Investigation by Electron Tunneling of the Superconducting Energy Gaps in Nb, Ta, Sn, and Pb

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Electron tunneling between two superconductors separated by a thin potential barrier gives rise to nonlinear current vs voltage characteristics, from which a direct measurement of their energy gaps can be obtained. The temperature dependence of the $I:V$ characteristics for sandwiches of Ta/barrier/Pb and Nb/barrier/Sn has been studied and the energy gaps of tin and tantalum determined up to their transition temperatures. Good agreement has been obtained between the temperature dependence observed experimentally, and the predictions of the Bardeen, Cooper, and Schrieffer (BCS) theory of superconductivity.

The full limiting values of the superconducting energy gaps obtained are $2\epsilon_{\mathrm{Nb}}=(3.05\pm0.05)\times10^{-3}$ eV, $2\epsilon_{\mathrm{Ta}}=(1.40\pm0.05)\times10^{-3}$ eV, and $2\epsilon_{\mathrm{Sn}}=(1.15\pm0.06)\times10^{-3}$ eV. The lead apparently exhibited two prominent energy gaps with values of $2\epsilon_{\mathrm{Pb}}^{(1)}=(2.67\pm0.05)\times10^{-3}$ eV and $2\epsilon_{\mathrm{Pb}}^{(2)}=(2.90\pm0.05)\times10^{-3}$ eV, at 0°K. This behavior is tentatively ascribed to anisotropy.

Theoretical characteristics have been computed, using the BCS density-of-states expression, $\rho=E/(E^2-\epsilon^2)^{1/2}$, and compared with the experimental results. Possible reasons for the deviations observed are discussed.

INTRODUCTION

THE technique of electron tunneling has been successfully applied to the study of superconducting energy gaps. A number of authors have reported values for the superconducting energy gaps of Sn, In, Pb, Al, and Nb,[1–7] using both normal metal/barrier/superconductor and superconductor/barrier/superconductor systems. The direct determination of energy gaps is only possible when the two superconductor system is used. With niobium ($T_c=9.20$°K) or tantalum ($T_c=4.47$°K) as one element of a superconducting sandwich, it should be possible to obtain a direct measure of the energy gaps of the majority of the elemental superconductors up to their transition temperatures. The superconductors niobium and tantalum are very susceptible to oxygen and nitrogen impurity, and because of their high boiling points it is extremely difficult to prepare evaporated films with good superconducting characteristics. The results presented here have been obtained using bulk samples of these metals.

EXPERIMENTAL TECHNIQUES

The specimens consisted of strips of niobium or tantalum with a thermally grown oxide, ~15 Å thick, acting as the potential barrier. Tunneling areas were formed by the cross evaporation of tin or lead strips.

Zone-refined ingots of niobium and tantalum were prepared by Metals Research, Limited, Cambridge. They were rolled into sheets 0.005-in. thick which were cut into strips 3 in.×0.1 in. Platinum electrodes were spot welded on the ends, and the strips given a chemical polish to remove any impurities introduced in the rolling operation. They were then mounted in a vacuum system and enclosed within a copper cylinder cooled with liquid nitrogen. The strips were outgassed by resistive heating, their temperature being raised over a period of 4 h to the melting point, with the residual pressure in the vacuum system never exceeding 5×10^{-6} mm of Hg. When the outgassing procedure was completed, the specimen was cooled to 60°C and the vacuum system flushed with pure oxygen at atmospheric pressure. These oxidation conditions were maintained for 2 h and resulted in the formation of a continuous oxide. The estimated thickness of the resulting tantalum oxide was 15 Å.[8] The higher tunneling resistances observed with the niobium system suggest a somewhat thicker oxide.

Each oxidized strip was secured with collodion to a glass substrate 3 in.×½ in. and the specimen geometry adopted is shown in Fig. 1. The collodion not only served as a glue, but was also painted over the edges of the strip to provide a continuous path for the cross evaporation of the second superconductor. These evaporations were carried out at 5×10^{-5} mm of Hg and a mask was used to define three tunneling areas ~1 mm square. X-ray absorption measurements indi-

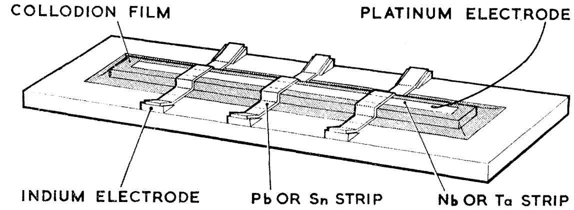

FIG. 1. A schematic drawing of a typical specimen showing three tunneling areas.

