IV. CONCLUSIONS

The good agreement between our calculations and our data indicates that the model used contains the essential features of the problem. The fact that results from the solution of the linearized Ginzburg-Landau equations can be extended to the full temperature range[4] so readily is due to the fact that we are dealing with local or "dirty" alloys, for which an equation of the Ginsburg-Landau type exists at all temperatures.[10] The discrepancies which exist between the data and the calculated results for the higher κ material may be attributed to an inadequacy of the constant thickness of the sheath approximation, and to deviations from the simple two-fluid model temperature dependence.[19]

ACKNOWLEDGMENTS

We wish to thank H. Hanson for his assistance throughout this work. We wish to especially thank Dr. G. Fischer of RCA Laboratories, Zurich, Switzerland, for providing us with all of the X-band data.

[19] There may also be deviations from the assumed temperature dependence of κ. See D. E. Farrell and B. S. Chandrasekhar, Bull. Am. Phys. Soc. 11, 710 (1966).

PHYSICAL REVIEW VOLUME 155, NUMBER 2 10 MARCH 1967

Density of States of a Short-Mean-Free-Path Superconductor in a Magnetic Field by Electron Tunneling

JAMES L. LEVINE
IBM Watson Laboratory, Columbia University, New York, New York
(Received 13 October 1966)

Measurements of the density of states of a thin-film, short-mean-free-path superconductor in a magnetic field are reported. The measurements were made on indium-tin films by a conventional tunneling technique. Temperatures near 0.5°K were used, in order to minimize thermal smearing. The magnetic field was in the plane of the film, and the film thickness was such that the order parameter was expected to be substantially independent of position. The results are in excellent agreement with theoretical calculations of Maki, except very close to the critical field, where small discrepancies occur. Maki's calculations predict gapless superconductivity close to the critical field, but thermal smearing prevented a direct verification. An attempt to fit the data to a BCS density of states with a field-dependent energy gap was completely unsuccessful except at zero field, where the two theories agree.

I. INTRODUCTION

SEVERAL years ago, Abrikosov and Gor'kov[1] pointed out that the addition of magnetic impurities to a superconductor should have a profound effect on its excitation spectrum. Their most startling prediction was the possibility of gapless superconductivity, that is, the existence of superconductivity without a gap in the excitation spectrum. Measurements by Woolf and Reif[2] appear to have confirmed their prediction. More recently, Maki,[3] and Maki and Fulde[4] have treated the effect of a magnetic field and/or transport current on a superconductor containing nonmagnetic impurities and have found essentially identical results. In this paper, we report on measurements made on superconducting films with a magnetic field in the plane of the film, and with the film thickness and mean free path chosen in such a way as to satisfy the conditions implicit in Maki's paper. The density of states in these films was measured by a conventional electron-tunneling technique[5] and the data were found to be in rather good agreement with calculations based on Maki's theory. In contrast, an attempt to fit the data to a BCS-type[6] density of states with field-dependent energy gap was completely unsuccessful, except at zero field.

II. THEORY

A. Density of States

The geometry of a tunnel junction of the type used in our experiment is shown in Fig. 1. Here, metal 1 is a normal metal, the "insulator" is a mixture of oxide and adsorbed gases having a thickness of ≈ 20 Å, and metal

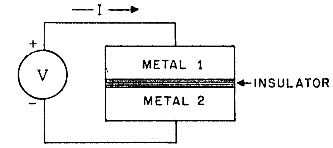

FIG. 1. Schematic representation of the tunneling experiment.

[1] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 39, 1781 (1960) [English transl.: Soviet Phys.—JETP 12, 1243 (1961)].
[2] M. A. Woolf and F. Reif, Phys. Rev. 137, A557 (1965).
[3] K. Maki, Progr. Theoret. Phys. (Kyoto) 31, 731 (1964). References to earlier work are given here.
[4] K. Maki and P. Fulde, Phys. Rev. 140, A1586 (1965).
[5] I. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1961).
[6] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

