SOME FEATURES OF THE TEMPERATURE DEPENDENCE OF THE SPECIFIC HEAT OF A NIOBIUM-TITANIUM ALLOY AT THE TRANSITION TO THE SUPERCONDUCTING STATE

B. Ya. SUKHAREVSKIĬ, A. V. ALAPINA, and Yu. A. DUSHECHKIN

Physico-technical Institute for Low Temperatures, Academy of Sciences, Ukrainian S.S.R.

Submitted December 8, 1967

Zh. Eksp. Teor. Fiz. **54**, 1675–1679 (June, 1968)

The specific heat of a type-II superconductor ($Nb_{0.25}Ti_{0.75}$ alloy) is measured between 4.2 and 17°K. It is suggested that the smearing of the superconducting transition in this sample is due to its inhomogeneity. A method for treating the experimental data is proposed. The method permits one to determine the transition interval to the superconducting state, the temperature dependence of the superconducting phase concentration in this interval, and the coefficients in formula (3) of the BCS theory for the electronic heat capacity of a homogeneous superconductor near T_c.

IN measuring the temperature dependence of the specific heat near the Curie point one often observes smearing of the transition which is due as a rule to the inhomogeneity of the sample.[1,2] A similar smearing may be expected in the case of a transition to the superconducting state in a type-II superconductor, especially if in preparing the sample of the alloy no special measures are taken to homogenize the solid solution carefully.

We have investigated the specific heat of the solid solution 25 at.% Nb + 75 at. percent Ti in the temperature range 4.2–17°K. The measurements were carried out in an adiabatic calorimeter. A germanium thermometer prepared and calibrated at the VNIIFTRI served as the temperature detector. The adiabaticity conditions were controlled with the aid of gold-cobalt-copper thermocouples. The error in the specific heat measurement was ~3% in the 4–6°K temperature range, ~1% between 6 and 9°K, and ≤0.5% above 9°K.

The temperature dependence of the total specific heat of the alloy is shown in Fig. 1 (curve a).

The separation of the electronic component of the specific heat is usually accomplished by plotting at sufficiently low temperatures a graph in C/T-T^2 coordinates. The electronic specific heat $C_e(T) = C - BT^3$ where B is the slope of the straight line on this graph.

In our instance this procedure must be justified for two reasons. First, the investigated sample is a solution with an atomic mass ratio of ~2. This may lead to an increase of the specific heat whose magnitude $\Delta C(T)$ can be estimated by using the results of Kagan and Iosilevskiĭ[3]. An estimate shows that the characteristic temperature of the vibrations of the "impurity" atoms ($T_0 \sim 100°$K) is larger by an order of magnitude than the temperature in the range of interest to us (up to 10°K), and the specific heat of the lattice with an account of ΔC remains proportional to T^3. Thus the presence of atoms with different masses apparently does not lead in this instance to any complications. Secondly, the indicated graphical treatment is only valid in the temperature range where $\Theta = \Theta_0 = $ const.

Inasmuch as we can plot the dependence of C/T on T^2 (Fig. 2) only at temperatures exceeding 8°K, at which the sample is certainly in the normal state, it is essen-
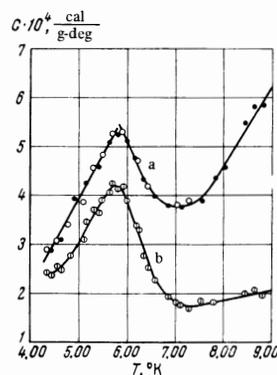

FIG. 1. The total specific (a) and electronic (b) heat capacity of an alloy near the transition to the superconducting state. The light and dark points on curve a refer to two different experiments.
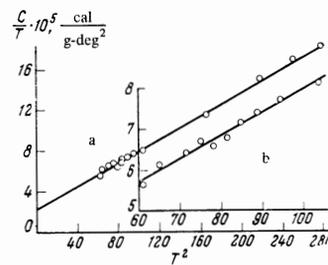
FIG. 2. The dependence of C/T on T^2. Points obtained in the range 7.8–10°K are plotted in b whose scale is four times as large as that of a.

