temperature-dependent coherence length of de Gennes) is not satisfied, it can be estimated that Δ varies by no more than 5% over the film. We also note that the two dirty films with similar mean free paths give identical results, while the clean film gives a different result. Therefore the change observed in the conductivity is presumed to be caused by a different mean free path.

Theoretical curves for a small finite temperature can be estimated from

$$\sigma(\omega)=\int_0^\infty \frac{N(\omega')}{N_0}\frac{d}{d\omega'}[f(\omega-\omega')-f(\omega+\omega')]d\omega', \quad (40)$$

where

$$f(E)=[\exp(E/T)+1]^{-1}. \quad (41)$$

In Fig. 8 we have plotted theoretical curves $\sigma(0)$ for $l/\xi_0=0$, 0.314, and 1.256, respectively. A comparison between the experimental points and the theoretical curves of Fig. 8 shows that the theory developed for $l\neq 0$ predicts a deviation from the case $l\rightarrow 0$ even for $l/\xi_0\simeq 0.1$ which is in qualitative agreement with experiments. A more extensive analysis of the experimental data will be given elsewhere.[14]

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Tunneling into Superconducting Films in a Magnetic Field*

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Tunneling experiments were performed on thin superconducting films in the presence of a magnetic field. The experiments were done at He^3 temperatures on tin and tin-indium alloy films with thicknesses between 600 and 2000 Å. As expected theoretically, the effect of the field on the density of states is, for dirty films, similar to the effect of paramagnetic impurities with the square of the magnetic field playing a role analogous to the paramagnetic impurity concentration. The data are compared with the theoretical results of Maki for the limit of zero mean free path, and agreement is fair. The difference between these results and those of this experiment is attributed to the finite mean free path. Strässler and Wyder have calculated the field dependence of the density of states for small particles with arbitrary mean free path. We find that their calculations are in good agreement with experiment.

I. INTRODUCTION

In 1960 Abrikosov and Gor'kov[1] published a theory that described the behavior of superconductors containing paramagnetic impurities. They derived the surprising result that, for an impurity concentration equal to 91% of the concentration which reduces T_c to zero, the energy gap Ω_g vanishes at all temperatures while the order parameter Δ remains finite over a finite temperature range. In this range the metal is a superconductor, capable of carrying persistent currents, but it has no energy gap in the excitation spectrum. This phenomenon, gapless superconductivity, has been observed in tunneling experiments by Woolf and Reif.[2] They measured the density-of-states spectrum for various concentrations of gadolinium in lead and found good agreement with the theory as worked out in detail by Skalski *et al.*[3]

The theoretical density-of-states spectrum $N(\omega)$ in the presence of magnetic impurities is strongly modified from that found in the BCS theory,[4] namely, $N(\omega)/N_0=\omega/(\omega^2-\Delta^2)^{1/2}$ for $\omega>\Delta$, and zero for $\omega<\Delta$, where N_0 is the density of states in the normal metal. The change is more profound than can be described by simply using some field-dependent gap parameter in the BCS formula. Rather, the shape of $N(\omega)$ is smeared out, the edge of the gap in the state density becoming less sharp. This behavior is exemplified by the existence of gapless superconductivity, mentioned above, whereas the BCS formula requires that there be a gap if the state density is not completely normal. In view of these drastic changes, interpretation of experimental measurements on magnetically perturbed superconductors in terms of BCS theory with a reduced, field-dependent gap has only qualitative or, at best, semiquantitative significance.

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[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)].

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In a series of papers on currents and fields in superconductors, Maki[5] showed that the effect of a magnetic field on a thin dirty superconductor is in many ways the same as the effect of paramagnetic impurities. The same conclusion was reached independently by de Gennes[6] using a less formal method. (It should be noted, however, that the two situations need not be equivalent for all purposes. For example, Maki and Griffin have recently shown[7] that the effect on the Tomasch oscillations of the two types of magnetic perturbations should be quite different.) The parameter analogous to the magnetic impurity concentration is the square of the magnetic field. Thus, a dirty superconductor should become gapless at a field H satisfying $(H/H_c)^2=0.91$. In a similar way, the density-of-states spectrum calculated by Skalski *et al.* for the paramagnetic impurity situation, rather than a BCS spectrum with a field-dependent gap, should also apply to the magnetic field case. Hence, it is evident that the BCS theory with simply a field-dependent gap parameter also has only limited validity for describing the properties of thin films exposed to magnetic fields. For example, interpretations of data on thermal conductivity,[8] microwave absorption,[9] and electron tunneling[10,11] using this point of view should be viewed as having only limited quantitative significance. This conclusion had been anticipated[9] from the inconsistency of the $\Delta(H)$ values inferred from these various experiments.

