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Gap Energy of Superconducting Niobium Carbide*

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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-

ity, $\kappa_{es}/\kappa_{en}=g(T/T_c)$. The theory is meant to apply to an ideal superconductor in which the adiabatic approximation holds.

Extensive measurements of the low-temperature thermal conductivity of several transition-metal carbides by Radosevich and Williams[5] showed that for carbides with high vacancy concentration ($x \cong 0.8$) the adiabatic approximation fails. This result was inferred from the fact that the relaxation rate for phonon-electron scattering in these carbides exhibits a frequency dependence proportional to ω^2 rather than to the usual ω. However, this frequency dependence is predicted by a scattering theory of Pippard[6] which applies for $q\lambda \ll 1$, where q is the dominant phonon wave number, and λ is the electron mean free path. Because of the high concentration of point defects (carbon vacancies) in these compounds, the value of λ is small (~ 50 Å) and the Pippard condition is satisfied. The adiabatic approximation requires the opposite condition, $q\lambda \gg 1$. Thus one would hold little hope that BRT theory, which assumes that the adiabatic approximation holds, would apply to transition-metal carbides with high vacancy concentrations.

However, in a later paper, Radosevich and Williams[7] reported measurements of thermal conductivity of a niobium carbide with a lower vacancy concentration, $NbC_{0.96}$, which has a superconducting transition in the range of their measurements, $T_c = 9.8\,^{\circ}K$. Below T_c the thermal conductivity *increased* over 100-fold (Fig. 1). Residual resistivity measurements indicated a much longer electron mean free path, than for $NbC_{0.76}$, and some ω^2 had to be included in the relaxation rate for phonon-electron scattering to fit thermal conductivity data using a Callaway analysis. These results indicated that the adiabatic approximation was on the verge of being satisfied, and some hope was held for the applicability of BRT theory to $NbC_{0.96}$.

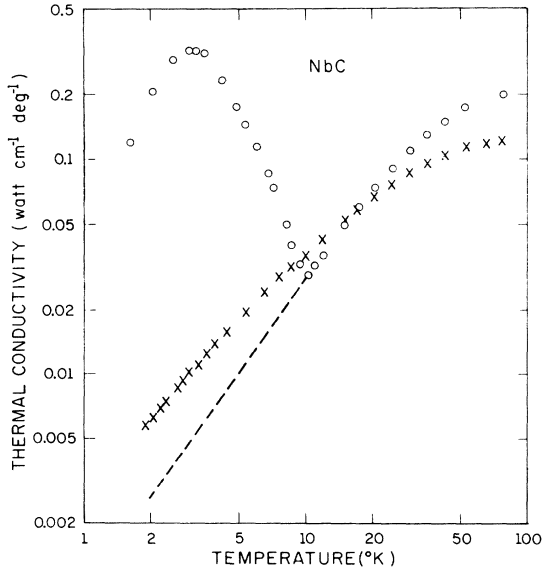

FIG. 1. Measured thermal conductivity κ of $NbC_{0.96}$ (circles) and $NbC_{0.76}$ (crosses). Note 100-fold *increase* of κ below superconducting transition for $NbC_{0.96}$ (from Ref. 7).

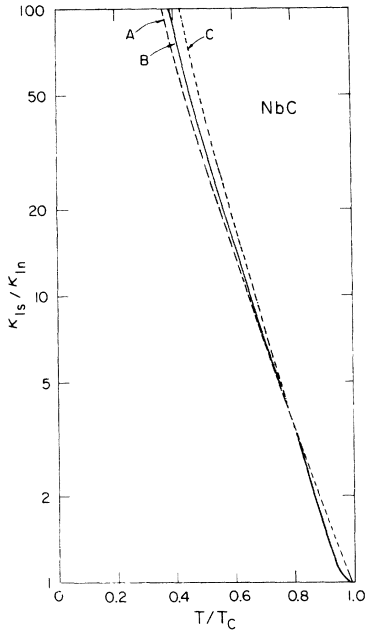

FIG. 2. Comparison of derived experimental results with BRT prediction for change in lattice conductivity below T_c. A: derived data. B: BRT calculated curve including point-defect correction. C: BRT calculated curve without correction. Value of 4.0 used for $2\epsilon(0)/kT_c$ to give best fit (from Ref. 7).