[1] I. Giaever, Phys. Rev. Letters **5**, 147, 464 (1960).
[2] J. Nicol, S. Shapiro, and P. Smith, Phys. Rev. Letters **5**, 461 (1960).
[3] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[4] M. D. Sherril and H. H. Edwards, Phys. Rev. Letters **6**, 460 (1961).
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[7] N. V. Zavaritskii, Soviet Phys.—JETP. **14**, 470 (1962).
[8] D. A. Vermilyea, Acta. Met. **6**, 166 (1958).

cated film thicknesses of $\sim 3\,\mu$. Indium electrodes, soldered to the glass slide prior to the evaporation, enabled contacts to be made between the evaporated films and the current and potential leads in the cryostat.

The cryostat used for the measurements on the Ta/barrier/Pb specimens was a conventional double helium Dewar in which temperatures from 1 to 4.5°K could be attained by controling the helium vapor pressure. The temperatures were determined either from the helium vapor pressure or from a carbon resistance thermometer included in the specimen chamber. Temperatures above 4.2°K were obtained by pressurizing the outer helium Dewar and were reproducible to better than 0.01°K. For measurements on the Nb/barrier/Sn specimens a simple glass Dewar was used in which temperatures from 1.5 to 4.2°K were reached, and within this range temperatures were measured with an estimated accuracy of 0.1°K.

The current vs voltage characteristics were plotted automatically on a Moseley 2S XY recorder, the current being varied by a motor driven rheostat. In measuring nonlinear characteristics at these low-voltage levels, the influence of noise must be kept to a minimum and extreme care was taken in screening the entire circuit. Even so, some loss of detail in the measured characteristics must be attributed to noise.

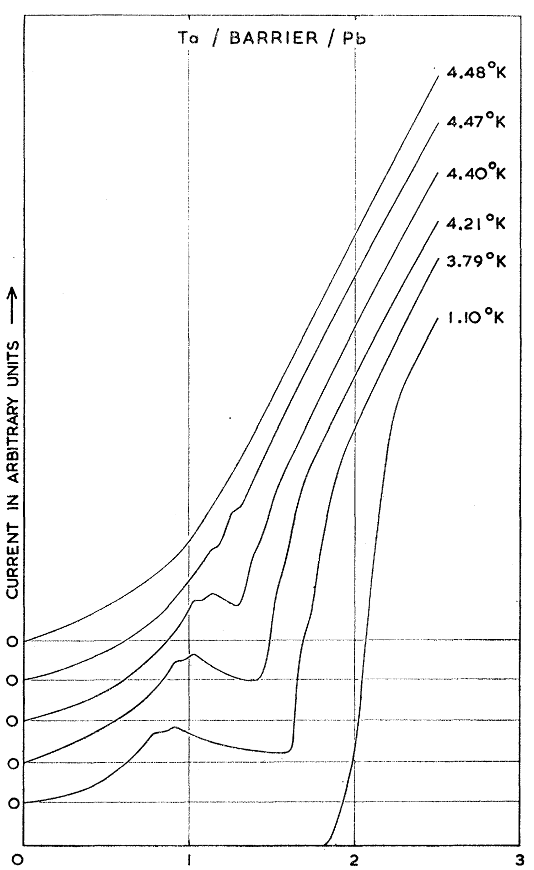

FIG. 2. $I:V$ characteristics for a Ta/barrier/Pb sandwich as a function of temperature.

