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PHYSICAL REVIEW B VOLUME 4, NUMBER 1 1 JULY 1971

Pressure Dependence of the Specific Heat of a Superconductor Derived from Critical-Magnetic-Field Data*

J. P. Carbotte
Physics Department, McMaster University, Hamilton, Ontario, Canada
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The low-temperature variation of the critical magnetic field of a superconductor is related to the normal-state electronic specific-heat coefficient γ. Measurements of the critical magnetic field at zero and finite pressure are used to obtain a value for the volume Ω dependence of γ. We show that strong-coupling corrections must be included in such an analysis. For example, in Pb, ignoring such corrections leads to an error of almost a factor of 2 in $d\ln\gamma/d\ln\Omega$.

The temperature variation of the critical magnetic field $H_c(T)$ of strong-coupling superconductors, like Pb and Hg, is known to deviate from the predicted BCS behavior.[1,2] It is customary to introduce a function $D(t)$ defined by

$$D(t) = H_c(T)/H_c(0) - [1 - (T/T_c)^2] \ , \qquad (1)$$

where t is the reduced temperature T/T_c and T_c is the critical temperature. For Pb, $D(t)$ is found to be positive, in contrast to Al for which $D(t)$ is negative in close agreement with BCS theory.

When the electron-phonon interaction becomes particularly large, the details of the interactions involved become of some importance and the Eliashberg[3] formulation of pairing theory must be used instead of the simple BCS model.[4] On the basis of the Eliashberg gap equations, it is possible to understand quantitatively[5] not only the observed variation of $D(t)$ with t but also many other anomalous properties of superconducting Pb.[6-8] For instance, the very large value observed for the ratio

$$2\Delta_0/K_B T_c$$

(where Δ_0 is the energy gap at zero temperature, and K_B is the Boltzmann constant) is explained.

On application of hydrostatic pressure P, the critical temperature of Pb is observed to decrease. The ratio $2\Delta_0/K_B T_c$ is also found to decrease[9] and tends toward the weak-coupling BCS value of 3.53. These effects are understood[10] theoretically and are a simple consequence of a reduction in the electron-phonon interaction as P increases. Thus, we would also expect that the shape of $D(t)$ vs t would change under pressure and tends toward the BCS temperature variation. This would mean a breakdown of the "similarity principle" which is sometimes introduced in discussions of the pressure dependence of $H_c(T)$.[11,12] According to this principle the shape of $D(t)$ would be invariant. It is the purpose of this paper to make an estimate of the volume dependence of the shape of $D(t)$ vs t and to explore the consequences of such an estimate. We will limit the discussion to very low temperature (i.e., $t \to 0$) and consider only Pb.

Denote the slope of the low-temperature behavior of $D(t)$ vs t^2 by α. For small t we have

$$D(t) \cong \alpha t^2 .$$

The following thermodynamic relationship involving α is easily obtained[8]:

$$\gamma = [H_c^2(0)/2\pi T_c^2](1 - \alpha) , \qquad (2)$$

where γ is the coefficient of the electronic specific heat in the normal state at low temperature. The relation (2) is often used to obtain information on the volume dependence of the specific heat from the critical-field data.[11,12] We will return to this important point later. For the moment we proceed with an estimate of the volume dependence of α.

Recently Carbotte and Vashishta[13] have calculated the zero-temperature condensation energy U of a number of superconductors. Their results are obtained from detailed solutions of the Eliashberg equations based on realistic values for the interaction kernels. The kernels can be obtained accurately by "inversion" of superconducting tunneling data.[7] The value of U obtained in this way is expected to be quite reliable. It is convenient to write the results for U as

$$U = RU^{BCS}, \tag{3}$$

where U^{BCS} is the BCS value for the condensation energy and R is a correction factor coming from strong-coupling effects.

The condensation energy U is of course closely related to $H_c^2(0)$, and in the notation of Carbotte and Vashishta[13] we can write

$$\gamma T_c^2/H_c^2(0) = 0.168/Rx^2, \tag{4}$$

where x is defined by

$$2\Delta_0/K_B T_c = 3.53x.$$

For a weak-coupling superconductor, $R = x = 1$, and Eq. (4) reduces to a very familiar result. Comparing (4) with (2) it follows that

$$(1-\alpha)/2\pi = 0.168/Rx^2. \tag{5}$$

This last equation can conveniently be used to evaluate the volume dependence of α.

Carbotte and Vashishta[14] have calculated R for finite as well as zero pressure. They have also calculated the change in x with volume and obtained results in close agreement with the previous estimate of Trofimenkoff and Carbotte.[10] Quoting from these works, we have

$$\frac{d\ln R}{d\ln\Omega} \cong -1.8, \tag{6a}$$

$$\frac{d\ln x}{d\ln\Omega} \cong 1.9, \tag{6b}$$

where Ω is the volume. From (6) it follows on differentiating (5) that

$$\frac{d\ln(1-\alpha)}{d\ln\Omega} \cong -2. \tag{7}$$

This is a substantial variation and indicates a breakdown of the "similarity principle" which assumes α to be volume independent. Next we need an estimate of the volume dependence of the specific heat γ.

