Superconductivity and electron structure of a solid solution of titanium in niobium

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Extensive information on the electronic and superconducting characteristics of a solution of Nb + 7.23 at.% Ti is obtained by measuring the temperature dependence of the specific heat in the temperature range from 2.5 to 18° K. It is established that the alloy is a superconductor with strong electron-phonon interaction. This is confirmed by the magnitude of the specific-heat discontinuity and by the temperature behavior of the thermodynamic critical magnetic field. An anomalous behavior of the low-temperature specific heat is observed and can be described satisfactorily by the theory of superconductivity which takes into account overlapping of the energy bands. The main parameters of the bands are obtained by treating the experimental data in the two-band model. It is shown that the alloy studied is an interesting case in which the coupling is weak in one band (the d band), of the BCS type, and strong in the other. The applicability of the Anderson criterion to two-band superconductors, when formulated for one-band anisotropic superconductors, is discussed.

In the present work, the results are given of an investigation of superconducting and electronic characteristics of the solid solution Nb + 7.23 at.% Ti, obtained by measurement of the temperature dependence of the specific heat.

The measurement of the specific heat was performed on an annealed sample[1)] in the temperature range 2.5—18° K, which included the region of the phase transition into the superconducting state. Several series of measurements (about 200 experimental points) have been carried out, which permits us to give a very reliable temperature dependence of the specific heat of the alloy studied (Fig. 1). The points of the different series of measurements lie in a row or coincide; the maximum error is ~3% at temperatures 2.5—5° K, about 1% in the region 5—8° K, and less than 1% for higher temperatures. In Fig. 1, the open circles denote the experimental values of the total specific heat, and the continuous lines represents the electronic component of the specific heat, determined by plotting C/T as a function of T^2 for $T > T_c$ (the validity of such an operation was discussed in[1,2]). The slope of the straight plot of C/T against T^2 lets us determine the characteristic Debye temperature θ_D, which is equal to 245° K, and the intercept of the line with the ordinate axis characterizes the coefficient for the electronic specific heat of the normal state: γ = 11.2 mJ/mole-deg.[2] The density of electronic states on the Fermi surface is therefore N(0) = 4.75 levels/eV-atom.

Analyzing the plot of the specific heat (Fig. 1), we note that a discontinuity in the specific heat is observed in our alloy at the temperature T_c = 9.53° K, which defines the temperature of the superconducting transition. The discontinuity in the specific heat is sufficiently strong, with a sharp maximum, which demonstrates the homogeneity of the sample. Special measures were used in this case: the sample was annealed for 100 hours in a vacuum at the optimal temperature. Control was maintained by means of chemical and x-ray analysis.

The value of the ratio of specific heats in our case, $\alpha = C_{es}(T_c)/C_{en}(T_c) = 2.66$, exceeds the value $\alpha = 2.43$ which follows from the microscopic theory of superconductors with weak coupling. The anomalously large discontinuity in the specific heat is explained within the framework of the theory of Geĭlikman and Kresin,[3,4] who took into account the strong electron-phonon interaction.

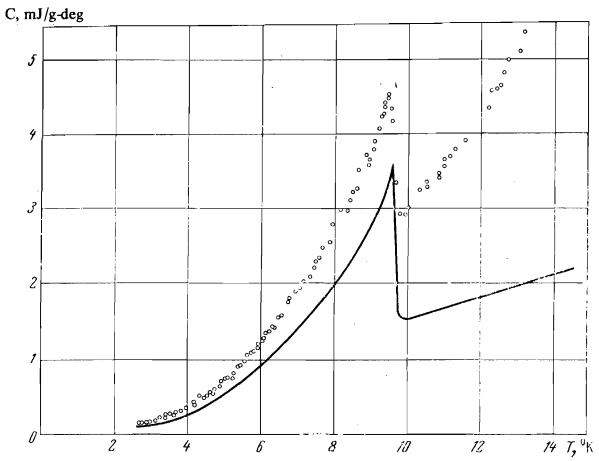

FIG. 1. Temperature dependence of the specific heat of the solid solution Nb + 7.23 at. % Ti; open circles—experimental points for the total specific heat; solid line—electronic component of the specific heat.

Thus the solid solution Nb + 7.23 at.% Ti, also pure niobium, must be regarded as a superconductor with strong coupling. This is confirmed by the character of the temperature dependence of the thermodynamic magnetic field $H_c(T)$, which has been calculated by us from experiments on the specific heat of the sample. To calculate $H_c(T)$ we used the relation

$$F_n - F_s = H_c^2/8\pi, \qquad (1)$$

which relates the difference in the free energies of the normal (F_n) and superconducting (F_s) states (computed from the corresponding specific heats) with the value of the critical field. The strong electron-phonon interaction is evidenced by the positive departure of $H_c(T)$ from a parabolic dependence—see Fig. 2. The figure shows also the corresponding dependences for lead and mercury, which are also characterized by strong coupling, and also the curve plotted from the BCS theory.