THEORY

Bardeen[9] has written that the probability per unit time of an electron in a state (a) on one side of a potential barrier tunneling to a state (b) on the other side is given by

$$P_{ab}=(2\pi/\hbar)|M_{ab}|^2\rho_b' f_a(1-f_b), \tag{1}$$

where ρ_b' is the density of states at (b), and f_a and f_b are the appropriate Fermi functions. $|M_{ab}|$, the matrix element for the transition, vanishes unless the component of the wave number transverse to the tunneling direction is conserved in the transition. Although the component of the wave number in the tunneling direction, k_z, does not have to be conserved in the transition, a change in k_z will result in a reduced tunneling probability.[10] The resulting current is given by

$$j=\frac{4\pi e}{\hbar}\sum_{k_T}\int_{-\infty}^{+\infty}|M_{ab}|^2\rho_a'\rho_b'(f_a-f_b)dE. \tag{2}$$

The integral is taken over fixed transverse wave num-

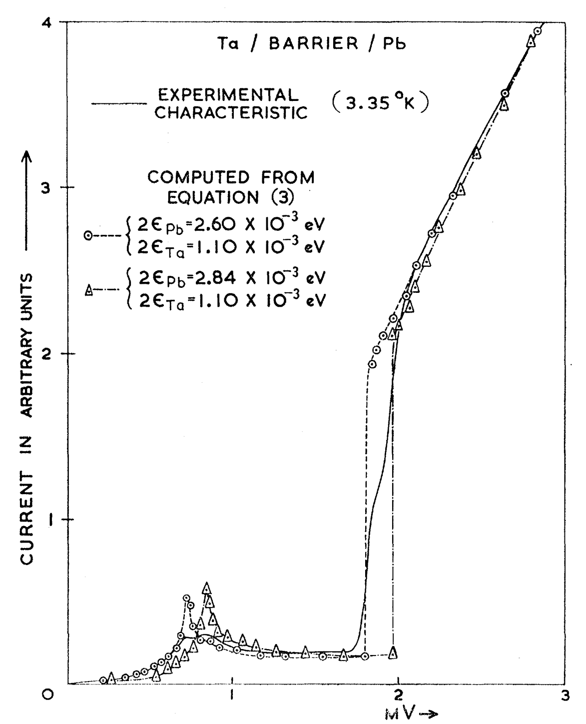

FIG. 3. Comparison of an experimental $I:V$ characteristic for the Ta/barrier/Pb system at 3.35°K and theoretical points calculated from Eq. (3).

[9] J. Bardeen, Phys. Rev. Letters **6**, 57 (1961).
[10] P. J. Price and J. M. Radcliffe, IBM J. Research Develop. **3**, 364 (1959).

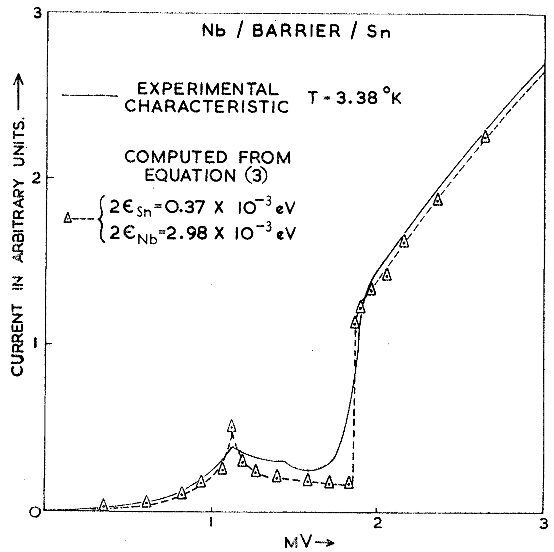

FIG. 4. Comparison of an experimental characteristic for the Nb/barrier/Sn system at 3.38°K and theoretical points calculated from Eq. (3).

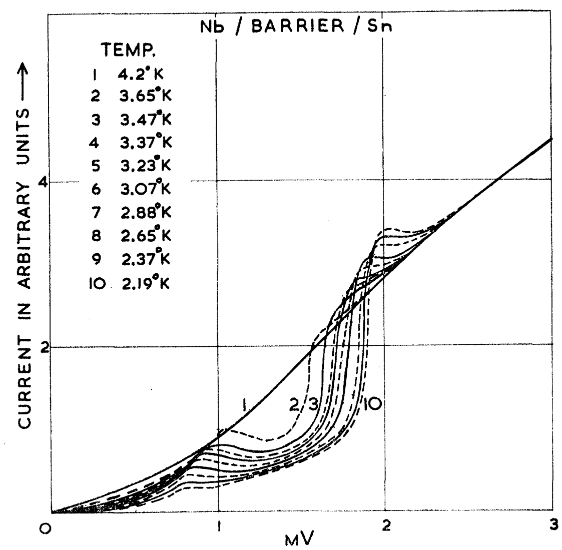

FIG. 5. The temperature dependence of the $I:V$ characteristics for a Nb/barrier/Sn sandwich in which an insufficiently outgassed niobium strip was used.

ber k_T, and ρ_a' and ρ_b' are the density of states for fixed k_T.

