and the value of the gap of the p-band, determined with the aid of the line b (Fig. 2), differ noticeably from the values obtained by Keesom and Van der Hoeven[10] from the experimental dependence (line a in Fig. 2).

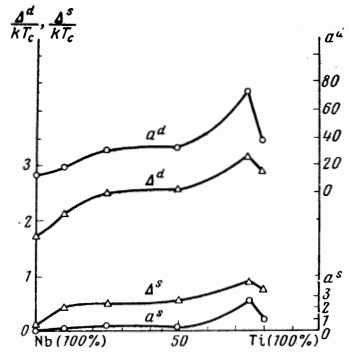

FIG. 3. Behavior of energy gaps Δ^d/kT_c and Δ^s/kT_c and of the pre-exponential factors a^d and a^s as functions of the concentration of titanium in the solid solution; Δ^d and Δ^s–behavior of the energy gaps of the d- and s-bands (in relative units) as functions of the titanium concentration; a^d and a^s–behavior of the pre-exponential factors for the d- and s-bands as functions of the titanium concentration.

The fact that the specific heat of each of the bands is described sufficiently well by an exponential function in a wide temperature interval $T_c/T > 1.5$ agrees with the results of[17], in which it was shown that in the case of strong coupling the value of the gap $\Delta(0)$ extends to higher temperatures than for superconductors with weaker coupling[6,7]. The latter is confirmed also by investigations of the temperature dependence of the gap of niobium, performed by the method of absorption of ultrasound[18], and from data of magnetic measurements[19]. Judging from the diagram shown in[19], the gap remains practically constant up to $0.7\,T_c$.

The similarity of the temperature dependence of the specific heat of lead (Fig. 2) and of solid solutions of the niobium-titanium system (e.g., Fig. 1) allows us to assume that for these solutions the presence of two linear sections on the diagrams, just as in the case of lead, is due to the presence of two-band superconductivity.

Starting from this assumption, the specific heat of the investigated solid solutions of the niobium-titanium system was analyzed using a model of two partly overlapping bands (2). The results of such an analysis are shown in Fig. 3 and in the table, which gives the values of the energy gaps of the d- and s-bands and the corresponding pre-exponential factors in the dependence on the concentration of the titanium in the solution.

We note that there is an explicit correlation between the values of the gaps and the pre-exponential factors.

Dependence of the superconducting parameters of the niobium-titanium system on the concentration

Sample composition, at.%	T_c, °K	Δ^{d*}/kT_c	Δ^d/kT_c	Δ^s/kT_c	Δ^d/Δ^s	a^{d*}	a^d	a^s	a^d/a^s
Nb [8,9]	9.26	1.46	1.73	0.12	14.4	7.0	12.7	0.0066	2000
$Nb_{90}Ti_{10}$	8.90	1.60	2.13	0.42	5.07	9.6	18.5	0.250	74.0
$Nb_{75}Ti_{25}$	9.72	1.68	2.50	0.45	5.56	11.6	31.5	0.428	73.6
$Nb_{50}Ti_{50}$	9.32	2.05	2.55	0.50	5.10	19.5	32.8	0.300	109.3
$Nb_{25}Ti_{75}$	6.09	1.67	3.15	0.89	3.54	11.6	73.7	2.800	26.3
$Nb_{20}Ti_{80}$	6.95	2.06	2.90	0.73	3.97	19.1	35.6	1.060	34.5
Pb [10,11]	7.19	1.68	2.17	0.55	4.00	10.7	19.1	0.367	52.1

*Values obtained without subtracting the specific heat due to the s-band.

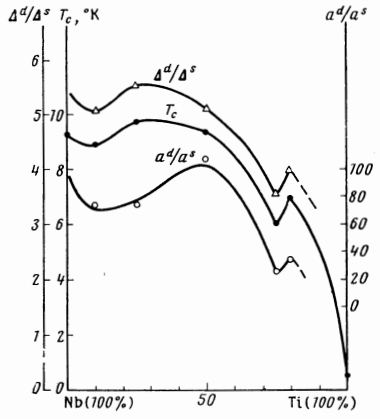

FIG. 4. Concentration dependence of the ratio of the energy gaps of the d- and s-bands, Δ^d/Δ^s, of the transition temperature T_c, and of the ratio a^d/a^s of the pre-exponential factors.

At a concentration ~ 80 at.% Ti all the relations obtained by us have a singularity which, like the singularities of the other characteristics (critical temperature, density of states, Debye temperature, jump of specific heat[1]), is probably connected with the appearance of traces of the second phase at these concentrations; this does not contradict the known diagram of states for the niobium-titanium system[20].

Figure 4 reveals a distinct correlation between the ratio of the energy gaps, of the pre-exponential factors, and the critical temperature, in agreement with the conclusions of the theory of two-band superconductivity[12,13,17]. However, the interpretation of the specific heat of alloys of the niobium-titanium system in the model of two overlapping bands is subject to a certain doubt, for in the case of a large impurity-atom concentration the scattering by the impurities intermixes the states corresponding to different bands, and consequently such a superconductors should behave like single-band ones. The same conclusion is reached also by a theoretical analysis of the influence of contamination on two-gap superconductivity[21-23]. Moreover, experimental investigations of the specific heat indicate that an alloy of lead with 5.93 at.% indium behaves like a single-band superconductor, although at a concentration of 1.71 at.% indium the two-band superconductivity is still retained[11].

We note, however, that the situation with niobium, and apparently with solid solutions on its basis, is unusual. Thus, numerous investigations of ~ 99.8—99.9% pure niobium point to the existence of two-band superconductivity[8,9,24], in spite of the fact that the electron mean free path in such niobium samples is $\sim 4 \times 10^{-7}$ cm, i.e., of the same order as in solid solutions of the niobium-titanium system ($\sim 10^{-7}$ cm[25,26]). In this connection, it is interesting to note that, as stated in[27], the electron mean free paths in niobium and in solid solutions of the niobium-titanium system are commensurate with the coherence length.

On the other hand, in spite of the doubts expressed above, we see no other explanation for the temperature dependence observed by us in the electronic specific heat of niobium-titanium solid solutions. We note that in view of the lack of theoretical studies of the electronic structure of superconducting alloys with large impurity concentrations, we are forced to leave open the question of the cause of the possible appearance of two-band superconductivity in our case.

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