Radosevich and Williams calculated the electronic contribution to κ using the Wiedemann-Franz law for the normal state κ_{en} and BRT theory for the superconducting state κ_{es}. Then the appropriate κ was subtracted from the total measured κ to give the lattice component above and below the transition temperature, κ_{ln} and κ_{ls}, respectively. In most superconductors the electronic contribution dominates the total thermal conductivity, and the uncertainty in the lattice component is high since

TABLE I. Results of three determinations of gap energy of superconducting $NbC_{0.96}$.

Method	$2\epsilon(0)$ (meV)
Thermal conductivity, BRT theory (Ref. 7)	3.4 ± 0.2
Tunneling, probe	3.3 ± 0.2
Tunneling, film	3.2 ± 0.1

TABLE II. Values of energy parameter from BCS theory obtained for superconductors containing niobium.

Material	$2\epsilon(0)/kT_c$	Reference
$NbC_{0.96}$	3.8	Present work (film)
$NbC_{0.96}$	4.0	7
NbN	4.08	11
Nb	3.84	10

it must be determined by the subtraction of two numbers of similar size. However, in the transition-metal carbides, where the lattice contribution dominates, the reverse is true. This favorable circumstance offered the possibility of making an indirect determination of the gap energy, provided of course, that the applicability of BRT theory could be demonstrated. The ratio κ_{1s}/κ_{1n} was plotted against the reduced temperature T/T_c (Fig. 2). A comparison of this predicted curve and that obtained from BRT theory is also shown in Fig. 2, taken from the work of Radosevich and Williams.[7] The fit is very good, particularly when a correction for the influence of point defects, calculated by Klemens and Tewordt,[8] is introduced.

A parameter in BRT theory is $2\epsilon(0)/kT_c$. The best value of this parameter for fitting the derived data was found to be 4.0. This value is at the upper limit of values allowed by BCS weak coupling theory. The corresponding value of the gap energy is $2\epsilon(0) = 3.4 \pm 0.2$ meV.

This result for the gap energy was based on a good fit between experiment and BRT theory, but in view of the unusual and indirect way in which the value was obtained and the initial reservation about the applicability of BRT theory to nonstoichiometric carbides, it was felt necessary to verify the finding with direct tunneling measurements. We now describe the results of two such measurements.

TUNNELING MEASUREMENT USING PROBE

The probe technique of Levinstein and Kunzler[9] was employed first. Anodized tips of Ta and Nb were used to make point contact with a single crystal of $NbC_{0.96}$. Contact pressure was controlled with a micrometer screw after the crystal and probe were immersed in liquid helium. Measurements of I vs V were taken at the normal helium boiling point and over a range of temperature extending down to 1.6 °K.

Although some structure appeared in the tunneling curve, the highest-voltage inflexion point was taken to represent the sum $\epsilon_1(T) + \epsilon_2(T)$. Values of $\epsilon_{Ta}(T)$ and $\epsilon_{Nb}(T)$ were taken from the BCS curve of $\epsilon(T)/\epsilon(0)$ vs T/T_c using $2\epsilon_{Ta}(0) = 1.4$ meV and $2\epsilon_{Nb}(0) = 3.05$ meV.[10] The correction of the gap energy for $NbC_{0.96}$ measured at 4.2 to 0 °K is small because of the relatively high value of T_c (9.8 °K).

The result is $2\epsilon_{NbC_{0.96}}(0) = 3.3 \pm 0.2$ meV.

THIN-FILM TUNNELING MEASUREMENT

A second tunneling measurement was made using evaporated films for improved leakage characteristics. The technique employed phase-sensitive detection and gave values of dI/dV. The film was lead, $2\epsilon_{Pb}(0) = 2.67$ meV.[10] The resulting value of $2\epsilon_{NbC_{0.96}}(0)$ is 3.2 ± 0.1 meV.

DISCUSSION

All three methods of evaluating the gap energy for superconducting $NbC_{0.96}$ agree within the limits of error assigned to each method. Of the three, tunneling with an evaporated film is the most direct and accurate. The results are compared in Table I.