The BCS theory[11] assumes that the metal has a spherical Fermi surface and an isotropic superconducting energy gap. The density of states ρ_a' and ρ_b' can then be identified with the total density of states $\rho = E/(E^2-\epsilon^2)^{1/2}$ and if $|M_{ab}|$ is assumed constant over the energy range of interest, the current density can be written

$$j = C\int_{-\infty}^{+\infty} \frac{E^2 - EV}{\{(E^2-\epsilon_1^2)[(E-V)^2-\epsilon_2^2]\}^{1/2}} \times [f(E)-f(E-V)]dE, \quad (3)$$

where E is the energy measured from the Fermi level, V is the energy equivalent of the applied voltage, and ϵ_1 and ϵ_2 are the half-energy gaps of the two superconductors. A program has been written to allow computation of characteristics from this equation for any values of ϵ_1 and ϵ_2.

RESULTS AND THEIR INTERPRETATION

Figure 2 shows typical $I:V$ characteristics for the Ta/barrier/Pb system at the temperatures indicated. Figure 3 shows the experimental characteristic measured at 3.35°K, together with theoretical points computed from Eq. (3), using the experimental values of the energy gaps. In Fig. 4 a typical experimental curve for the Nb/barrier/Sn system at 3.38°K is compared to the theoretical characteristic.

Although the experimental curves and the theoretical points are similar in form, there are marked deviations at the high- and low-voltage ends of the negative-resistance regions. Neither the pronounced cusp at $(\epsilon_1-\epsilon_2)$ nor the discontinuous rise in current at $(\epsilon_1+\epsilon_2)$ evident from the simple theory, is present in the experimental characteristics. Since Bardeen[9] has shown that the nonlinear characteristics obtained in this type of experiment arise entirely from the variation of the density of states in the superconductors, the deviations between theory and experiment must be attributed to an effective density of states in the superconductors different from that given by the BCS theory. Thus, a modification of the BCS density of states expression is necessary to provide agreement. Possible mechanisms which might be responsible for the deviations are discussed below.

(1) Nonhomogeneous Superconductor Surfaces

In considering any real surface, the amount of impurity and its distribution over the surface is important. Variations in impurity concentration occurring over distances which are large compared to the coherence length, will lead to regions of varying transition temperature and energy gap. This effect was detected in the Nb/barrier/Sn system where different characteristics were obtained from different parts of a niobium strip. Figure 5 shows the temperature dependence of the characteristics obtained from a sandwich in which insufficiently outgassed niobium was used. The detailed explanation of the effect is not clear; in particular, the mechanism responsible for the appearance of the second negative resistance region is not known. Tantalum systems have not shown the same phenomenon. This is probably due to the higher melting point of Ta (2850°C) compared with Nb (1950°C) which allows a more

[11] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

effective outgassing procedure. The transition temperature of the tantalum surface at all the junctions, determined from the behavior of the characteristics, was 4.47°K, indicating a very high purity.[12] This was confirmed from measurement of the lattice parameter from which it was possible to set an upper limit of 40 parts per million of oxygen and nitrogen impurity. Therefore, while an impure surface on the niobium strip may be responsible for the observed rounding of the Nb/barrier/Sn characteristics, it does not seem to be a likely explanation for the behavior of the Ta/barrier/Pb system.

(2) Lifetime Effects

The BCS density of states function is valid only so long as the electronic energy levels are infinitely well defined. Such a concept is untenable physically and it would seem reasonable to smear the energy levels by a factor Δ. Assuming that the uncertainty principle can be applied to the energy levels in a superconductor, then $\Delta\sim\hbar/\tau$ where τ is the lifetime of the state. Hebel and Slichter[13] and Redfield[14] have measured the density of states in superconducting aluminum by nuclear spin relaxation time experiments. To obtain a better agreement between experiment and theory, they smear the BCS density of states expression with a square function of width 2Δ and height $(2\Delta)^{-1}$. Excellent agreement is obtained when $\epsilon_0/\Delta=15$. They reach no conclusions as to the origin of this spread, but suggest that as it is largely temperature independent, it might arise from boundary scattering or from anisotropy. Anderson[15] has shown that impurity scattering and boundary scattering will serve only to reduce the energy gap and transition temperature, and cannot be used to calculate an uncertainty in energy of the individual levels.

