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# Superconducting Energy Gap of Thorium Determined by Electron Tunneling*

B. A. Haskell, W. J. Keeler, † and D. K. Finnemore
*Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa* 50010
(Received 6 October 1971)

Electron-tunneling measurements have been performed over the temperature range 0.4–1.4 K on Th-$ThO_2$-Au tunnel junctions fabricated on the surface of polycrystalline thorium substrates. Both the temperature dependence of the energy gap and the voltage dependence of the tunneling density of states agree rather well with the theoretical predictions for a weak-coupling superconductor. No significant phonon-induced structure was observed in the tunneling density of states.

## I. INTRODUCTION

Transition-metal superconductors form a class of materials with widely varying properties, and as a class they are one of the least understood. Because their properties are dominated by the presence of *d* bands at the Fermi level, they frequently show characteristics which differ from those of the *s*-*p*-band superconductors.[1] In fact, it has been suggested that the fundamental mechanism responsible for superconductivity in these materials is different from that in the *s*-*p*-band materials.[2] Unfortunately, however, experimental work to confirm or refute this suggestion has been scarce because the superconducting properties of the transition metals are very sensitive to oxygen impurities and samples are difficult to prepare.

Early measurements for Ta and Nb[3] showed a well-behaved energy gap but high-quality tunnel junctions were more difficult to prepare than in the *s*-*p*-band superconductors. Attempts to prepare junctions by evaporation of the transition metal have been largely unsuccessful, but Shen[4] has shown that it is possible to obtain high-quality junctions by depositing a thin film of silver over a freshly cleaned and oxidized surface of bulk tantalum. One of his junctions showed less than 0.3% of the normal-state conductance in the region of the gap, and several also showed structure in the tunneling density of states at higher voltages which correlated well with the neutron-diffraction phonon density of states. Shen concluded that the electron-phonon interaction is the only mechanism needed to explain the superconducting properties of tantalum.

MacVicar[5] and Hafstrom and MacVicar[5] have used a similar method to prepare single-crystal niobium junctions, and find evidence for a highly anisotropic energy gap. They interpret their data in terms of the two-band model of Suhl, Matthias, and Walker[6] and suggest the presence of two distinct gaps in "clean" samples. For these cases, the magnitude of the energy gap associated with the *d* band is ten times the magnitude of the one associated with the *s* band. Similar measurements for rhenium[7] also show anisotropy but the magnitude is smaller than for Nb, less than 30%.

We have prepared Th-$ThO_2$-Au junctions by a method similar to that of Shen and report here the first electron-tunneling measurements of the energy gap of superconducting thorium. Results for polycrystalline samples show an excitation spectrum fairly close to the BCS[8] prediction.

## II. EXPERIMENTAL

Tunnel junctions were prepared on the surface of parallelepiped-shaped ($1\times12\times12$-mm) pieces of pure thorium which were provided by Peterson of the Ames Laboratory.[9] Spectroscopic analysis of the starting material showed that the main impurities were C and O at 46 and 122 ppm by weight, respectively. The most prevalent magnetic impurities were Cr, Mn, and Fe at levels less than 20, 20, and 6 ppm, respectively. To prepare the junction, the sample was mounted in a high-vacuum system and the surface was cleaned by electron bombardment from a hot tantalum filament. During

