Far-Infrared Study of Superconductors Containing Magnetic Impurities*

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(Received 9 January 1969)

A new far-infrared method has been developed to study the energy-gap properties of a thin superconducting film containing magnetic impurities, and which is thus capable of exhibiting gapless superconductivity. The method allows the direct determination of the real part σ_1 of the conductivity of the superconductor by measuring calorimetrically the infrared radiation absorbed by the film. The systems studied were quenched films of lead containing either Gd or Mn impurities. The experimentally observed frequency dependence of σ_1 (which exhibits the properties of the energy gap) is found to be distinctly different from that expected for nonmagnetic impurities. In the case of lead films containing Gd impurities, whose spins are due to $4f$ electrons, the behavior of σ_1 is in good quantitative agreement with the behavior predicted by Skalski *et al.* on the basis of the Abrikosov-Gorkov theory. In the case of lead films containing Mn impurities, whose spins are due to $3d$ electrons, the behavior of σ_1 is affected more drastically than predicted by this theory. These results agree with conclusions obtained in previous tunneling measurements on these systems.

I. INTRODUCTION

A. Magnetic Impurities in Superconductors

SUPERCONDUCTORS containing magnetic impurities exhibit very unusual behavior. For example, the critical temperature of a superconductor is influenced only slightly by the presence of nonmagnetic impurities; on the other hand, the addition of magnetic impurities has a drastic effect, depressing the critical temperature to zero for impurity concentrations as small as a few percent. This effect has been studied by the Göttingen group,[1] who investigated the critical temperatures of quench-evaporated films of lead and tin containing various magnetic impurities. These workers found that the depression of the critical temperature is large and is a linear function of the impurity concentration. A more detailed study of the critical temperature in bulk superconducting samples was undertaken by Matthias *et al.*[2] In this study, the superconductor lanthanum was alloyed with small amounts of the other (magnetic) rare-earth elements. (The resulting situation is particularly simple because the magnetic moments of the impurities are due to their localized $4f$ electrons and because only the number of $4f$ electrons changes from element to element.) It was found that the depression of the lanthanum critical temperature by a rare-earth impurity is related to the spin rather than to the magnetic moment of the impurity. This result indicates that the interaction between the impurities and the superconducting electrons is spin-dependent, i.e., presumably due to exchange rather than to a local magnetic field.

The theoretical description of superconductors containing magnetic impurities is also unusual and leads to some remarkable predictions. To understand the theoretical peculiarities, let us first review the description of an ordinary superconductor. If this superconductor is pure, its ground state, as described by the BCS theory,[3] consists of correlated pairs of electrons with opposite spins and momenta. This theory was extended by Anderson to include superconductors containing nonmagnetic impurities.[4] (His procedure was to generalize the BCS pairing scheme by replacing it with one in which each electron in a given eigenstate of the normal metal is paired with another electron in the corresponding time-reversed state.) Both the BCS and the Anderson theories predict that the electronic excitation spectrum of the superconductor has an energy gap Ω which is equal to the order parameter Δ and which (in the weak-coupling limit) is proportional to the critical temperature T_c. However, in the presence of spin-dependent interactions involving the conduction electrons, the time-reversed state is no longer an eigenstate of the system. Thus the ground-state pairs of the Anderson theory would have a limited lifetime and this theory should no longer provide a good description of the superconductor.

A new theory suitable for treating the case of superconductors containing magnetic impurities was therefore proposed by Abrikosov and Gorkov[5] (henceforth denoted by AG). This theory is based on the model of randomly oriented localized impurity spins coupled weakly to the conduction electrons. Calculations[6] based on this theory predict, in agreement with the experimental evidence, a nearly linear decrease of the critical temperature with increasing impurity concentration. However, in contrast to the simpler cases treated by the BCS and Anderson theories, the energy gap Ω is *not* equal to the order parameter Δ. Furthermore, as the magnetic impurity concentration is increased, the predicted energy gap Ω approaches zero more rapidly than

* Work supported in part by the U. S. Office of Naval Research.

[1] See N. Barth, Z. Physik **148**, 646 (1952); also K. Schwidtal, *ibid.* **158**, 563 (1960), and references therein.

[2] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 93 (1958); J. Phys. Chem. Solids **13**, 156 (1960).

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

[4] P. W. Anderson, Phys. Rev. **112**, 1900 (1958).