The density-of-states results obtained from the Abrikosov-Gor'kov theory, as calculated by Skalski *et al.* and applied to the magnetic field problem by Maki (we shall henceforth abbreviate the preceding by AGSM) are valid only in the dirty limit, i.e., when $l/\xi_0=0$, where l is the electronic mean free path and $\xi_0=\hbar v_F/\pi\Delta(0)$ is the coherence length. In the opposite limit, Larkin[12] solved the Gor'kov equations including the effect of a magnetic field for the unrealistic case of pure spherical and cylindrical superconductors with specular surface scattering and no volume scattering. His calculation is restricted to particles small compared to λ and ξ_T, where λ is the penetration depth and ξ_T is the de Gennes coherence length governing spatial variations of the gap parameter Δ. He found results that are different from AGSM; in particular, the reduced field at which a pure superconductor becomes gapless is predicted to be much smaller than the corresponding field for a very dirty superconductor. Roughly speaking, the state density smears out even faster in clean than in dirty superconductors exposed to a magnetic field.

Strässler and Wyder[13] have used Larkin's approach to treat superconductors of arbitrary intermediate purity. As did Larkin, they derive results for spherical samples with specular reflection at the surface and diameter small compared to ξ_T, so that Δ may be taken to be independent of position, and small compared to λ, so that the applied field penetrates uniformly. However, they carried out numerical calculations to find the spectrum of state density for values of l/ξ_0 intermediate between the Larkin limit of a pure metal with $l/\xi_0=\infty$, and the AGSM limit $l/\xi_0=0$.

The major prior experimental work testing these theories of the effect of magnetic fields is that of the Orsay group,[14] which was almost entirely confined to the gapless subcritical range of magnetic fields and to comparison with the de Gennes–Maki theory for the limit $l/\xi_0=0$. This work demonstrated clearly the inapplicability of a BCS-like state density to these systems. In particular, it showed that in the gapless subcritical region $N(\omega)$ had an energy scale independent of H, whereas any BCS-like approach with simply a field-dependent gap parameter would lead to a field-dependent energy scale for $N(\omega)$.

Note added in proof: While the present paper was in press, a report of rather similar work was published by James L. Levine [Phys. Rev. **155**, 373 (1967)]. The present paper differs in that it offers data on $T_c(H)$ and comparison with theory for nonzero values of l/ξ_0.

In the experiments reported here, we measure the density-of-states spectrum in superconducting films over a much wider range of magnetic fields, including field values for which the spectrum still shows a gap. In this way we can make a more thorough test of the theory, including the new results of Strässler and Wyder for finite values of l/ξ_0 which have not previously been tested.

II. EXPERIMENTAL TECHNIQUES

The samples, which consisted of a normal metal and a superconducting metal separated by a thin oxide layer, were vacuum deposited onto crystal quartz substrates. The normal metal was an Al-Mn alloy. Al was used because it oxidizes easily to form a durable insulating layer; a small amount of Mn was added to keep the film normal at the low temperatures of the experiment. The superconducting film was either Sn or a Sn-5%In alloy. It was evaporated onto a substrate whose temperature was about −150°C; the pressure at the beginning of the evaporation was between 10^{-7} and 10^{-6} mm Hg. The alloy pellet was evaporated to

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[14] E. Guyon, A. Martinet, J. Matricon, and P. Pincus, Phys. Rev. **138**, 746 (1965).

TABLE I. Film properties.

	$H_{c\parallel}$ (Oe)	$H_{c\perp}$ (Oe)	$(R_{300}/R_{4.2})$	Δ_0 (meV)	T_c (°K)	d (Å)	ξ_T (Å)	l_R (Å)	$(l_R)_H$ (Å)
Sn-In 1	1840	620	4.45	0.605	3.77	850	730	320	360
Sn 1	1535	500	6.2	0.628	3.85	920	800	490	480
Sn 2	880	260	13.7	0.620	3.79	1150	1130	1190	1260

[a] $H_{c\parallel}$ and $H_{c\perp}$ are the parallel and perpendicular critical fields of the film at $\sim$0.3°K; $R_{300}/R_{4.2}$ is the measured resistance ratio; Δ_0, the fitted gap parameter n zero field and at $\sim$0.3°K; T_c, the critical temperature; d, the film thickness; ξ_T, the low-temperature value of the temperature-dependent coherence length of de Gennes; l_R and $(l_R)_H$, the electronic mean free path as determined from normal-state resistance and from critical-field values as indicated in the Appendix.

completion so that the ratio of Sn to In was the same in the film as in the pellet. Since diffusion at room temperature between the two metals takes place quite readily,[14] we expect the local composition of the film everywhere to approximate that of the pellet.

Before the sample was mounted in the cryostat, the edges of the superconducting film were trimmed (except at the junction) in order to eliminate the thinner parts of the film and thus sharpen the resistive transition in a magnetic field.[15]

Measurements of the ac resistivity of the junctions were made using a small, constant amplitude ac current and a lock-in amplifier. The arrangement is similar to that described by Giaever *et al.*[16] The "normal" differential resistivity used for normalization was taken to be that in the superconducting state at a voltage many times the gap.