tial that the T^3 law be valid at least up to 10°K. It follows from the data of measurements of the specific heat of titanium and niobium published in[4,5] that for the initial components the required constancy of the effective Debye temperature occurs up to 10°K. This circumstance, as well as the positions of the experimental points on Fig. 2 (a and b) permit one to hope that the T^3 law is valid for the investigated alloy in the entire temperature range of interest.

It follows from Fig. 2 that in the normal state the specific heat of the alloy is described by the relation

$$C_n(T) = 5.45\,T + 0.143\,T^3\ \text{mJ/mole-deg}\,(T \leqslant 17°\,\text{K}).$$

The Debye temperature of the alloy $\Theta_0 \approx 239°$K; the coefficient for the electronic specific heat $\gamma = 5.45$ mJ/mole-deg^2.

Making use of the generally accepted conception concerning the unchanged nature of the lattice specific heat at the superconducting transition, we calculate the electronic specific heat of the alloy in the entire investigated temperature range (Fig. 1, curve b), subtracting from curve a (Fig. 1) the lattice specific heat of $0.143T^3$ mJ/mole-deg = $0.575 \times 10^{-6}T^3$ cal/g-deg. In accordance with numerous experimental data and the

BCS theory (see, for example,[6]) the electronic specific heat should experience a sharp jump at the transition point T_c. On the other hand, in our instance the nature of the temperature dependence allows one to assume that the transition to the superconducting state is smeared out and occurs within a temperature range of $\sim 2°$K.

Such smearing is apparently due to some inhomogeneity of the sample, for instance an inhomogeneity of the composition or of the mechanical stresses. In such a case one can consider the sample as a mixture of "homogeneous volumes," each of which has a definite transition temperature τ. The relative size of the volumes whose transition points lie in the interval between τ and $\tau + d\tau$ is $(\partial x/\partial \tau)d\tau$ where x(T) is the concentration of the superconducting phase in the sample at a temperature T. Assuming that the inhomogeneity of the sample is sufficiently small, so that the coefficient γ for the electronic specific heat of the normal state has the same value in all "homogeneous" volumes, we write

$$C_e(T) = \gamma T(1-x) + \int_{T_1}^{T} \frac{\partial x}{\partial \tau} C(T, \tau) d\tau, \tag{1}$$

where $C(T, \tau)$ is the specific heat of a homogeneous superconductor with a transition temperature τ at a temperature T; T_1 is the temperature at which the transformation begins: $x(T_1) = 0$, $\partial x/\partial T|_{T \geq T_1} = 0$.

Relation (1) is also valid for a sharp transition when x(T) changes jumpwise from zero to unity. In this case

$$\frac{\partial x}{\partial \tau} = -\delta(\tau - T_c),$$

$$\int_{+\infty}^{\infty} \frac{\partial x}{\partial \tau} d\tau = -1, \quad \lim_{\tau \to T_c} \frac{\partial x}{\partial \tau} = -\infty, \quad \frac{\partial x}{\partial \tau} = 0 \quad \text{for } \tau \neq T_c,$$

and expression (1) transforms into

$$C_e(T) = \gamma T \quad \text{for} \quad T > T_c,$$

$$C_e(T) = \int_{-\infty}^{\infty} \delta(\tau - T_c) C(T, \tau) d\tau = C(T, T_c) \quad \text{for } T \leqslant T_c.$$

Differentiating (1), we obtain

$$\frac{\partial C_e}{\partial T} = \gamma(1-x) - \gamma T \frac{\partial x}{\partial T} + C(T, T) \frac{\partial x}{\partial T} + \int_{T_1}^{T} \frac{\partial x}{\partial \tau} \frac{\partial C(T, \tau)}{\partial T} d\tau, \tag{2}$$

whence it follows that the dependence $C_e(T)$ is smooth to the extent to which x(T) is smooth, i.e., in a smeared transition $C_e(T)$ has a continuous curvature and not a jump.