2 is a superconductor. The differential conductance of such a sandwich is given by

$$\frac{dI}{dV}=\left(\frac{dI}{dV}\right)_{nn}\int_{-\infty}^{\infty}\frac{N(E)}{N(0)}\left[\frac{1}{kT}\frac{e^x}{(1+e^x)^2}\right]dE, \qquad (1)$$

$$x=(E-eV)/kT.$$

Here, $N(E)$ is an effective density of states at energy E (measured from the Fermi surface), k is the Boltzmann constant, T is the temperature, e is the electronic charge, and V is the applied bias voltage. $N(0)$ is the density of states in the normal state at the Fermi surface. The function in brackets is the derivative of the Fermi function and is a bell-shaped curve of width $\approx 2kT$ peaked around $E=eV$, and having an integrated value of unity. In the limit of zero temperature, it approaches a delta function, so that dI/dV at voltage V becomes proportional to $N(E=eV)$. At nonzero temperatures, a certain amount of smearing occurs because of the width of the function. With both metals in the normal state, the conductance is represented by $(dI/dV)_{nn}$ and is essentially constant over the voltage range of interest (several tens of millivolts).

In a pure superconductor, electrons of equal and opposite momenta are paired. If nonmagnetic impurities are added, pairing takes place between time-reversed "scattered" states.[7] In either case, the lifetimes of the pair states are effectively infinite and $N(E)$ is given by the BCS relation:

$$N(E)/N(0)=\begin{Bmatrix} 0 & |E|<\Delta_0 \\ |E|/(E^2-\Delta_0^2)^{1/2} & |E|>\Delta_0 \end{Bmatrix}. \qquad (2)$$

Here, $2\Delta_0$ is the energy gap, essentially the minimum energy required to break up a pair. The application of a field or current or the introduction of magnetic impurities breaks the time-reversal symmetry of the system, giving a finite lifetime to the pairs, and thus decreasing the degree of ordering. These effects are handled by a Green's-function technique. The results have been fully discussed elsewhere.[8,9] We will present only the relevant formulas here, in order to establish a consistent notation. The density of states is given by[8]

$$N(E)/N(0)=|(E/\Delta)(1/Z^{1/2})\,\mathrm{Im}(X-Z)^{-1}|. \qquad (3)$$

Here, Im stands for "imaginary part of," and Z is a parameter which depends on the applied field and/or transport-current density, and on the concentration of magnetic impurities. If only nonmagnetic impurities are present and a magnetic field is applied in the plane of the film, Z may be expressed in terms of a Fourier transform of the vector potential inside the film.[10] Under the con-

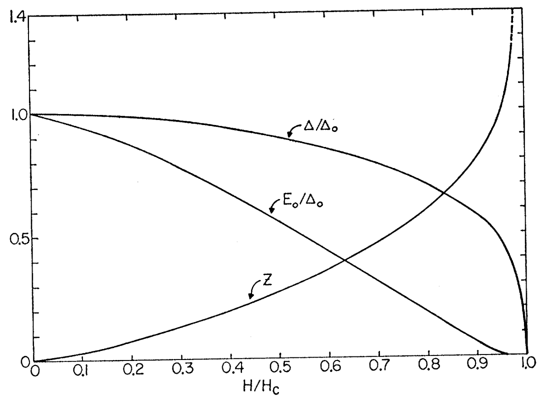

FIG. 2. The parameters Z, Δ/Δ_0, and E_0/Δ_0 as functions of the reduced field strength H/H_c.

ditions of the present experiment (see Sec. II.B), it may be put in the convenient form

$$Z=[\tfrac{1}{2}(\Delta_0/\Delta)(H/H_c)^2]^{2/3}. \qquad (4)$$

The variable ζ used by Maki is equal to $Z^{3/2}$. The quantity $2\Delta_0$ is now the zero-field energy gap. Δ is essentially an order parameter, and may be thought of as specifying the density of "superelectrons" or the degree of pair correlation. It is normalized here such that $\Delta=\Delta_0$ in zero field, and is given by[3]

$$\begin{aligned}\ln(\Delta/\Delta_0)&=-\tfrac{1}{4}\pi Z^{3/2}, & Z\lesseqgtr 1\\ &=-\cosh^{-1}(Z^{3/2})-\tfrac{1}{2}[Z^{3/2}\sin^{-1}(1/Z^{3/2})\\ &\quad-(1-1/Z^3)^{1/2}], & Z>1. \qquad (5)\end{aligned}$$

Equations (4) and (5) form a set of transcendental equations which must be solved numerically in order to obtain Δ and Z as functions of H/H_c. The variable X in Eq. (3) is obtained by solving the quartic equation

$$E/\Delta=(1-X^2Z)^{1/2}(1-Z/X). \qquad (6)$$

A complex root is required in order that $N(E)$ be nonzero because the other quantities appearing in Eq. (3)