The experiments were performed in a He^3 cryostat so that thermal smearing of the density of states was minimized. Care was taken to keep superconducting solders at least 5 in. from the sample block to ensure the field near the sample was not distorted by their diamagnetism. Alignment parallel to the field within 0.1° was easily possible by monitoring the resistive transition. The possible existence of trapped flux was investigated by comparing data taken at $H=0$ before and after a large field was applied. No difference was observed, confirming the absence of significant trapped flux effects. We feel that this measurement also excludes any important effect of any small perpendicular field component producing flux quanta penetrating through the film, since such flux is strongly hysteretic.[17]

III. RESULTS

The quantity measured was the inverse of the differential conductivity, σ^{-1}. The data were inverted to yield σ, which is related to the density of states by the following expression[18]:

$$\sigma=\frac{(dI/dV)_S}{(dI/dV)_N}=e^{-1}\int_0^\infty \frac{N(\omega)}{N_0}\frac{d}{dV}[f(\omega-eV)-f(\omega+eV)]d\omega, \quad (1)$$

where $N(\omega)$ is the superconducting density of states as a function of energy ω, N_0 is the density of states at the Fermi level, and $f(x)=[1+\exp(x/kT)]^{-1}$ is the Fermi function.

At zero temperature, the conductivity $\sigma(V)$ is directly proportional to the density of states $N(eV)$. At a finite temperature T the conductivity is proportional to an average of $N(\omega)$ over a range $\sim kT$ about the energy eV. Evidently, to resolve structure of the order of the energy gap Δ one must have $kT\ll\Delta$. In our experiments, Sn and the Sn-In alloys have a zero-field gap of about 600 μeV, while the thermal energy kT at He^3 temperatures is of the order of 30 μeV. Thus, this condition is well satisfied in these measurements until the magnetic field has reduced the gap by a factor of order 10.

We shall concentrate on the tunneling results for a representative sample of Sn-In, namely Sn-In 1. The properties of this film are given in Table I, together with the properties of two films of nominally pure tin. The methods used for obtaining the numbers in this table are explained in the Appendix.

The tunneling results in zero field are shown in Fig. 1, together with points from Eq. (1) using the BCS density of states, $N(\omega)=N_0\omega(\omega^2-\Delta_0^2)^{-1/2}$. Agreement between theory and experiment for the zero-field case is evidently quite good. The theoretical curve was fitted to the experimental curve by adjusting Δ_0 and T. The temperature obtained this way agreed, within experimental accuracy, with the temperature indicated by the McLeod gauge measuring the He^3 vapor pressure.

The tunneling results for finite fields are shown in Fig. 2 together with the theoretical curves of AGSM, $l/\xi_0=0$, and of Strässler and Wyder, $l/\xi_0=\pi/10$. The AGSM curves are obtained from the expressions in Skalski *et al.*[3] using $\Gamma=(\Delta_0/2)(H/H_{c\parallel})^2$. Both the AGSM curves and the Strässler-Wyder curves are calcu-

[15] E. H. Rhoderick, Proc. Roy. Soc. (London) **267**, 231 (1962).

[16] I. Giaever, H. R. Hart, Jr., and K. Megerle, Phys. Rev. **126**, 941 (1962).

[17] This situation contrasts with that observed in far-infrared studies of films in magnetic fields in which trapped flux effects were noted. [M. Tinkham, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland Publishing Company, Amsterdam, 1966), p. 431.] We believe this greater difficulty with trapped flux can be attributed to the following factors: the far-infrared experiments require thinner and larger films, leading to a much more unfavorable demagnetizing factor; also, the field of the superconducting solenoid was less homogeneous than the field of the iron-core magnet used in the present experiments.

[18] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).

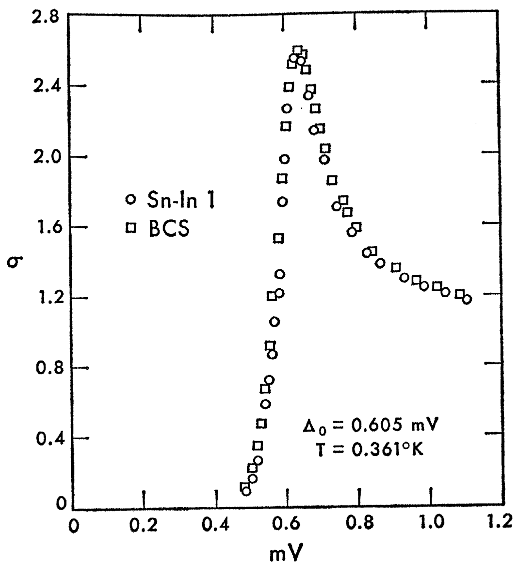

FIG. 1. Energy dependence of measured σ for zero magnetic field compared with BCS theory. Δ_0 is the energy-gap parameter at $H=0$, $T\approx 0$.