According to BCS theory $C(T, \tau)$ is a universal function with one parameter—the transition temperature. In the range $0.7T_c < T < T_c$ which practically covers the temperature range of interest to us, the deviation of this function from a linear dependence of the form

$$\gamma^{-1} C(T, \tau) = \alpha \tau + \beta(T - \tau) \tag{3}$$

does not exceed 1 percent (see Table IV in[6]).

According to BCS theory the coefficients α and β are universal constants with values of 2.4 and 4.8 respectively. However, the empirical values of these coefficients for various superconductors differ somewhat from these values. Nevertheless, assuming the inhomogeneity of the sample to be sufficiently small, we shall assume that the BCS conclusion regarding the universal nature of α and β can be extended to all "homogeneous volumes" of the investigated sample.

Employing (2) and (3), we have

$$\partial C_e / \partial T = \gamma \beta \quad \text{for} \quad T \leqslant T_2,$$
$$\partial C_e / \partial T = \gamma \quad \text{for} \quad T \geqslant T_1$$

[T_2 is the temperature at which the transition ends: $x(T_2) = 1$, $\partial x/\partial T|_{T \leq T_2} = 0$] which makes it possible to find from the data shown on curve b of Fig. 1 that $T_1 \approx 7.4°$K, $T_2 \approx 5.6°$K and $\beta = 7.6$ [from the slope of the linear portion of $C_e(T)$ for $4.8 < T < 5.6$].

In order to estimate α, we integrate the second term in (1) by parts and apply the mean-value theorem. As a result we find

$$\alpha = \left[\frac{C_e(T_2)}{T_2} + x(\Theta) \frac{T_1 - T_2}{T_2} \beta \right] / \left[1 + x(\Theta) \frac{T_1 - T_2}{T_2} \right], \tag{4}$$

where $T_2 < \Theta < T_1$. Since $C_e(T_2)/\gamma T_2 \approx 3$ (see curve b on Fig. 2), it follows from (4) that $3 < \alpha < 4.1$.

It is also easy to show with the aid of (1) that for $\beta > \alpha$ the value $\alpha_{exp} = C_e(T_m)/\gamma T_m$ found from the height of the maximum of curve b (Fig. 1) is certainly less than the actual ratio of the specific heat of the superconducting and normal states at the transition point α.

Substituting (3) in (2), we obtain a differential equation with respect to x(T):

$$\frac{\partial x}{\partial T} + \frac{x}{T} \frac{\beta - 1}{\alpha - 1} = \left(\frac{1}{\gamma} \frac{\partial C_e}{\partial T} - 1 \right) / T(\alpha - 1), \tag{5}$$

whose solution is

$$x = \frac{1}{\alpha - 1} T^{-(\beta-1)/(\alpha-1)} \int_{T_1}^{T} \left(\frac{1}{\gamma} \frac{\partial C_e}{\partial T} - 1 \right) T^{(\beta-1)/(\alpha-1)} dT. \tag{6}$$

For calculating $\partial C_e/\partial T$ the $C_e(T)$ curve (Fig. 1, curve b) in the range $T_2 \leq T \leq T_1$ is approximated with an accuracy of ~ 1 percent by two parabolas $[0.419 - 0.609(T - 5.78)^2] \times 10^{-3}$ cal/g-deg and $[0.172 + 0.123(T - 7.30)^2] \times 10^{-3}$ cal/g-deg smoothly joined to one another at $T = 6°$K and to the sections of $C_e(T)$ which are outside the transition interval (at the points T_1 and T_2).