For the determination of the temperature dependence of the energy gap, it is first necessary to find the value

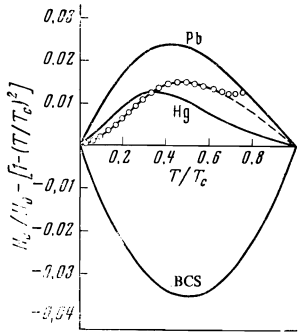

FIG. 2. Difference in the thermodynamic critical fields H_c/H_0 obtained by experiment and the parabolic dependence $1-(T/T_c)^2$. The open circles indicate the critical field for the composition Nb + 7.23 at. % Ti (H_0 = 2200 Oe).

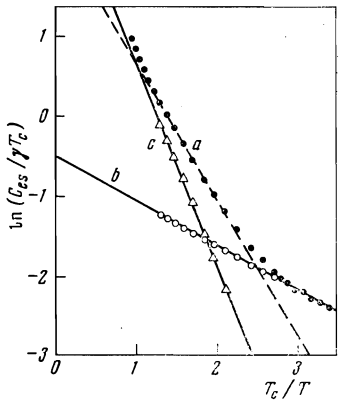

FIG. 3. Temperature dependence of the electronic specific heat in semi-logarithmic coordinates: filled circles–experimental values of the specific heat; open circles–the contribution to the specific heat from the s band for higher temperatures; triangles–values of the specific heat of the d band. The slope of the dashed line a determines the value of the effective energy gap $\Delta^*(0)$, which represents the superposition of the gaps of the s and d bands. The lines b and c give values of the gap in the s and d bands, respectively.

of the gap at zero, $\Delta(0)$. For this purpose, we constructed a semi-logarithmic graph of the experimental values of $C_{es}/\gamma T_c$ as a function of T_c/T (Fig. 3). The slope of the dashed straight line a on this diagram gives the value of the effective energy gap, which is equal to 1.78 kT_c in our case. The temperature dependence of the gap near T_c is given by the square-root relation[3,4]

$$\frac{\Delta(T)}{T}\Big|_{T\to T_c} = \beta\left[1-\frac{T}{T_c}\right]^{1/2}, \qquad (2)$$

in which the coefficient β is connected with the discontinuity of the specific heat by the relation

$$a = C_{es}(T)/C_{en}(T) = 1 + (3/2\pi^2)\beta^2. \qquad (3)$$

Using the experimentally found values of the discontinuity of the specific heat and $\Delta(0)$, we obtain the temperature dependence of the energy gap for the solid solution Nb + 7.23 at.% Ti (Δ^* on Fig. 4).

Attention should be called to the strong positive deviation of the specific heat at low temperatures from linearity (Fig. 3). A similar behavior of the specific heat is observed in pure two-band semiconductors (Pb, Nb, etc.). This singularity of the specific heat at low temperatures cannot be due to experimental errors, inaccuracy of separating the electronic component of the specific heat, presence of inhomogeneities, etc. More acceptable from our point of view is the interpretation

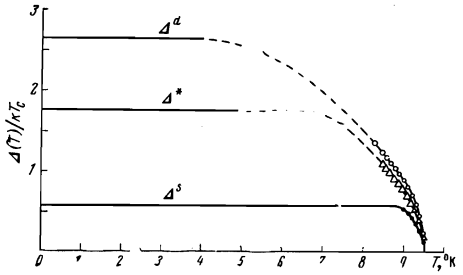

FIG. 4. Temperature dependence of the energy gap in the d band (Δ^D), the effective value (Δ^*) and in the s band (Δ^*).

of the experimental data on the specific heat in the model of two overlapping energy bands, proposed by V. A. Moskalenko.[5]

The basic argument against such an interpretation for impurity superconductors and alloys is connected with the problem of the relation of the free path length l and the coherence length ξ, inasmuch as such objects generally have a small free path length and the Anderson criterion relating these quantities may not hold.[6] Namely, if the free path length is greater than or of the order of the coherence length, then the scattering by impurities will be rather small in this case and anisotropy of the energy gap may be observed. The presence of impurities smooths out the anisotropy. However, there is today no single, quantitative, theoretically-based criterion whereby a superconductor can be regarded as either pure or impure (in the sense of the appearance of a two-band character), while experiments quite definitely indicate in many cases the appearance of two bands in impurity superconductors and alloys.[7-11]

It is possible that in some solid solutions, even for a high impurity content, the free path length remains greater than the coherence length, and the criterion is not violated. This evidently occurs in solid solutions of the niobium-titanium system. Thus it is shown[12] that for the alloys Nb + 17% Ti, Nb + 37% Ti etc., the free path length is of the order of the coherence length. A similar ratio of l/ξ_0 can be expected also in the case of a solid solution with 7% titanium.

Actually the estimates of the coherence length ξ_0 and the free path length of the electrons l for the alloy with 7.23% Ti confirm that our sample lies in the pure range. The coherence length has been determined from the relation

$$\xi_0 = \hbar v_F/\pi\Delta(0), \qquad (4)$$

where v_F is the velocity on the Fermi surface.