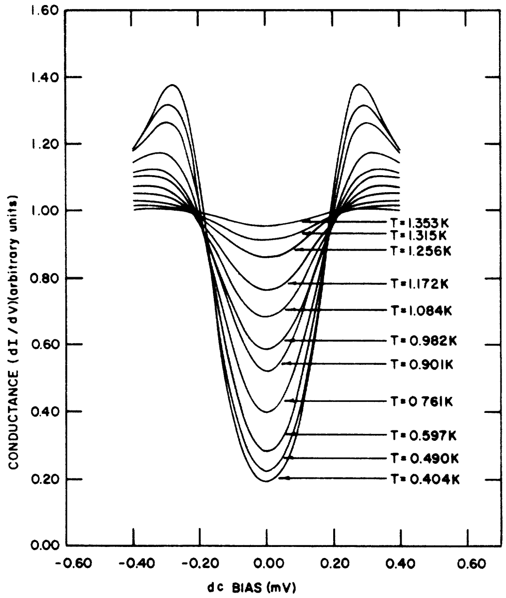


FIG. 1. Normalized conductance curves for a polycrystalline Th-$ThO_2$-Au tunnel junction (BAH-2). The transition temperature $T_c$ for this junction is 1.387 K.

the cleaning process the temperature was slowly increased to about 1200 °C while maintaining a pressure always lower than $4\times10^{-8}$ Torr. In the early stages of the cleaning process, there was copious outgassing from the sample surface. After two days of cleaning at temperatures near 1200 °C and pressures lower than $1\times10^{-8}$ Torr, the sample was cooled to room temperature and the surface was oxidized *in situ* with dry oxygen at 0.1 atm for about 20 min. This initial oxide layer reduced subsequent oxidation when the substrate was removed from the high-vacuum system. Many samples prepared in this way showed distinct thermal faceting and the grain sizes were often as large as several millimeters. Samples with very small grain size, on the order of a few hundredths of a millimeter, showed the most reproducible tunneling results and only these are reported here. After oxidation, Cu leads were attached to the thorium with indium solder. Part of the surface of the thorium was then coated with collodion and a second pair of contacts was placed on top of the collodion. The substrate and lead connections were then placed in a conventional bell-jar evaporator and a strip of Au was deposited to complete the junction. The resistance of the junction was monitored during evaporation. The final junction area was approximately 2 $mm^2$. Electron-tunneling conductance curves were obtained using a bridge system reported by Rogers.[10] This circuit has the advantage of yielding directly the conductance, $dI/dV$, and its derivative, $d^2I/dV^2$.

## III. RESULTS

Normalized conductance curves for one of the polycrystalline junctions reported here (BAH-2) are shown in Fig. 1. There appears to be an additional conductance in parallel with the tunneling processes, which, if Ohmic, could be subtracted from the data as a constant, independent of bias voltage and temperature. For the junctions reported here, this parallel conductance ranges between 14 and 19% of the normal-state conductance. The origin of this parallel conductance is not well understood but we believe the effect is due to very small metallic bridges through the oxide layer.[11]

If this single factor, a constant for any one junction, is subtracted from the data, then one obtains the results in Fig. 2, shown for five representative temperatures. The data, represented by the open circles, are in good agreement with the BCS theoretical curves derived by a technique outlined by Bermon[12] and shown by the solid lines. At the lowest temperatures, the experimental conductance rises less abruptly in the region of 0.1-mV bias than BCS predict, but this would be expected for a superconductor with an anisotropic energy gap. Anderson, Peterson, and Finnemore[13] have shown from measurements of the transition temperature $T_c$ as a function of electronic mean free path that thorium has a mean-squared anisotropy constant of $\langle a^2\rangle = 0.021$.[14] Therefore, the energy gap over different parts of the Fermi surface might vary between 3.1 and $3.9kT_c$, where $k$ is the Boltzmann

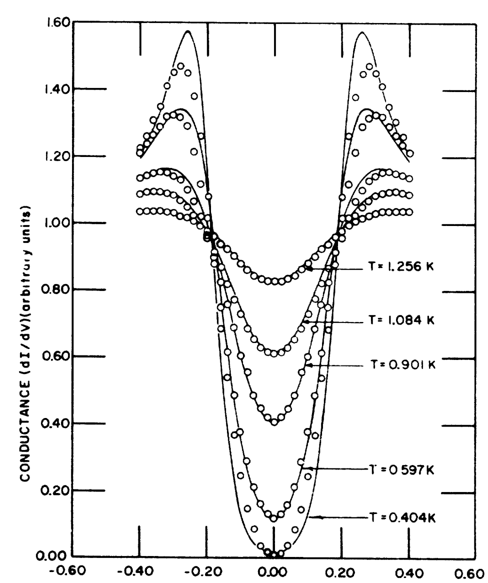


FIG. 2. Comparison of the data (open circles) and the theoretical BCS curves for polycrystalline Th-$ThO_2$-Au tunnel junction (BAH-2).