The critical temperature of a superconductor is quite a sensitive function of the electron-phonon mass-renormalization parameter λ.[15] Since the theory of Trofimenkoff and Carbotte[10] accounts very well for the observed volume dependence of T_c, we conclude that their value for

$$\frac{d\ln\lambda}{d\ln\Omega} \cong 4.8 \quad \text{(very roughly)} \tag{8}$$

should be accurate. But the specific heat γ is related to λ by

$$\gamma = \tfrac{2}{3}\pi^2 K_B^2 N(0)(1+\lambda), \tag{9}$$

where $N(0)$ is the one-spin density of electrons states at the Fermi surface. Using the free-electron model for $N(0)$, differentiating (9), and making use of (8), we get

$$\frac{d\ln\gamma}{d\ln\Omega} \cong 2.4. \tag{10}$$

This result is in reasonable agreement with the experimental value obtained from thermal-expansion data.[16] Rather large errors are associated with the experimental value, however.

So far our estimates have been based on theory. Before proceeding to a discussion of the experimental situation, it is useful to derive one more result. Combining (2), (7), and (10) we find that

$$\frac{d\ln[H_c^2(0)/T_c]}{d\ln\Omega} \cong 4.4. \tag{11}$$

This value is consistent with experiment,[14] giving us confidence in our theoretical work.

Garfinkel and Mapother[11] have studied the effect of pressure on $H_c(T)$ in Pb. They have employed Eq. (2) to derive from the data a value for $d\ln\gamma/d\ln\Omega$. We need not repeat the details of their analysis. It is sufficient to point out that, in essence, they find the data to be consistent with zero volume dependence for α; i.e., the "similarity principle" which has a basis in BCS theory seems to hold. They deduce a value of 4.9 for $d\ln\gamma/d\ln\Omega$. This is a factor of 2 larger than the expected value (10). The experimental situation is, however, far from straightforward. The measurements appear to be very difficult and the data are not very accurate. Because of this we cannot say that our predicted volume dependence of α [Eq. (7)] is in serious disagreement with experiment. More measurements of greater precision at lower temperatures are needed. It is nevertheless clear that, if the volume dependence of α is ignored when deducing a value for $d\ln\gamma/d\ln\Omega$ from (2), we would be led to the equation

$$\frac{d\ln\gamma}{d\ln\Omega} \cong \frac{d\ln[H_c^2(0)(T_c^2)]}{d\ln\Omega} \cong 4.4, \tag{12}$$

which is close to the result of Garfinkel and Mapother. This is not unexpected since, as we have implied, their analysis seems to be consistent with neglecting any volume dependence of α. We know, however, that (12) is not even approximately correct. To get the right answer we must add to the right-hand side of (12) the term $d\ln(1-\alpha)/d\ln\Omega \cong -2$ [Eq. (7)].

In conclusion, we have demonstrated that strong-coupling corrections lead to an important violation of the familiar "similarity principle" for superconducting lead. We believe that this observation explains, at least partially, why past values of the volume dependence of the specific heat derived from a critical-field analysis have not agreed with values deduced by other methods. When strong-coupling effects are included in the analysis of Pb data, the discrepancy disappears.

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PHYSICAL REVIEW B VOLUME 4, NUMBER 1 1 JULY 1971

Gap Energy of Superconducting Niobium Carbide*

L. W. Shacklette, L. G. Radosevich†
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

and

Wendell S. Williams
Department of Physics, Department of Ceramic Engineering, and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

(Received 25 February 1971)

The first estimate of the superconducting energy gap in a transition-metal carbide was recently made from thermal conductivity data on $NbC_{0.96}$. The quantity $2\epsilon(0)/kT_c$ was treated as an adjustable parameter in fitting the data to Bardeen-Rickayzen-Tewordt (BRT) theory, and a good fit was found for $2\epsilon(0)kT_c = 4.0$. The resulting value of the gap energy has now been verified by tunneling measurements using both probe and thin-film techniques. The best value is $2\epsilon(0) = 3.2 \pm 0.1$ meV. The result supports the applicability of BRT theory to the transition-metal carbides having low vacancy concentrations and demonstrates that under favorable circumstances, which may be unique to nonstoichiometric compounds, thermal conductivity data can be used to evaluate the gap energy of a superconductor.

INTRODUCTION

The transition-metal carbides are usually regarded as high-temperature refractory compounds. However, some of them are notable superconductors with high critical fields. The superconducting properties of these solids have been studied by Toth *et al.*,[1] Giorgi *et al.*,[2] and Geballe *et al.*[3] Data have been reported on values of the transition temperature T_c for carbides of various transition metals, and on the variation of T_c with carbon/metal ratio x in MeC_x, where Me is a given transition metal. However, no direct measurements of gap energies for this group of superconductors have been reported.

The gap energy at $T = 0\,^\circ K$, $2\epsilon(0)$, is an important physical characteristic of a superconductor and also an important parameter in the BCS microscopic theory of superconductivity and in the Bardeen-Rickayzen-Tewordt (BRT) theory of the thermal conductivity of superconductors. Hence, a fuller characterization and understanding of superconductivity in the transition-metal carbides requires that gap energies be determined.

USE OF THERMAL CONDUCTIVITY DATA AND BRT THEORY

The BRT theory[4] predicts that for a superconductor, in the weak coupling limit, the ratio of the lattice conductivity in the superconducting state κ_{ls} to that in the normal state κ_{ln} will be given by a universal function of reduced temperature, $\kappa_{ls}/\kappa_{ln} = f(T/T_c)$. A corresponding prediction is made for the electronic contribution to the thermal conductiv-