The best choice of $2\epsilon(0)/kT_c$ for fitting the derived thermal conductivity data was found to be 4.0. This value is at the upper limit of values allowed by BCS weak coupling theory. Strong coupling deviations lead to higher values as shown for lead. For comparison, the values of $2\epsilon(0)/kT_c$ for Nb and NbN are given in Table II.

The tunneling measurements support the evaluation of $2\epsilon(0)$ from thermal conductivity data and BRT theory and illustrate the adequacy of that theory to deal with a complex solid.

In most superconductors, the increase in lattice conductivity as T falls below T_c is a minor feature of the change in κ, which is dominated by the *decrease* in κ_e; for $NbC_{0.96}$ electron-vacancy scattering limits κ_e and allows κ_l to dominate. Below T_c paired electrons cease to scatter phonons, and hence κ_1 increases by as much as two orders of magnitude. This dramatic and unusual increase in κ below T_c is accurately predicted by BRT and, as a by-product, leads to a value for $2\epsilon(0)/kT_c$.

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Tunneling into Weakly Coupled Films of Tin and Aluminum in Proximity. II. From the Tin Side*

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Tunneling experiments have been performed into the tin side of aluminum-tin proximity sandwiches evaporated at room temperature onto an oxidized aluminum electrode B. The coupling between the aluminum and tin films in proximity was made weak by allowing slight oxidation of the tin to occur at the interface. Using the McMillan model of the proximity structure, values of the electron-transmission probability α at the interface may be derived from the experiments. The α value is related to the critical temperature of the sandwich and also to the positions of peaks in the McMillan density of states. These peaks are reflected in the tunneling currents when the electrode B is superconducting. Values of α derived from these two kinds of measurements are found to be consistent and, qualitatively, to vary as expected with the oxidation conditions. Although the calculated curves of tunneling conductance as a function of applied voltage, when B is superconducting, exhibit sharper structure than the experimental curves, they are otherwise in good agreement. In contrast to tunneling from the aluminum side of the proximity sandwich, the tunneling characteristics into the tin side, when B is in the normal state, are similar to those into a BCS superconductor. On the whole, the experimental results are in good agreement with the predictions of the McMillan model.

INTRODUCTION

In recent papers[1,2] tunneling experiments into the aluminum side of aluminum-tin proximity sandwiches, when the aluminum thickness d_N was less than the tin thickness d_S, were reported. The occurrence of double-peaked structure was correlated with the predictions of the McMillan[3] tunneling model of the proximity effect and substantial quantitative agreement was obtained.

In a continuation of this work, measurements of the tunneling currents into the tin side of aluminum-tin proximity sandwiches with $d_s < d_N$ have been performed. The electron coupling between the metals was made weak by allowing slight oxidation of the tin to occur before the aluminum was deposited. The electron-transmission probability α at the proximity interface may be crudely controlled with the oxidation conditions and is qualitatively similar to that obtained by oxidation of aluminum.[1] The tunnel characteristics from a normal-state metal look like those into a BCS superconductor and do not offer any information about the properties of the sandwich. This is in contrast to the situation when tunneling into the aluminum side of the sandwich. The tunneling currents between a superconductor and the tin side of the proximity sandwich, on the other hand, exhibit a double-peaked structure over a considerable range of tin thickness. Again, in this investigation the experimental results are compared with calculations based on the McMillan model.

CALCULATIONS FOR TIN-ALUMINUM SANDWICHES

All the equations necessary for computer calculations with the McMillan model are presented in Ref. 1. Here, we present graphically the results of calculations with the McMillan model when $d_N > d_S$. An analysis of the tunneling density of states in the tin film is given. Again, we refer to aluminum as the normal-state metal (even when it is superconducting) and tin as the superconductor.

The double-peaked density of states seen in the aluminum side also exists in the tin side of the sandwich when α is sufficiently small. The exact shape and energy position of the peaks depend on the parameters Γ_S, Γ_N, Δ_S^{ph}, and Δ_N^{ph}. The behavior is illustrated in Fig. 1 for three different values of