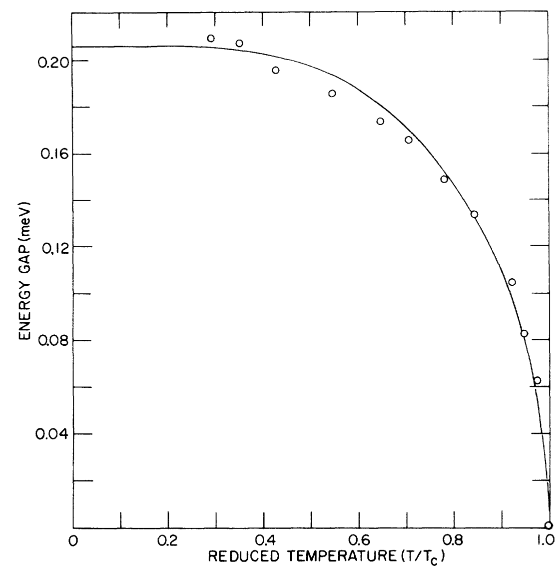


FIG. 3. Experimental energy-gap parameter for junction BAH-2 compared to the BCS curve for $2\Delta(0)=3.47kT_c$.

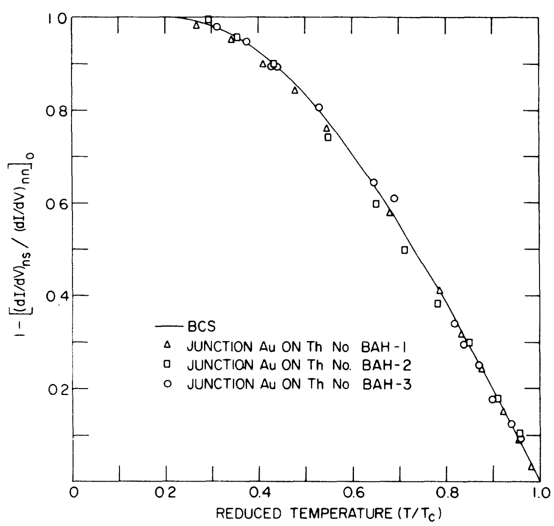


FIG. 4. Temperature dependence of the zero-bias conductance for polycrystalline thorium tunnel junctions. Transition temperatures for BAH-1 and BAH-3 are 1.316 and 1.39 K, respectively.

constant. With this much anisotropy, it is not surprising that the low-temperature and low-bias-voltage measurements differ from the BCS prediction.

The values of the energy-gap parameter which cause the measured and theoretical conductance curves to coincide at zero bias voltage are shown in Fig. 3. These yield a value for the energy gap of $2\Delta(0)=3.47kT_c$, in good agreement with critical-field measurements due to Decker and Finnemore.[15]

The characteristics of the other junctions (BAH-1 and BAH-3) are very similar to those shown for junction BAH-2. The conductance curves for different junctions agree well when compared at common temperatures. In addition, Fig. 4 shows that the zero-bias conductance values of the three junctions agree well with each other over the whole temperature range, and that the temperature dependence is close to the BCS prediction. It should be stressed that the three junctions agree with the BCS curve even though different amounts of parallel conductance have been subtracted from each junction.