Burstein *et al.*[16] have obtained an estimate of the electron-hole radiative recombination lifetime for lead at 2°K, using the theory of van Roosbroeck and Shockley. They obtain a value for $\tau_{\rm opt}$ of 0.4 sec which leads to a Δ of 1.6×10^{-15} eV which is many orders of magnitude smaller than the observed spreads. Theoretically, the electron-phonon lifetime should be the appropriate one for calculating Δ. This would result in a strongly temperature-dependent spread, which was not apparent. It must, therefore, be concluded that lifetime effects are not an important contribution to the deviation of the effective density of states from the BCS value.

(3) Anisotropy

The Fermi surface of all metals is complex, and the assumption made in the BCS theory that the Fermi surface is spherical and that the superconducting energy gap is not a function of crystal orientation, is an approximation. Anderson[15] has proposed that in order to observe anisotropy, $(\hbar/\tau)<\epsilon_g$, where ϵ_g is the energy gap and τ is the lifetime against scattering from chemical and physical impurities. Assuming the BCS relation $\xi_0=2\hbar v_0/\pi\epsilon_g$, where v_0 is the Fermi velocity, Anderson's criterion may be expressed as $\lambda>1.6\xi_0$, where λ is the electron mean free path. This criterion has been verified by Richards,[17] who has measured the superconducting energy gaps of pure and "dirty" single-crystal tin by far-infrared techniques.

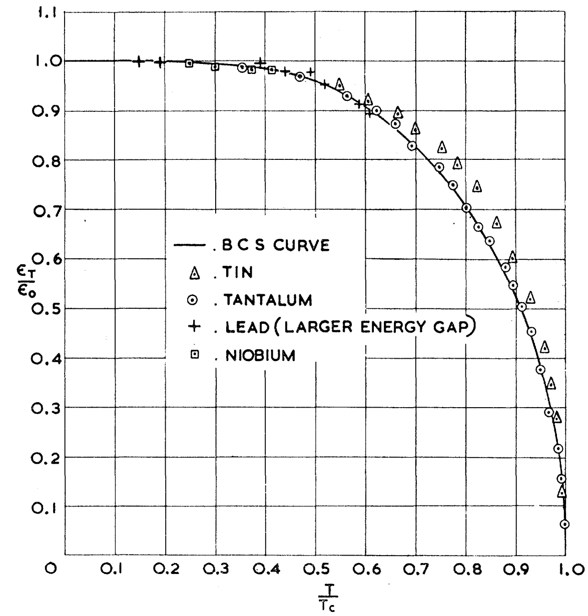

FIG. 6. Reduced values of the energy gaps for lead, tin, tantalum, and niobium as a function of reduced temperature, and compared to the theoretical curve (solid line) of BCS.

X-ray analysis of the evaporated tin films indicates crystal sizes within the range 1–10 μ, i.e., very much greater than the coherence length $\xi_0=2300$ Å. The fact that anisotropy is not resolved in the Nb/barrier/Sn system is probably due to a high chemical impurity content in the tin film, which would make it a dirty superconductor. Alternatively, the nonhomogeneous niobium surface may have obscured any fine structure in the effective density of states of the tin.

The $I:V$ characteristics for the Ta/barrier/Pb system, (Fig. 2) show two peaks near the low-voltage end of the negative-resistance region, and two regions of maximum slope at the high-voltage end. The small temperature dependence of the voltage separation of the peaks, up to the transition temperature of the tantalum, indicates that this behavior is characterictic of the lead film. The characteristics can only be explained by assuming two maxima, or a plateau preceding the maximum, in the effective density of states of the

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[17] P. L. Richards, Phys. Rev. Letters **7**, 412 (1961).

TABLE I. Full limiting values of the energy gaps, $2\epsilon_0$, and $2\epsilon_0/kT_c$.