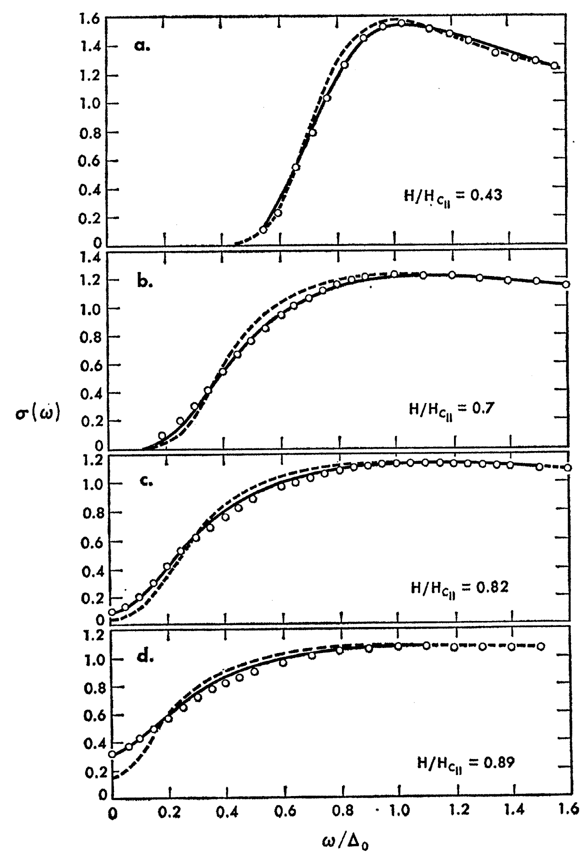

FIG. 2. Energy dependence of σ for Sn-In 1 in parallel magnetic field at $T=0.361$°K. Dashed curve is AGSM theory ($l/\xi_0=0$); solid curve is Strässler-Wyder theory for $l/\xi_0=\pi/10$.

lated in two steps. First the zero-temperature density of states is found; then the curve is corrected for the effect of thermal smearing by using Eq. (1). This procedure is valid so long as the temperature is small compared to the critical temperature in the presence of the magnetic field.

The agreement between AGSM and experiment is fair, as can be seen from Fig. 2. The difference is somewhat similar to the effect that would result from thermal smearing at a temperature of 0.5 or 0.6°K. The samples actually were at about 0.36°K, however, as is verified by the good agreement between theory (for $T=0.36$°K) and experiment in the zero-field case. Also, the He^3 vapor pressure corresponded to a temperature of 0.36°K.

An effect of this kind is predicted by Strässler and Wyder[13] if the films are not in the extreme dirty limit.

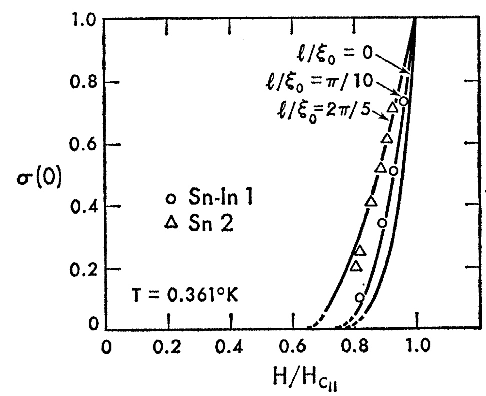

FIG. 3. Magnetic field dependence of $\sigma(0)$ in parallel field. The solid lines were calculated using the Strässler-Wyder theory with the values of l/ξ_0 indicated. ($l/\xi_0=0$ reproduces the AGSM result. The dashed parts are extrapolations.) Independent estimates suggest $l/\xi_0\approx 0.14$ for Sn-In 1 and $l/\xi_0\approx 0.55$ for Sn 2. Note that these are in a ratio of 1:4 just as are the values for the theoretical curves.

They have calculated the density-of-states spectrum for arbitrary field and purity at $T=0$. For Sn-In 1, $l/\xi_0\approx 0.14$, but we compare the data with theoretical curves for $l/\xi_0=\pi/10=0.31$, which gave the best fit of those calculated. Figure 2 shows that the fit is really quite good. The discrepancy of a factor of 2 between the two l/ξ_0 values is of limited significance because of the uncertainty in the definition of a mean free path in small samples and because of the use of a spherical idealization of the film by Strässler and Wyder.

Figure 3 shows measured values of $\sigma(0)$ for various values of $H/H_{c\parallel}$ for the film Sn 2 as well as for Sn-In 1. The systematic divergence of the two sets of points clearly shows the existence of a mean-free-path effect. Temperature-corrected, theoretical curves are shown for $l/\xi_0=0$, $\pi/10$, and $2\pi/5$, the latter two values differing by the same factor of 4 that independent experiments give for the ratio of l values of the two films. The good agreement suggests that the theory accounts for finite-l effects apart from a numerical factor of about 2.

More generally, the entire $\sigma(\omega)$ curves for the cleaner film Sn 2 (not shown) are "smeared" more than the corresponding curves for Sn-In 1, in qualitative agreement with the results of Strässler and Wyder. A quantitative fit to these curves has not been made. For a given reduced field, the maximum in the curve is higher for the clean than for the dirty film. This aspect of the results is not in accord with the Strässler-Wyder calculations. A possible explanation for the disagreement may lie in the film boundaries. The Strässler-Wyder equations assume a spherical particle with specular reflection at the surface. An actual film is not spherical, but in the dirty limit, where scattering from impurities is much more frequent than scattering from the surface, the exact shape of the surface would not be expected to be crucial. For a cleaner film, however, surface scattering becomes comparable to impurity scattering, and it may be necessary to take this into account.