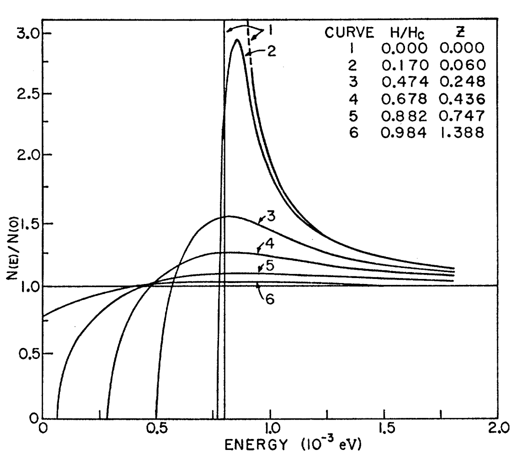

FIG. 3. Effective density of states versus energy for the field strengths indicated.

[7] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
[8] P. Fulde, Phys. Rev. **137**, A783 (1965).
[9] S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. **136**, A1500 (1964).
[10] R. S. Thompson and A. Baratoff, Phys. Rev. Letters **15**, 971 (1965).

are real. The existence of an energy gap is associated with the fact that the roots of Eq. (6) are all real if $Z<1$ and if E is less than an energy E_0 given by

$$E_0=\Delta(1-Z)^{3/2}. \qquad (7)$$

Here, $2E_0$ plays the role of an energy gap. For $Z \gtrsim 1$, a complex root of Eq. (6) exists for all E, and the energy gap is zero. In Fig. 2, we show Z, Δ, and E_0 as functions of H/H_c. Note that the energy gap vanishes for $H/H_c \gtrsim 0.955$, whereas Δ remains nonzero until H/H_c is equal to 1. The region $0.955<H/H_c<1$ is referred to as a region of "gapless superconductivity." In the limit as $H/H_c \to 0$, $N(E)$ reduces to the BCS density of states, Eq. (2).

In Fig. 3, we show $N(E)/N(0)$ for several values of H/H_c. The calculations were performed on a digital computer. Note the absence of a singularity in the density of states for $H/H_c>0$. This feature, and the subsequent spread of the density-of-states peak, is a result of the finite lifetime of the pairs brought about by the field. An interesting feature of these curves is that the maximum in the density of states still occurs in the vicinity of the zero-field energy gap. The density of states given above was derived for the case of zero temperature, and can be extended to nonzero temperatures by introducing thermal Green's functions. The errors involved in neglecting the effect of temperature on $N(E)$ are uncertain, but should be small and of the order kT/Δ_0. This quantity was less than 0.1 in the present experiments.

B. Experimental Considerations

In order to simplify his calculation, Maki made several assumptions which restrict the range of film thickness D, and mean free path l, over which the theory is expected to be valid. The first restriction is that the transport mean-free-time τ satisfy

$$\tau\Delta_0 \ll \hbar. \qquad (8)$$

Introducing the Fermi velocity v_0 and the coherence length of the pure material ξ_0, setting $\tau=l/v_0$, and making use of the BCS relation $\xi_0=\hbar v_0/\pi\Delta_0$, this becomes

$$l \ll \hbar v_0/\Delta_0=\pi\xi_0. \qquad (9)$$

Apart from simplifying the calculation, a short mean free path serves to eliminate anisotropy in $N(E)$. This is fortunate because the angular variation of tunneling probability is not known with any degree of certainty in real junctions. The second assumption is that the order parameter Δ is essentially constant across the thickness of the film. A magnetic field tends to depress Δ more near the surface of the film than in the interior because the induced velocities are higher near the surfaces. However, rapid spatial variation of Δ is energetically unfavorable. As discussed, for example, by deGennes and Tinkham,[11] Δ will be very nearly independent of position if the film thickness is much less than a characteristic length ξ_Δ, i.e.,

$$D \ll \xi_\Delta \cong (\xi_0 l)^{1/2}. \qquad (10)$$

Finally, Maki assumed the electrodynamics to be local, thus implying that the vector potential varies slowly over distances of the order of the electrodynamic coherence length ξ_a. In a thin film, the vector potential varies with a length scale equal to the film thickness D, so that this would require[11]

$$D \gg \xi_a=(\xi_0^{-1}+l^{-1})^{-1}\approx l, \quad l \ll \xi_0. \qquad (11)$$