[5] A. A. Abrikosov and L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [English transl.: Soviet Phys.—JETP **12**, 1243 (1961)].

[6] S. Skalski, O. Betbeder-Matibet, and P. R. Weiss, Phys. Rev. **136**, A1500 (1964).

the critical temperature.[7] Therefore, when the impurity concentration becomes sufficiently high, there exists a concentration range where the energy gap vanishes, but where the order parameter and critical temperature are still nonzero. Thus the theory leads to the remarkable prediction of the phenomenon of "gapless superconductivity."

B. Experimental Gap Studies

The previous comments show that studies of the energy gap are of crucial importance for a detailed microscopic understanding of the effects of magnetic impurities on superconductors. The two experimental techniques capable of investigating the energy gap most directly are those of electron tunneling and far-infrared spectroscopy. Since the first of these techniques has been applied previously to study superconductors containing magnetic impurities, we shall make a few remarks about the results thus obtained before discussing the far-infrared method of primary interest to us.

A typical tunneling experiment involves a junction formed between a superconductor and a normal metal which are separated by a very thin insulating layer. Except for effects due to thermal excitations, no current will flow through such a junction until the voltage V applied across the junction is such that $eV \geq \Omega$. Furthermore, the current I through the junction is related to V by the proportionality $dI/dV \propto N(eV)$, where $N(eV)$ is the electronic density of states at an energy eV above the Fermi level. Measurements of the current-voltage characteristics of such a tunnel junction provide, therefore, very direct information about the energy gap and density of states.

Using the tunneling technique, Woolf and Reif[8] demonstrated that, as predicted by the AG theory, the density-of-states curve is broadened and the energy gap rapidly depressed as the magnetic impurity concentration is increased. In particular, they found satisfactory agreement with this theory for lead containing impurities of the rare-earth element Gd, whose spin is due to $4f$ electrons. On the other hand, the agreement with the theory was found to be less good in some other cases. For example, the broadening of the density-of-states curve markedly exceeds theoretical predictions in the case of Mn or Fe impurities which have spins due to $3d$ electrons. Other recent tunneling work shows that La-Ce alloys also exhibit an anomalously large broadening.[9] (In comparison with other rare earths, Ce also causes an anomalously large depression of the critical temperature of lanthanum.[2]) Thus the tunneling experiments suggest that the AG theory describes best those cases where the spin-dependent coupling between the impurities and the conduction electrons is expected to be weak.

Let us now turn to far-infrared spectroscopy, a method which can also be used to examine directly the energy gaps of superconductors. This general technique involves the study of the energy spectrum of the electrons in a superconductor by an investigation of their response to electromagnetic radiation. In particular, at frequencies less than the "gap frequency" $\omega_g \equiv 2\Omega/\hbar$, no radiation will be absorbed by the superconductor. In general, the response of the conduction electrons to electromagnetic radiation can be characterized by a complex conductivity $\sigma(\omega)=\sigma_1(\omega)-i\sigma_2(\omega)$ (where σ_1 and σ_2 are real). The existence of the energy gap influences most directly σ_1, which corresponds to the "in-phase" or absorptive part of the electronic response. Thus σ_1 vanishes at frequencies less than the gap frequency ω_g. On the other hand, σ_1 approaches σ_{1n}, the conductivity of the normal metal, at frequencies sufficiently high so that $\omega \gg \omega_g$. Many of the characteristic superconducting properties of the electrons are most directly related to σ_2, the out-of-phase response of the electrons. Thus, at low frequencies where $\omega \ll \omega_g$, the quantity σ_2 is proportional to ω^{-1} and gives rise to the constant penetration depth and "infinite conductivity" observed at very low frequencies.

The directly observable properties of a superconducting sample, such as its absorption or transmission of far-infrared radiation, can be related to σ_1 and σ_2 by Maxwell's equations. Hence a study of these infrared properties provides information about σ_1 and σ_2, and thus allows one to infer characteristics of the energy gap.