Gapless Region

It is interesting to compare, for a given field, the extent to which the states are filled in at low energy with the resistance of the film. Figure 4 is a plot of $\sigma(0)$ and R versus H for Sn 2. From this figure one can see that the states are quite well filled in before there is any appearance of resistance.

For high fields in the gapless region, $H>0.95H_{c\parallel}$, AGSM and, independently, de Gennes,[6] predict that the density of states at $T\approx0$ can be written

$$N(\omega)=N_0\left[1+2\left(\frac{\Delta(T=0,H)}{\Delta_0}\right)^2\frac{(2\omega/\Delta_0)^2-1}{[(2\omega/\Delta_0)^2+1]^2}\right]. \quad (2)$$

From Eq. (1) σ then takes the form

$$\sigma(V)=1+f(H)g(V). \quad (3)$$

Thus, if we plot $[\sigma(V)-1]/|\sigma(0)-1|$ versus V, the resulting curves should be field-independent in this region. The results for Sn-In 1 are shown in Fig. 5 for several parallel fields. The data lie on a single curve as expected. However, in contrast to the prediction of AGSM, this behavior is true for fields as low as $0.89H_{c\parallel}$.

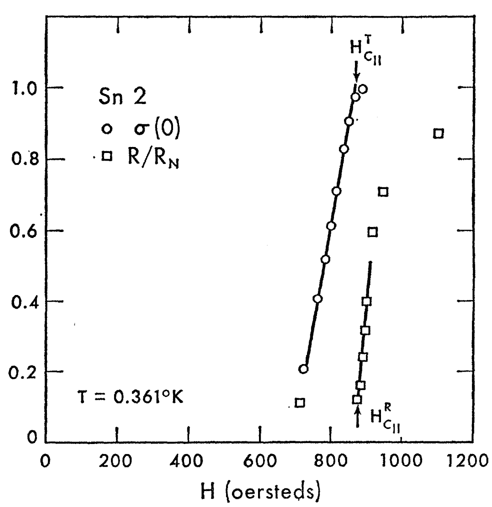

FIG. 4. Magnetic field dependence of $\sigma(0)$ and film resistance in parallel field. $H_{c\parallel}{}^T$ and $H_{c\parallel}{}^R$ are the critical fields determined by tunneling and by resistance, respectively. In this case, $H_{c\parallel}{}^R\approx1.01\,H_{c\parallel}{}^T$. (The finite resistance below $H_{c\parallel}{}^R$ is due to contacts.)

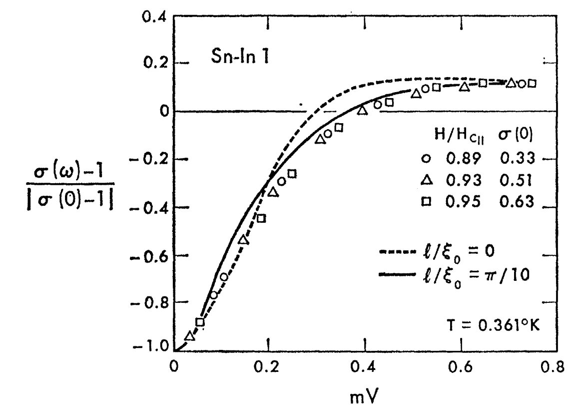

FIG. 5. Energy dependence of $(\sigma-1)/|\sigma(0)-1|$ for Sn-In 1. The theoretical curves are corrected for thermal smearing.

The experimental curve is different from that predicted by AGSM and de Gennes, which is shown in the same figure. An important feature of this difference is the voltage V_0, defined by $g(V_0)=0$. From Eq. (2) the theory predicts $V_0=\Delta_0/2$ at $T=0.0$°K.[19] This is about 0.3 mV, but we consistently find $V_0\approx0.4$ mV. Guyon *et al.*,[14] working at higher temperatures and using thicker samples, have done tunneling experiments in high fields and find good agreement with theory. In an effort to duplicate their work we made a thicker film and took data at higher temperatures (1.44°K) as well as at the usual He^3 temperatures. The low-temperature data yielded $V_0=0.41$ mV. For the higher temperature the predicted value of V_0 is 0.39 mV, while the experiment yielded 0.47 mV. We attribute the difference in values found for V_0 by Guyon *et al.* and by us as due to a difference in the dirtiness of the films. Apparently their films are very close to the dirty limit, whereas our films, as shown in the previous section, are less so. The Orsay group also finds that V_0 for a clean film is greater than V_0 for a dirty film,[20] in qualitative agreement with our results.

A numerical calculation for $l/\xi_0=\pi/10$ shows that a relation of the form of Eq. (3) but with a different $g(V)$ also holds to a good approximation for the theory of Strässler and Wyder in this impurity region. The results of this calculation are shown in Fig. 5. The agreement with the data is better for this theory than for AGSM; in particular, V_0 corresponds more closely to the experimental value.

Another interesting feature of these curves is that the total number of states found by integrating $N(\omega)$

[19] The figure shows V_0 slightly less than $\Delta_0/2$ because, following Guyon *et al.* (Ref. 14) we have used T_c rather than Δ_0 to normalize the energy dependence of the temperature correction.