In practice, it is difficult to satisfy Eqs. (10) and (11) simultaneously $[l \ll D \ll (\xi_0 l)^{1/2}]$. As shown by Thompson and Baratoff,[10] however, inequality (11) is unduly restrictive, and can be replaced by the much weaker inequality

$$D \gg l(l/\xi_0). \qquad (12)$$

It is also desirable to make the film thickness somewhat less than the weak-field penetration depth for the following reason. The parameter Z discussed above depends on a Fourier transform of the vector potential inside the film. If the film thickness is comparable to or greater than the penetration depth λ, the vector potential will depend on λ because of screening effects. Therefore, Z will depend on λ. Since λ itself is field-dependent, tending towards infinity as $H \to H_c$, Z will vary in a complicated manner with field. While it is possible to take these complications into account,[12] it is more convenient to avoid them. We require[11]

$$D \lesssim \lambda_w \approx \lambda_{Lp}(\xi_0/l)^{1/2}, \quad l \ll \xi_0. \qquad (13)$$

Here, λ_w is the weak-field penetration depth and λ_{Lp} is the London penetration depth for the pure material. The relation between Z and H given in Eq. (4) applies only if Eq. (13) is satisfied. In Fig. 4, we show ξ_Δ, $l(l/\xi_0)$, and λ_w plotted as functions of mean free path and tin impurity concentration for indium, the material used in our experiments. The unshaded region of the figure corresponds to acceptable values of l and D (where D is taken from the vertical axis). We have used the zero-temperature value for the various parameters discussed above. The errors introduced thereby are negligible in the present experiment.

III. EXPERIMENTAL

A. Sample Preparation

Indium with tin as an impurity was found to be a convenient choice for study as stable solid solutions exist having suitable mean free paths. In addition, $N(E)$ for these alloys in zero field is well approximated

[11] P. G. deGennes and M. Tinkham, Physics **1**, 107 (1964).

[12] An expression for the penetration depth as an implicit function of field strength is given in Ref. 3.

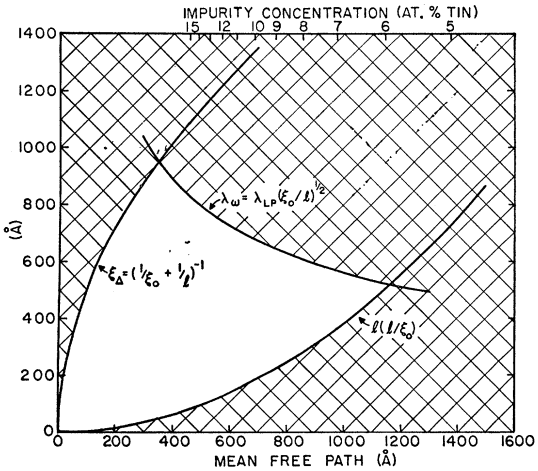

FIG. 4. The length scale for order-parameter variation ξ_Δ, the weak-field penetration depth λ_w, and the nonlocal parameter $l(l/\xi_0)$ as functions of mean free path. The necessary parameters were taken from A. M. Toxen [Phys. Rev. **127**, 382 (1962)] and A. M. Toxen and M. J. Burns [*ibid.* **130**, 1808 (1963)]; $\xi_0 \approx 2600$ Å, $\lambda_{Lp} \approx 350$ Å, and $l \approx 6900$ Å/(at.% tin).

by the BCS relation with only weak phonon structure,[13] thus simplifying a comparison with theory. The relevant parameters for indium are given in the caption of Fig. 4. The mean free paths in our sample appear to have been reduced somewhat by grain-boundary scattering. This will be discussed in Sec. III.C. Alloys covering the range 0–12 at.% tin were prepared by melting the components under vacuum. The alloys were held above their melting temperature for several days to ensure homogeneity.

Aluminum was used as the normal metal because of its well-behaved oxide layer. A few percent of manganese was added to the aluminum in order to suppress its superconductivity.[14] Commercial aluminum foil with a layer of vacuum-deposited manganese was found to be a suitable starting material for this purpose. The evaporation rates of the two components are very nearly the same, and the resulting alloy was found to be normal at the lowest temperature reached (0.5°K). There was no evidence that the presence of manganese in the aluminum affected the superconducting properties of the indium films. An attempt to use magnesium as the normal metal was partly successful, but the normal-state resistance of the resulting junctions was difficult to control and increased very rapidly with time.