C. Present Experiment

Although far-infrared techniques have been fruitfully used to investigate many superconductors, they have not previously been applied to the study of superconductors containing magnetic impurities. Such an application of far-infrared techniques promises, however, to be valuable for the following reasons. Up to now, the tunneling method is the only one which has been used to study directly the remarkable energy-gap properties of these superconductors; it would therefore seem useful that the conclusions derived from these experiments be verified by an independent method. The interpretation of the tunneling measurements is also subject to the possible objection that the observed results might be artifacts caused by the presence of magnetic impurities in the tunnel junction itself; infrared measurements would be free from any such criticisms. The tunneling measurements indicate that the AG theory is fairly successful in predicting the effects on superconductors of rare-earth impurities such as Gd, but fails to account properly for the larger effects produced by impurities having $3d$ electrons; it is therefore of interest to check whether infrared measure-

[7] Qualitatively, this rapid decrease of Ω can be regarded as due to the filling of the energy gap when the BCS pair states suffer an energy broadening as a result of their reduced lifetimes.

[8] M. A. Woolf and F. Reif, Phys. Rev. **137**, A557 (1965).

[9] A. S. Edelstein, Phys. Rev. Letters **19**, 1184 (1967).

ments reveal similar differences between the effects produced by the two types of impurities. Finally, there exist calculations of $\sigma(\omega)$ performed by Skalski *et al.*[6] on the basis of the AG theory; the results of infrared measurements can therefore be compared in detail with specific theoretical predictions.

The present paper will discuss such an infrared study of superconductors containing magnetic impurities. We shall begin by describing a method designed to yield directly the real part σ_1 of the conductivity of a superconductor. This method involves a direct measurement of the far-infrared radiation absorbed by a thin film, this absorption being detected by the resulting temperature rise of the film and its substrate. Lead is chosen as host superconductor because it has been well studied and because its energy gap is large. (Hence the gap frequency ω_g can be depressed appreciably by the addition of magnetic impurities before it becomes smaller than the lowest frequency attainable with our apparatus.) The impurities studied, Gd and Mn, are representative of impurities with $4f$ and $3d$ electrons and are the same impurity elements which have been studied by tunneling methods. Finally, we shall compare our experimental results with the theoretical predictions and with the previous tunneling measurements.

II. EXPERIMENTAL ASPECTS

A. Choice of Far-Infrared Method

It is desirable that far-infrared measurements on a superconductor allow one to deduce unambiguously the frequency dependence of its complex conductivity $\sigma(\omega)$, the fundamental parameter characterizing the response of the metal to electromagnetic radiation.[10] When infrared radiation is incident on a metal, quantities accessible to direct experimental measurement are various powers, e.g., the power P_I incident on the metal, the power P_R reflected by it, or the power P_A absorbed by it. The power P_T transmitted by the metal can also be measured if this metal is in the form of a film sufficiently thin ($\lesssim 100$ Å) to transmit appreciable radiation. The ratio of any two such powers represents a quantity characteristic of the metal sample and can always be expressed in terms of σ_1 and σ_2 by using Maxwell's equations. The task is then to deduce from such experimentally measured quantities the parameter σ_1 which is most directly related to the energy gap of the superconductor.

Since measurement of a single power ratio (for example, P_T/P_I) gives a quantity related, in general, to *both* σ_1 and σ_2, such a measurement does not allow one to deduce σ_1 itself without using additional information. Information of this kind can be obtained by noting that σ_1 and σ_2 are not completely independent, but are interrelated by certain "integral relations." These are the Kramers-Kronig relations[11]

$$\sigma_2(\omega)=\frac{-2\omega}{\pi}\int_0^\infty \frac{\sigma_1(\omega')d\omega'}{\omega'^2-\omega^2} \tag{1a}$$

and

$$\sigma_1(\omega)-\sigma_1(\infty)=\frac{2}{\pi}\int_0^\infty \frac{\omega'\sigma_2(\omega')d\omega'}{\omega'^2-\omega^2}, \tag{1b}$$

which can be derived from very general arguments based on the assumptions of linearity and causality of the electromagnetic response; and the Ferrell-Glover "sum rule"[12]

$$\int_0^\infty \sigma_1(\omega')d\omega'=\int_0^\infty \sigma_{1n}(\omega')d\omega', \tag{2}$$

which involves the real conductivity σ_{1n} of the normal metal and which follows from (1a) by noting that, for $\omega\gg\omega_g$, the response of the metal must be the same in its superconducting and normal states [so that $\sigma_2(\infty)=\sigma_{2n}(\infty)$]. The sum rule (2) must be used since σ_1 of a lossless system of electrons has, at $\omega=0$, a singularity of the form $\sigma_1(\omega)=A\delta(\omega)$.[13] Thus (2) can be used to determine the coefficient A by