[20] Groupe de Supraconductivité d'Orsay, Physik Kondensierten Materie **5**, 141 (1966).

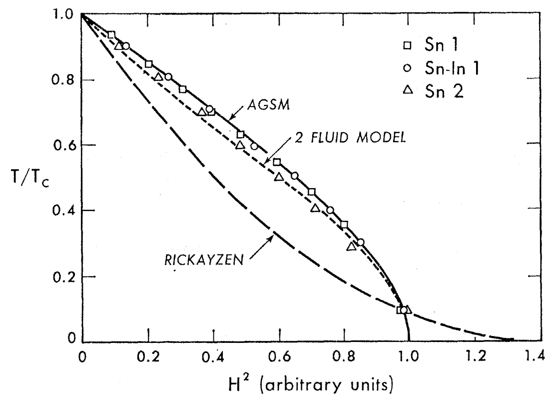

FIG. 6. Data on temperature dependence of parallel critical fields for three films compared with theory. Sn 1 and Sn-In 1 are relatively dirty; Sn 2 is relatively clean. Magnetic field scale for all theoretical curves is determined by fitting the points at $T/T_c \approx 0.1$.

appears to be somewhat less than the number of states for the normal metal, if one assumes that the normal-metal density of states is constant through the entire relevant range of energies. The difference is such that the discrepancy would be nullified if $\sigma(V)$ were greater by 1–2% over an energy range of twice the gap. This difference depends on the experimental determination of the normal-state conductivity, which is done at a voltage far above the gap. A slight variation of this quantity with voltage would be sufficient to explain the discrepancy. Rowell and Shen[21] have reported finding a variation of this kind in many types of normal-metal tunnel junctions.

Temperature Dependence of the Parallel Critical Field

The theoretical temperature dependence of the parallel critical field for a dirty superconducting film has been calculated by AGSM and also by de Gennes and Tinkham,[22] with the result that the critical condition is given by the implicit relations:

$$\ln\frac{T_c(H)}{T_c(0)}=\Psi(\tfrac{1}{2})-\Psi\left[\frac{1}{2}+\frac{\hbar}{4\pi k_BT_c(H)\tau_K}\right], \quad (4a)$$

$$\hbar/\tau_K=1.76k_BT_c(0)[H_{c\parallel}(T)/H_{c\parallel}(0)]^2, \quad (4b)$$

where Ψ is the digamma function.

Figure 6 shows the measured dependence of $H_{c\parallel}$ for two dirty films, Sn-In 1 and Sn 1, and for one cleaner film, Sn 2. For comparison, three theoretical curves are shown, with the normalization parameter $H_{c\parallel}(0)$ being in each case determined by fitting the lowest-temperature data point to the theoretical curve. The curve labeled AGSM is that given by Eq. (4). That labeled "two-fluid model" is a plot of

$$H_{c\parallel}(t)=H_{c\parallel}(0)[(1-t^2)/(1+t^2)]^{1/2}, \quad (5)$$

which follows from elementary theory, using the empirical approximations that $H_{cb}(t)\sim(1-t^2)$ and $\lambda(t)\sim(1-t^4)^{-1/2}$. The third curve is one given by Rickayzen.[23] Evidently, AGSM describes the dirty-film behavior quite well. As expected, the cleaner film Sn 2 does not conform quantitatively to the prediction of AGSM; in fact, its critical field is given better by the two-fluid curve, but the difference is not great. The agreement with the Rickayzen curve is comparatively unsatisfactory, a conclusion opposite to that reached in recent results of Chaudhari.[24] In assessing the significance of this discrepancy, attention should be paid to the shapes of the three theoretical curves. All give a nearly linear variation of $T_c(H)$ with H^2 down to $T_c(H)/T_c(0)\approx0.5$, below which very different curvatures set in. Thus a very-low-temperature data point is necessary to fix the magnetic field scale so that a critical test can be made. Since the present data go down to $\sim0.1T_c$, whereas those reported by Chaudhari[24] go only to $\sim0.35T_c$, the present data should offer a more critical discrimination among the various theoretical curves.

IV. CONCLUSION

The tunneling results reported here reconfirm theoretical expectations and previous experimental results showing that the effect of a magnetic field on the density of states $N(\omega)$ in a superconducting film is more profound than can be described by the BCS theory with a field-dependent gap. Rather, the sharp rise in $N(\omega)$ above the gap, characteristic of BCS, is smeared out, leading to gapless superconductivity over a significant range of magnetic field below the critical field value $H_{c\parallel}$ at which the resistance and tunneling characteristic of the film return to those of the normal state.