Tunnel junctions were formed in the usual manner.[5] A 0.25-mm-wide strip of the aluminum alloy was deposited onto a substrate cut from a standard microscope slide, and allowed to oxidize in air for several hours. A weighed charge of the indium-tin alloy was then evaporated to completion forming a cross strip. The substrate was cooled to 150°K during this deposition to prevent agglomeration. Prior to the latter evaporation, part of the aluminum strip was coated with thick Formvar insulation in such a way as to eliminate tunneling from the tapered edges of the indium film. The resulting junctions had dimensions of 0.25 mm by approximately 0.50 mm and normal-state resistances near 3 kΩ. Junctions formed without the Formvar insulation had very broad magnetic-field transitions and were completely unsuitable for quantitative measurements. The alloy films were annealed for several days at room temperature in order to eliminate possible gradients in the tin concentration caused by the different evaporation rates of the two components. Film thicknesses were 750 ±50 Å as determined by a multiple-beam interferometer. The pressure in the evaporator remained below 2×10^{-5} Torr during the indium evaporation.

B. Cryogenics and Electronics

Temperatures down to 0.5°K were provided by a simple "one-shot" helium-3 refrigerator. An electronic regulator held the temperature constant to ±1 mdeg K. A carbon-resistor thermometer was calibrated against the vapor pressure[15] of helium 4 in the vicinity of 1.5°K and the Clement-Quinnell[16] formula used to extrapolate into the region of interest. No attempt was made to achieve great accuracy because the temperature was inferred directly from the observed tunneling characteristics at zero field. This will be discussed in detail in Sec. III.C. The magnetic field was produced by a conventional iron-pole magnet and measured with a Hall-effect Gaussmeter, which was linear to approximately 1%. The field was set parallel to the surface of the film to within a few tenths of a degree. This was necessary because of the very large demagnetizing factor of a thin film in the direction normal to the surface. The adjustment was made with the sample in place and consisted of finding the angular position of the magnet which produced the least change in the density of states with a field of $\approx\frac{1}{4}H_c$.

The differential conductance was measured by a simple ac technique. A dc bias voltage and a small 400-Hz sine-wave voltage were applied to the sample from a low-impedance circuit. The in-phase component of the ac current through the junction, which is proportional to the differential conductance, was measured with a phase-sensitive detector, and displayed on an X-Y recorder as a function of bias voltage. The ac voltage was limited to 15-μV rms, in order to prevent loss of resolution. Very careful attention was given to the shielding and ground connections in order to prevent induced power-line voltages from appearing across the junction. rf pickup from nearby radio transmitters was found to be particularly objectionable and was finally

[13] J. G. Adler and J. S. Rogers, Phys. Rev. Letters **10**, 217 (1963), and the present work.

[14] G. Boato, G. G. Gallinaro, and C. Rizzuto, Rev. Mod. Phys. **36**, 162 (1964).

[15] F. G. Brickwedde *et al.*, Nat. Bur. Std. (U. S.), Monograph **10** (1960).

[16] J. R. Clement and E. H. Quinnell, Rev. Sci. Instr. **23**, 213 (1952).

eliminated by inserting low-pass filters in all leads entering the cryostat.

C. Experimental Results and Comparison with Theory

In Figs. 5 and 6, we show the conductance characteristics for an indium film containing a 12% tin impurity ($l \approx 575$ Å), for several field strengths. The conductance has been normalized to the normal-state value. The solid curves are tracings of the original data with the noise smoothed over. The temperature was low enough (approximately 0.5°K) that the conductance is nearly proportional to the density of states, although structure with an energy scale less than $2kT \approx 0.1$ mV is not well resolved.