Figure 3 shows the x(T) curves plotted in accordance with (6) for various values of α. As is seen from this
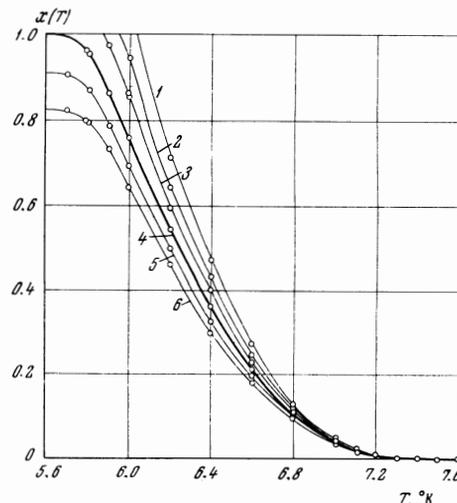

FIG. 3. The temperature dependence of the concentration x(T) of the superconducting phase for various values of the parameter α: curve 1—3.0, 2—3.2, 3—3.4, 4—3.6, 5—3.8, and 6—4.0.

figure, a value $\alpha = 3.6$ corresponds to the condition $x(T_2) = 1$.

Since, as follows from (5), $\partial x/\partial T |_{T = T_1, T_2} = 0$ (see also Fig. 3), an error in T_1 and T_2 affects $x(T)$ and the value of α for which $x(T_2) = 1$ very slightly. Direct calculations show that a change of the interval $T_1 - T_2$ by $\pm 0.2°$ results in a change of α by a value not exceeding 1 percent. More important is the course of $C_e(T)$ in the interval (T_1, T_2). However, relation (6) turns out to be very stable against variations of $C_e(T)$. Thus, a variation of the average slope of the section of curve b on Fig. 1 in the interval (T_1, T_2) within limits of ± 20 percent with a simultaneous change of $T_1 - T_2$ by $\pm 0.2°$ leads to values of α between 3.5 and 3.7. We note that such variations of the curve b (Fig. 1) are outside the limits of the error in measuring the specific heat, and are only justified if, regardless of all that was said at the beginning of this article, the lattice specific heat is described in the superconducting region by a function which differs from the function obtained on the basis of measurements of the specific heat in the region of the normal state.

Thus the proposed method of treatment of the experimentally obtained temperature dependence of the specific heat of an inhomogeneous sample makes it possible to determine the function $x(T)$ and to find the constants of Eq. (3) which describes the electronic specific heat of a homogeneous superconductor near the transition temperature.

It should be noted that a similar treatment of the experimental data on the specific heat can be used in studying second-order phase transitions in inhomogeneous samples, provided only that the function which describes the specific heat of a homogeneous crystal is determined by a single parameter—the Curie temperature.

[1] A. V. Voronel', S. R. Garber, A. P. Simkina, and I. A. Charkina, Zh. Eksp. Teor. Fiz. **49**, 429 (1965) [Sov. Phys.-JETP **22**, 301 (1966)].

[2] Yu. R. Chashkin, V. G. Gorbunova, and A. V. Voronel', Zh. Eksp. Teor. Fiz. **49**, 433 (1965) [Sov. Phys.-JETP **22**, 304 (1966)].

[3] Yu. Kagan and Ya. Iosilevskiĭ, Zh. Eksp. Teor. Fiz. **45**, 819 (1963) [Sov. Phys.-JETP **18**, 562 (1964)].

[4] M. H. Aven, R. S. Craig, T. R. Waite, and W. E. Wallace, Phys. Rev. **102**, 1263 (1956).

[5] A. Brown, M. W. Zemansky, and H. A. Boorse, Phys. Rev. **86**, 134 (1952).

[6] J. Bardeen and J. R. Schrieffer, Recent Developments in Superconductivity in Progress in Low Temperature Physics, North-Holland Publ. Co., Amsterdam, 1961, Vol. 3 (Russ. transl. Fizmatgiz, 1962).