$$A=\int_{0+}^\infty [\sigma_{1n}(\omega')-\sigma_1(\omega')]d\omega'. \tag{3}$$

It is clear that proper exploitation of (1) and (3) requires a knowledge of either σ_1 or σ_2 over the entire frequency spectrum, i.e., it necessitates an extrapolation outside the frequency range of the available instrumentation. The resulting difficulty is that small errors which occur over a very wide frequency range can give appreciable errors in values of σ deduced for frequencies near the gap edge ω_g. [The predominant reason is that the coefficient A of the δ function is, by (3), sensitive to errors in σ_1 at all frequencies, while this δ-function contribution to $\sigma_1(\omega)$ affects strongly the values of σ_2 deduced by (1a) for frequencies $\omega\lesssim\omega_g$.]

To avoid the difficulties arising from the use of the integral relations, one can measure *two* different power ratios (each depending on both σ_1 and σ_2) in order to deduce directly the two quantities σ_1 and σ_2. This method is feasible, although somewhat complicated.[14] Hence experimental approaches based on the use of the integral relations have been employed most commonly in the past.

Another way to circumvent the use of the integral relations is the method proposed and implemented in the present work. This method, which is very direct and simple in principle, involves the measurement of a

[10] Since the films used are very thin and characterized by very short electron mean free paths, the wave-number dependence of the complex conductivity is unimportant and only its frequency dependence is relevant in the experiments and the theoretical calculations.

[11] R. L. de Kronig, J. Opt. Soc. Am. **12**, 547 (1926); H. A. Kramers, Atti. Cong. Intern. Fis. Como **2**, 545 (1927).

[12] R. A. Ferrell and R. E. Glover, III, Phys. Rev. **109**, 1398 (1958).

[13] M. Tinkham, *Superconductivity* (Gordon and Breach, Science Publishers, Inc., New York, 1965), p. 22.

[14] L. H. Palmer and M. Tinkham, Phys. Rev. **165**, 588 (1968).

single ratio (the particular ratio P_A/P_T) which can be shown to be related to the quantity σ_1 *alone*, and which therefore yields directly the parameter of greatest interest to us. In the following paragraphs we shall first discuss the various considerations which led to the development of our infrared method as one particularly suitable for the investigation of superconductors containing magnetic impurities. We shall then outline the very simple theoretical basis of the proposed method and discuss the actual manner in which it has been implemented in practice.

The following considerations dictate the choice of a far-infrared method most suitable for the present investigation.

(a) The experiments should be sensitive to differences between the predictions of the BCS and AG theories. Since the low-frequency limit of our apparatus corresponds approximately to half the gap frequency of pure lead, we cannot hope to obtain information about the gapless region predicted by the AG theory. We can, however, work with lower impurity concentrations and aim to measure with quantitative precision the marked differences in σ_1 which are theoretically predicted to occur near the gap edge. To accomplish this aim, it is necessary to measure experimental quantities which allow an accurate determination of σ_1 even when σ_1 is small and σ_2 is large (as is the case when $\omega \lesssim \omega_g$). Accordingly, it seems best to choose an infrared method designed to measure directly the power absorbed by the sample, since this power is closely related to the real conductivity σ_1.

(b) The resort to integral relations, such as the Kramers-Kronig equations (1) and the sum rule (3), is best avoided, since it requires a knowledge of $\sigma_1(\omega)$ extrapolated to frequencies lying outside the range of the instrumentation. As this extrapolation is uncertain, particularly at low frequencies where σ_1 might be appreciably affected by the presence of the magnetic impurities, the integral relations cannot be expected to lead to accurate values of σ_1 near the gap edge.

(c) The impurity elements to be studied are not soluble in the host metal in thermal equilibrium. Hence the sample films are systems metastable at low temperatures and obtained by quench-evaporating the components onto a substrate maintained at liquid-helium temperatures.[15] Although the need for quench evaporation adds complications to the apparatus, it does not impose undue restrictions on the choice of the infrared method.