Before discussing the data, we will describe the procedure used to obtain the parameters needed for a comparison with the theory. These parameters are the zero-field energy gap Δ_0, the temperature T, and the critical field H_c. The parameters Δ_0 and T were obtained by fitting the zero-field conductance curve to the BCS density of states. The (normalized) conductance at the peak in the conductance curve (see Fig. 5) gave a value of Δ_0/T, while the voltage at which the peak occurred gave a value for Δ_0, so that both Δ_0 and T were obtained.[17] The dashed curve in Fig. 5 was calculated, using the above parameters, and is seen to agree rather well with the experimental curve. Only Δ_0 and the ratio Δ_0/T were needed for this and the remaining analysis; however, a comparison between the temperature determined in this way and that actually measured provided a useful check on the procedure. For most samples studied, the two values of temperature agreed within 1 or 2%. The critical field was taken to be the value which destroyed superconductivity as judged by the absence of structure in the conductance curves. A sensitive procedure was to plot the value of the conductance at zero bias as a function of field strength, as shown in Fig. 7. The sharp transition with no observable "tailing" indicates the high homogeneity of the films.

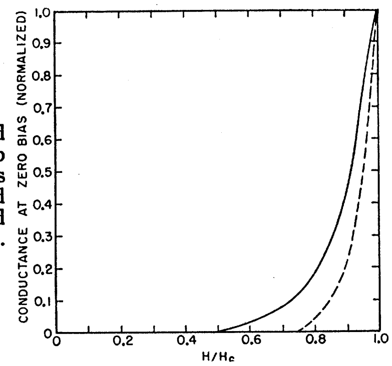

Fig. 7. Normalized conductance at zero bias voltage versus field strength (solid curve). The dashed curve is theoretical.

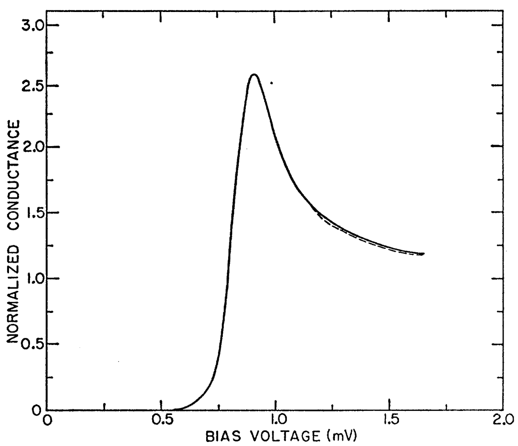

Fig. 5. Normalized tunneling conductance versus bias voltage at zero field (solid curve). The dashed curve was calculated from the BCS density of states with the energy gap and temperature chosen to fit the peak. Where the two curves overlap, only the experimental curve is shown.

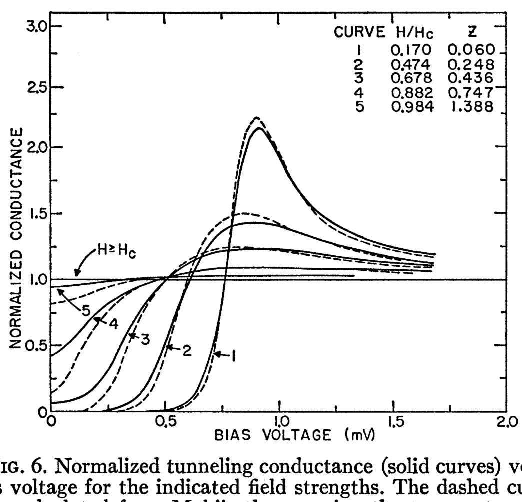

Fig. 6. Normalized tunneling conductance (solid curves) versus bias voltage for the indicated field strengths. The dashed curves were calculated from Maki's theory using the temperature and zero-field energy gap determined from Fig. 5.

With the parameters obtained in the above manner, a direct fit to the remaining data was made. The integral in Eq. (1) was evaluated numerically, using the density of states obtained from Eqs. (3)–(6). The results are shown by the dashed curves in Fig. 6. Note that the curves of $N(E)$ in Fig. 3 were calculated for the same values of H/H_c as in this figure. The agreement with experiment is satisfactory and in our opinion provides strong support for the theory in its present form. In contrast, an attempt to fit the data to the BCS density of states with a field-dependent energy gap failed completely. In Fig. 8, we show this clearly by exhibiting two possible fits to the data, using the BCS density of states, with the parameters determined in an obvious manner. Referring again to Fig. 6, the peak in the experimental curve is somewhat broader than expected, and the regions near zero bias are more nearly filled in. This is shown also by the theoretical curve in Fig. 7 (dashed

[17] Calculations in tabular form were used: S. Bermon, Technical Report No. 1, National Science Foundation Grant No. NSF-GP1100, Department of Physics, University of Illinois, 1964 (unpublished)