This velocity was obtained for the solid solution Nb + 7.23 Ti from data for the Fermi velocity of niobium ($v_F = 2.6\times10^7$ cm/sec[13,14]) and our experimental values on the density of the electronic states.

The correction to v_F, which is connected with the difference in the density of states of niobium (γ = 7.8 mJ/mole-deg^2) and the solid solution Nb + 7.23% Ti, is computed by the formula (see[15], p. 16)

$$v_F(\text{Nb}+7.23\%\ \text{Ti}) = v_F(\text{Nb})\,[\gamma(\text{Nb})/\gamma(\text{Nb}+7.23\%\ \text{Ti})]^{1/3} = 2.3\cdot10^7\ \text{cm/sec} \qquad (5)$$

The coherence length computed according to (4) for the solid solution Nb ± 7.23% Ti is $\xi_0 \approx 3\times10^{-6}$ cm. Using the relation

$$\bar{l} = 6\pi^2\hbar^3 / m^2e^2v_F^2\rho_0 \qquad (6)$$

with the substitution $\rho_0 = 7 \times 10^{-6}$ ohm-cm,[2)] we obtain the free path length $l = 3 \times 10^{-5}$ cm, whence $l/\xi_0 \approx 10$, so that, according to the Anderson criterion, the anisotropy should be preserved in such a sample.

Nevertheless, we consider it necessary to remark that superconductors with several overlapping bands are not the extreme case of single band of anisotropic superconductors, and the criteria for them should be different.

In two-band superconductors, the experimentally determined mean path length is itself the superposition of the band and interband mean free paths, which are proportional to the relaxation time. The relaxation time in the bands, τ_{11} and τ_{22}, exert no effect on the intermingling of the wave functions, since the electrons remain in their bands after being scattered. The interband relaxation time τ_{12} (or τ_{21}) and the corresponding free path length l_{12} are important. Consequently, the criterion for the appearance of overlapping bands will be a condition of the type

$$l_{12(21)} \gtrsim \xi_0. \qquad (7)$$

This criterion is apparently less stringent than the Anderson criterion. Actually, if we assume that the transition probability of electron from one band to the other as a result of scattering is less than the probability for the electron to remain in its band, then the relaxation time τ_{12} will be greater than τ_{11} and τ_{22}. Then the interband path length τ_{12} turns out to be greater than the mean value determined experimentally.

If we set $\tau_{11} = \tau_{22} = \tau_{12}$, we then obtain $l_{12} = 3\bar{l}$ from the relation

$$1/\bar{l} = 1/l_{11} + 1/l_{22} + 1/l_{12(21)} \qquad (8)$$

Furthermore, if $\tau_{12(21)} < \tau_{11}$ and τ_{22}, then $l_{12} > \bar{l}$, inasmuch as there is a positive contribution to the right side of (8), due to l_{11} and l_{22}.

Thus, two cases are possible: a) $l_{12} > \xi_0$, $\bar{l} > \xi_0$; b) $l_{12} \gtrsim \xi_0$, while $\bar{l} < \xi_0$, i.e., two-bandedness can evidently appear even when the mean free path is less than the coherence length.

Satisfaction of the stricter Anderson criterion in the solid solution Nb + 7.23% Ti means that the condition (7) is certainly satisfied. This allows us to treat the experimental data on the specific heat for the investigated material in the model of two overlapping bands.

Constructing a graph of the experimental values of the specific heat in semi-logarithmic coordinates (Fig. 3), we determine the energy gap of the s band from the slope of the straight line b; the value of this gap is $\Delta^s(0) = 0.57kT_c$. Calculating the contribution to the specific heat from the s band for higher temperatures, in accord with the method proposed in[10], we find the component of the specific heat from the d band which is adequately described by a straight line in semi-logarithmic coordinates. The angle of inclination of the line c in Fig. 3 gives the value of the gap of the d band: $\Delta^d(0) = 2.63\ kT_c$.

In correspondence with[16,17], we determine the factors β^s and β^d before the square root and establish the temperature behavior of the energy gaps of the s and d bands (the curves $\Delta^s(T)$ and $\Delta^d(T)$ in Fig. 4).

As is seen from the drawing, the temperature dependence of the energy gap of the d band is similar to the behavior of the gap in weak superconductors, i.e., the increase in the gap near T_c is sufficiently slow and reaches $\Delta^d(0)$ at temperatures $\sim(0.4-0.5)T_c$. The gap of the s band reaches the value $\Delta^s(0)$ at $T \lesssim 0.9T_c$. Such a dependence of the energy gap is typical of strong coupling.

Consequently, the presence of strong electron-phonon interaction in the alloy Nb + 7.23% Ti is determined by the strong coupling in the s band. This again indicates that the electronic structure of the given solid solution remains similar to that of pure two-band superconductors. The interpretation of the experimental data within the framework of the theory of overlapping energy bands allows us to obtain a noncontradictory picture.

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[2)]The authors express their gratitude to E. E. Anders and I. V. Shostakova, who measured the electrical resistance of the sample.

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