A careful search was made for phonon-induced structure in the tunneling density of states but no significant structure was found. One sample showed an apparent structure which ended at 11-mV bias, but this effect did not repeat in other samples. Reese, Sinha, and Peterson,[16] using neutron-diffraction techniques, have determined the phonon end point in thorium to lie at 13.1 mV, which correlates loosely with our observations. At these bias voltages, one expects the tunneling electrons to sample the bulk material only up to distances of approximately 100 Å,[17] and apparently these junctions are not sufficiently clean at those distances. This again reflects the difficulty of preparing good junctions.

The tunneling results reported here are somewhat preliminary in that we have not been able to eliminate parallel-conductance effects and we have not sorted out all the anisotropy effects. The data, however, do represent the first electron-tunneling measurements on thorium and they indicate an excitation spectrum fairly close to BCS.

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†Present address: Lakehead University, Port Arthur, Ontario, Canada.

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# Fluctuation-Induced Conductivity of Superconductors above the Transition Temperature: Regularization of the Maki Diagram*

Joachim Keller† and Victor Korenman

*Department of Physics and Astronomy and the Center for Theoretical Physics, University of Maryland, College Park, Maryland* 20742

(Received 2 August 1971)

The Maki contribution to the conductivity above the superconducting transition temperature is regularized within the framework of the BCS theory. This is achieved through the renormalization of the impurity-scattering vertex by inclusion of the effects of pair fluctuations. The conductivity is evaluated for a thin film. It depends only on the reduced temperature and the normal resistance per square. Fair agreement is found with Al films over a wide temperature range. Agreement is not found with experiments on Bi, Pb, and Ga films, which apparently contain a strong additional pair-breaking effect. The temperature range in which interactions among fluctuations become important in the Maki conductivity is generally larger than that given by the Ginzburg criterion.

## I. INTRODUCTION

Many experiments on the electrical conductivity of superconducting thin films above the transition temperature[1] can be successfully described by a phenomenological theory of superconducting fluctuations[2] or an equivalent microscopic calculation by Aslamazov and Larkin (AL).[3] According to this theory the excess conductivity $\sigma'$ due to superconducting fluctuations above the transition temperature $T_c$ of a thin film is given by the relation

$$\sigma' = \sigma'_{\rm AL} = e^2/16dt \quad , \tag{1}$$

where $t$ is the reduced temperature, $t = \ln(T/T_c) \simeq (T - T_c)/T_c$, and $d$ is the thickness of the film.

The AL theory is based on a diagrammatic expansion of the conductivity tensor in terms of independent fluctuations. Among the first-order diagrams, all of which are required for gauge invariance, there are two which give rise to a strongly temperature-dependent conductivity. One, generally called the AL diagram, leads to the expression in Eq. (1). The second, first discussed by Maki,[4] is shown in Fig. 1. The conductivity associated with this diagram in one and two dimensions is infinite for all temperatures above $T_c$. This unphysical divergence is removed if a pair-breaking effect is present in the system.[5] In fact, recent experiments on aluminum films[6,7] in the presence of a magnetic field are well described by a formula derived by Thompson[5]:

$$\begin{aligned} \sigma' &= \sigma'_{\rm AL} + \sigma'_{\rm MT} \quad , \\ \sigma'_{\rm MT} &= (e^2/8d)\ln(t/\delta)/(t-\delta) \quad . \end{aligned} \tag{2}$$

Here $\sigma'_{\rm MT}$ is the contribution to the electrical conductivity of the Maki diagram, and $\delta$ is the sum of the two pair-breaking parameters $\delta_H$ and $\delta_i$, corresponding to the well-known pair-breaking effect of the external magnetic field and an intrinsic pair-breaking mechanism, respectively. In Eq. (2) $t$ is defined as before but refers to the actual transition temperature $T_c$, which is related to the transition temperature $T_{c0}$ in the absence of pair-breaking effects by the relation $T_c = T_{c0}(1-\delta)$. In the case of aluminum films the intrinsic pair-breaking