The major new contribution of this work is to extend previous work[14] by making detailed quantitative measurements of $N(\omega)$ in the range of magnetic fields far below $H_{c\parallel}$, where there is still a gap in the density of states, as well as in the previously explored subcritical gapless region. These measurements show that $N(\omega)$ is much better described by the AGSM[1,3,5] than by BCS, but that quantitative discrepancies remain. These discrepancies apparently arise from the fact that in our films l/ξ_0, though smaller than unity, is not zero, as is assumed in AGSM. This conclusion is supported by the much better agreement between experimental data for an alloy film and the theory of Strässler and Wyder[13] (which generalizes AGSM to finite values of l/ξ_0) when an experimentally reasonable value of l/ξ_0 is used. Further support is offered by the data of Fig. 3, showing that the increased discrepancy from AGSM in a purer sample is in at least qualitative accord with theoretical expectations. The poorer quantitative agreement for the cleaner film may be due to the idealizations of the

[21] J. M. Rowell and L. Y. L. Shen, Phys. Rev. Letters **17**, 15 (1966).
[22] P. G. de Gennes and M. Tinkham, Physics **1**, 107 (1964).
[23] G. Rickayzen, Phys. Rev. **138**, A73 (1965).
[24] R. D. Chaudhari, Phys. Rev. **151**, 96 (1966).

Strässler-Wyder model, which become more important as l/d increases.

In addition to the density-of-states measurements, the temperature dependence of the parallel critical field for several films was measured. In the case of the dirtier films the results of these measurements are in good agreement with the predictions of Maki[5] and of de Gennes and Tinkham.[22] For the cleaner film, the agreement was significantly poorer, as expected. In all cases, the agreement with the theory of Rickayzen was unsatisfactory.

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APPENDIX: FILM PROPERTIES

Critical fields were measured resistively and by tunneling methods. The resistive critical field is taken to be that field at which an extrapolation of the linear part of the R-versus-H curve intersects the constant low-field contact resistance. The tunneling critical field was obtained by extrapolating the linear part of the $\sigma(0)$-versus-H curve to $\sigma(0)=1$. As shown in Fig. 4, there is good agreement between these two values, the discrepancy being typically only 2%. The resistively determined value is quoted in Table I.

The energy gap at zero temperature and zero-field Δ_0 is obtained from a fit of Eq. (1) to the zero-field tunneling data using the BCS expression for the density of states.

The parameters d (thickness) and ξ_T (the low-temperature value of the de Gennes temperature-dependent coherence length) were obtained from the measured values of $H_{c\parallel}$ and $H_{c\perp}$ using the relations

$$d_H=(6\phi_0H_{c\perp}/\pi H_{c\parallel}{}^2)^{1/2} \tag{A1}$$

and

$$\xi_T=(\phi_0/2\pi H_{c\perp})^{1/2}, \tag{A2}$$

which follow from

$$H_{c\parallel}=(24)^{1/2}H_{cb}\lambda/d, \tag{A3}$$

$$H_{c\perp}=4\pi\lambda^2H_{cb}{}^2/\phi_0=\phi_0/2\pi\xi_T{}^2, \tag{A4}$$

which should be approximately valid for the films studied.

As a check on this determination of the film thickness purely from critical field measurements, the thickness of each film was estimated from the resistance ratio assuming the temperature-dependent part of the resistivity to be the same as for pure bulk tin. This yielded a thickness d_R typically 10% less than the value d_H determined from the critical field. Considering the nonideal structure of thin films, this agreement is quite satisfactory. As a further check, thicknesses were determined optically by multiple-beam interferometry on two films similar to those reported here. In both cases the optical thicknesses agreed with the value d_H to within experimental error.

The electronic mean free path l was also determined in two independent ways, one from resistance measurements in the normal state and one from the critical field. Assuming Matthiessen's rule, the mean free path in the residual resistance region should be given by

$$l_0=l_{300}[(R_{300}/R_{4.2})-1]. \tag{A5}$$

Using the tabulated[25] values of ρ and ρl for tin from dc resistivity and anomalous skin-effect measurements, we estimate $l_{300}=94$ Å. The values of l_0 found in this way are listed in Table I as l_R.

To determine l from the critical fields, we solve Eq. (A4) for λ, and use the theory of the dependence of λ upon l. In the dirty local limit,

$$(\lambda/\lambda_L)^2=\xi_0/\xi_P=1+\xi_0/l, \tag{A6}$$

where the Pippard coherence length ξ_P is defined by $\xi_P{}^{-1}=\xi_0{}^{-1}+l^{-1}$. However, our films are not all so dirty as to justify use of this relation, which neglects the effects of nonlocality which arise if the vector potential varies significantly in a distance ξ_P. These effects can be roughly taken into account by using a shortened mean free path l^* in Eq. (A6). If we let l_∞ be the mean free path limited only by volume scattering, then from standard size effect theory we expect the resistively measured value l_R to be given by

$$1/l_R\approx1/l_\infty+3/8d. \tag{A7}$$

The same average dimension governs the effective localization of the vector potential (for diffuse boundary scattering) for the superconductor in the perpendicular field orientation, but the vortex structure also introduces an orthogonal variation of the vector potential in the plane of the film. Thus at $H_{c\perp}$ we expect

$$1/l_\perp{}^*\approx1/l_\infty+[(3/8d)^2+\tfrac{1}{2}\xi_T{}^{-2}]^{1/2}, \tag{A8}$$