Superconductor	T_c °K	This work $2\epsilon_0$ (eV×10^{-3})	This work $2\epsilon_0/kT_c$	Other tunneling experiments $2\epsilon_0$ (eV×10^{-3})	Other tunneling experiments $2\epsilon_0/kT_c$	Thermal conductivity $2\epsilon_0/kT_c$	Far infrared $2\epsilon_0/kT_c$
Sn	3.8[a]	1.15±0.06	3.51±0.18	1.02±0.02[b]	3.10±0.05		3.30±0.20[f]
				1.11±0.03[c]	3.46±0.10		3.60±0.20[g]
Pb	7.2	2.67±0.05	4.30±0.08	2.50±0.05[b]	4.04±0.10		4.00±0.50[f]
		2.90±0.05	4.67±0.08	2.68±0.06[c]	4.33±0.10		4.10±0.20[g]
Nb	9.2	3.05±0.05	3.84±0.06	3.02[d]	3.79	3.8±0.2[e]	
Ta	4.47[a]	1.40±0.05	3.60±0.10			3.5±0.2[e]	

[a] Measured values.
[b] S. Shapiro, P. H. Smith, J. Nicol, J. L. Miles, and P. F. Strong, IBM J. Research Develop. **6**, 34 (1962).
[c] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[d] M. D. Sherrill and H. H. Edwards, Phys. Rev. Letters **6**, 460 (1961).
[e] K. Mendelssohn IBM J. Research Develop. **6**, 27 (1962).
[f] D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).
[g] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).

lead films. This is thought to arise from anisotropy. X-ray diffraction and optical studies of the lead film revealed crystallite sizes of $1\,\mu \rightarrow 10\,\mu$ compared to a coherence length of 830 Å in lead. The mean free path for electron-impurity scattering in the film can be estimated from the measured ratio of room-temperature resistance to the residual resistance $R_{295}/R_{4.2}=250$. Using Chambers'[18] value of σ/λ for lead, and assuming $\sigma_{\text{evap}}=\sigma_{\text{bulk}}$, then $\lambda \sim 10\xi_0$. The lead film therefore satisfies Anderson's criterion for observing anisotropy.

Further evidence that this double structure is associated with the lead film and is consistent with anisotropy of the energy gap was obtained from a study of the Al/barrier/Pb system. A thin film of aluminum was used as an isotropic reference superconductor and the $I:V$ characteristics studied as a function of the thickness of the lead film. Films very much thicker than the coherence length resulted in a double structure, similar to that observed with Ta/barrier/Pb sandwiches, and gave two prominent energy gaps in good agreement with those reported. As predicted by Anderson's theory, this structure was not present for specimens in which the thickness of the lead film was of the order of the coherence length.

The reason for the existence of two peaks is not clear but it may result from preferential orientation in the evaporated lead film.

TEMPERATURE DEPENDENCE OF THE ENERGY GAPS

Interpretation of the measured characteristics to obtain values of ϵ_1 and ϵ_2 is complicated by the rounding effects discussed. It has been assumed that $(\epsilon_1-\epsilon_2)$ corresponds to the voltage at which the current is a maximum and $(\epsilon_1+\epsilon_2)$ to the voltage where (dI/dV) is a maximum. The lack of agreement between the results of various authors is thought to arise from their using different criteria to define the energy gaps. As long as the values ϵ_1 and ϵ_2 have the same temperature dependence as the 'true' energy gaps, then reduced values of ϵ/ϵ_0 should show the theoretical temperature dependence predicted by the BCS theory; but absolute values of ϵ_0 will show a systematic error.

In Fig. 6, the reduced energy gaps of Ta, Sn, Pb, and Nb are shown as a function of reduced temperature. The BCS variation of energy gap calculated from the equation given by Thouless,[19] $\epsilon_T/\epsilon_0=\tanh[(T_c/T)(\epsilon_T/\epsilon_0)]$, is shown for comparison.

The temperature dependence of the superconducting energy gap of tantalum shows excellent agreement with the predictions of the BCS theory, over a wide temperature range. The tin film shows a consistently greater temperature dependence near T_c, and this may be due to unresolved anisotropy. The values of the superconducting energy gaps at 0°K, $2\epsilon_0$, together with values of $2\epsilon_0/kT_c$ are tabulated in Table I and compared with the results obtained by other workers.

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[19] D. J. Thouless, Phys. Rev. **117**, 1256 (1960).