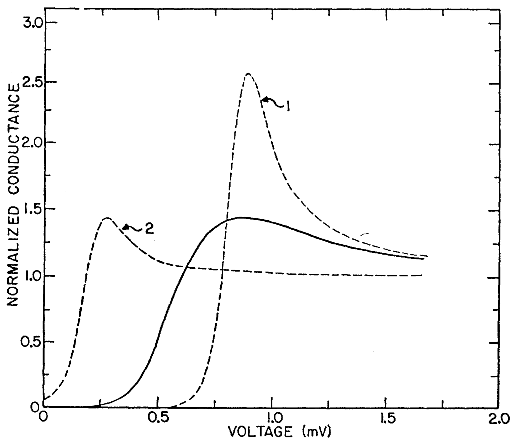

FIG. 8. Two attempted fits (dashed lines) to a conductance curve (solid line) at nonzero field strength, using the BCS density of states. For curve 1, the energy gap was determined from the peak location; for curve 3, the gap was determined from the peak height. The temperature was taken from the zero-field conductance curve.

line). This may be a result of neglecting the direct effect of temperature on the density of states, as discussed in Sec. II.A. In particular, Maki[3] has calculated the variation of Δ and E_0 with magnetic field for nonzero temperatures. For the reduced temperature of our experiments ($T/T_c \approx 0.13$) there are small but noticeable departures from the zero-temperature values near H_c. In addition, small variations of film thickness and mean free path across the sample would produce such effects. Similar, but in some cases far more pronounced, discrepancies were observed by Woolf and Reif[2] in their measurements on films containing various magnetic impurities. The fact that the agreement with theory is better in our case suggests that a more detailed treatment of magnetic scattering is required, since the present calculations predict identical results for the two cases (the addition of magnetic impurities affects only the parameter Z). Similar conclusions were reached by Woolf and Reif.

We have also made similar measurements on indium films of the same thickness containing lower concentrations of impurities (0% and 4% tin). If only scattering from the tin impurities was important in determining the electrodynamics of these films, both would have been in the nonlocal regime. In fact, the agreement with theory was nearly the same as in the case of the film containing 12% tin, although the discrepancies were slightly greater in the case of the nominally pure film. This suggests an additional scattering mechanism, possibly grain-boundary scattering, or scattering from dissolved gas atoms introduced during the deposition of the films. Such an explanation seems essential in the case of the "pure" film, since in this case nearly all the conditions discussed above should have been violated (see Fig. 4). An attempt to determine the mean free paths in these rather thin films by measuring the temperature dependence of the film resistivity did not yield consistent results in the purer films, because of the strong dependence of apparent mean free paths on the measured film thicknesses. In most cases, the mean free paths determined in this way were shorter than expected on the basis of scattering from the tin impurity alone. Similarly, calculations of the mean free path based on the measured critical fields gave consistent results only for the very impure films.

We stress that, in all cases studied, the major disagreement with Maki's calculations consists of a more rapid "filling in" of the conductance curves near zero bias, close to H_c, and can probably be attributed to small variations in H_c across the film due to variations in film thickness and mean free path. Such effects would be quite important near H_c because of the very strong dependence of Δ and E_0 on H/H_c in this regime. We note also that the main evidence for gapless superconductivity near H_c comes from the agreement with theory away from H_c. Near H_c, where the energy gap is expected to be small in any case (the transition of a thin film in a parallel magnetic field is known to be of second order), thermal smearing prevents a direct measurement of the energy gap. Thus, our data near H_c are not inconsistent with a small energy gap provided that the displaced states are distributed fairly smoothly at higher energies.

IV. CONCLUSIONS

We believe that the agreement between theory and experiment, discussed above, provides strong support for Maki's treatment of superconducting alloys. The discrepancies which do occur are small and may have been caused by neglecting the effect of temperature on $N(E)$ or by a variation in H_c across the samples. A calculation of this temperature dependence would be useful in deciding this question. Alternatively, the experiments could be repeated at lower temperatures, but a substantial improvement in this direction would probably require adiabatic demagnetization techniques. Because of thermal smearing, the existence of gapless superconductivity could not be directly verified. Measurements at much lower temperatures would also provide more information on this aspect of the theory.

ACKNOWLEDGMENTS

I would like to thank Dr. R. L. Garwin and Dr. P. J. Price for helpful comments on the manuscript.