where $\sqrt{2}\xi_T$ is the radius of a vortex cell at $H_{c\perp}$. For the parallel field orientation, the vector potential changes sign in going through the film, leading to a shorter characteristic length perpendicular to the plane, but there is no variation in the plane. We estimate

$$1/l_\parallel{}^*\approx1/l_\infty+1/d. \tag{A9}$$

In general, $l_\parallel{}^*\neq l_\perp{}^*$, so that $\lambda_\parallel\neq\lambda_\perp$. However, for these films the difference is only a few percent, so that our estimates of d_H made assuming a single value of λ_{eff} are not seriously upset. Combining Eqs. (A4) and (A6), values of $l_\perp{}^*$ can be computed from the measured critical fields using

$$\xi_0/l_\perp{}^*=(H_{c\perp}\phi_0/4\pi H_{cb}{}^2\lambda_L)^2-1. \tag{A10}$$

[25] J. L. Olsen, *Electron Transport in Metals* (Interscience Publishers, Inc., New York, 1962).

The bulk critical field H_{cb} of a Sn-5%In alloy is approximately equal to that of pure tin,[26] 304 Oe. For tin we take $\lambda_L = 355$ Å and $\xi_0 = 2300$ Å.[27] From l^* we compute $(l_\infty)_H$ using Eq. (A8), and from $(l_\infty)_H$ we compute $(l_R)_H$ using Eq. (A7); the latter is quoted in Table I for comparison with the value derived from the normal-state resistance measurements. (We quote l_R rather than l_∞ since l_R gives a better measure of the total surface-plus-volume scattering for comparison with the Strässler-Wyder theory, in which all scattering is treated by means of a mean free path. Evidently the concept of a mean free path is a bit indefinite in dealing with small real nonideal samples.) We note that the values based on superconducting properties agree well with the values determined from the normal-state resistance. There is no large systematic difference, which is reassuring. The close agreement is perhaps fortuitous, however, since the conductivity of tin is anisotropic by 50%, and there may be preferential crystal orientation in thin films. Further, the ρl value inferred from size-effect measurements is 1.9 times as large as the anomalous skin-effect value used above. Thus, l_{300} could range anywhere between 88 and 200 Å. If it were in the upper end of this range, it would lead to l/ξ_0 values in better agreement with those required for a fit to the Strässler-Wyder theory. We do not think such a large l value is likely, however, since it would destroy the agreement with $(l_R)_H$, it would be based on a less reliable and less appropriate technique (size effect versus anomalous skin effect), and further, the sweeping approximations of the Strässler-Wyder theory might well introduce an error as large as a factor of 2 in the appropriate choice of l/ξ_0.

The theory to which the tunneling data are compared requires that Δ, the order parameter, be constant across the film. For our films $d \approx \xi_T$, so it is not immediately obvious that this requirement will be fulfilled. One of us[28] has calculated the spatial dependence of Δ for a thin film in a parallel magnetic field, using a variational approach. This calculation shows that for Sn-In 1 at $H_{c\parallel}$ the total variation of Δ across the film should be $\sim$6%. Thus, we expect the theory to be reasonably applicable.

Because of the requirement that Δ be spatially constant, the film thickness cannot be too great. In fact, if d is much greater than ξ_T, surface superconductivity appears, and Δ may become much smaller in the interior of the film than on the surface. The films also cannot be very thin, since in that case the irregularities in the shape of the film and the nature of the surfaces have an effect on the density of states that is not easily calculable. The films studied in these experiments have thicknesses chosen to lie between these two limits.

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Bulk (H_{c2}) and Surface (H_{c3}) Nucleation Fields of Strong-Coupling Superconducting Alloys*

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The linearized self-consistency equation, in the electron-phonon model, for the nucleation of superconductivity in the presence of a magnetic field is studied. It is found that near the transition temperature this integro-differential equation is susceptible to analysis. The main results are that the ratio of surface to bulk nucleation fields is predicted to have the weak-coupling value of 1.695, thus not confirming a recent experimental suggestion of a value near 1.9 for strong-coupling superconductors. The slope $(\partial H_{c3}/\partial T)_{T_c}$ is worked out both in terms of integrals over the parameters of the bulk-strong-coupling theory and in terms of other experimental quantities. Comparison of this last result with existing experiments on pure lead is attempted, with good success. In the Appendix an implicit equation for $H_{c2}(T)$ for all T is derived, but the numerical work necessary to solve this equation has not been undertaken.

1. INTRODUCTION

In this paper we discuss the theory of critical magnetic fields for the nucleation of superconductivity in dilute alloys of materials in which the coupling between electrons and lattice vibrations is strong.

With a view to understanding some recent experiments discussed below, we have derived and studied the linearized self-consistency equation for the order parameter of a strong-coupling superconductor in an external magnetic field, allowing for spatial variations. We have found that this equation is rather more amenable to analysis than one might have imagined. The solution can always be written as the product of a position-dependent and a frequency-dependent function. Near the critical temperature (T_c) the position dependent part obeys a linearized Ginsburg-Landau equation, with its well-known solutions for surface and bulk nucleation. The ratio of the surface (H_{c3}) to bulk

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