Our infrared method, designed to satisfy all the previous criteria, is based on the following simple observation. Consider a *very thin* metal film located at an interface between two transparent media (which may have different indices of refraction). Suppose that radiation is incident normally on the "front" side of this film, so that some of it is absorbed by the film, while the radiation transmitted through the film passes on to infinity. (In practice, this situation can be realized by depositing the film on the "rear" side of a substrate so that no radiation transmitted through the film is reflected back to it.) In this case the electric field E existing in the film is essentially constant across its thickness (since this thickness is assumed to be small compared to both the skin depth of the film material and the wavelength of the radiation) and must also be equal to the field existing in the space immediately behind the film. The current density j produced in the film (and in phase with E) is then given by $j=\sigma_1 E$, where σ_1 is the real part of the conductivity of the film material. Hence the power P_A absorbed by the film is given by $P_A \propto jE \propto \sigma_1 E^2$. On the other hand, the power P_T transmitted by the film is given by the Poynting vector, so that $P_T \propto E^2$. Hence it follows that $P_A \propto \sigma_1 P_T$, so that[16]

$$\sigma_1 \propto P_A/P_T. \tag{4}$$

The relation (4) shows explicitly that we would achieve our goal of obtaining a direct measurement of σ_1 if we could measure both the radiation power P_A absorbed by, and the power P_T transmitted by, a thin film suitably deposited on a transparent substrate.[17]

The method thus suggested would be similar to that used by Norman,[18] who also measured directly the power absorbed by a superconducting sample; he could, however, measure only this one independent quantity, since his samples consisted of nontransmitting metal films with a thickness greater than 1000 Å. The method would also be similar to that used by Palmer and Tinkham,[14] who measured, in the case of thin lead films, the transmitted power P_T *and* the reflected power P_R in both the superconducting and normal states. Although their method avoids the use of integral relations in the data-reduction process, the small values of σ_1 which they obtain near the gap edge result from a cancellation between large quantities.[19] Hence small percentage errors in these measured quantities can give rise to a large error in σ_1.

[15] This technique is described by R. Hilsch, G. V. Minnegerode, and K. Schwidtal, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications Ltd., London, 1963), p. 155.

[16] More specifically, the power absorbed per unit area of a film of thickness d is given by $\sigma_1 E^2 d$ and the transmitted power flux by $cE^2/4\pi$. Hence $P_A/P_T=(4\pi d/c)\sigma_1$. To achieve the desirable condition that $P_A \approx P_T$, it thus follows that the quantity $(\sigma_1 d)^{-1}$ (which gives the resistance measured across opposite sides of a film of square shape) should be $4\pi/c$ statohms or 377 Ω. To approximate this value when σ_1 is reduced from its normal-state value, the film thickness d in our experiments is chosen so as to provide films with a normal resistance of approximately 200 Ω.

[17] The relation $A/T \propto \sigma_1$ connecting the absorbance A and transmittance T of a thin film was originally pointed out to us by M. Tinkham and L. H. Palmer. In our proposed geometry, this relation leads to (4) after taking into account multiple reflections in the substrate.

[18] S. L. Norman, Phys. Rev. **167**, 393 (1968).

[19] For example, if the substrate is neglected, $\sigma_1 \propto P_A/P_T = (P_I-P_R-P_T)/P_T$. Thus a small value of σ_1 can only result from a cancellation between the incident power P_I and the sum P_R+P_T.

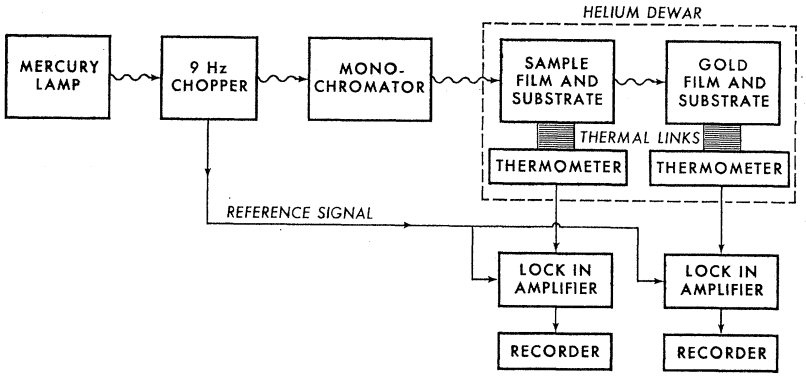

FIG. 1. Block diagram of the experimental apparatus.

Several major problems must be solved in order to implement our proposed infrared method. The first of these concerns the difficulty of measuring directly the power absorbed by the thin film. Not only is this power very small by virtue of the very weak radiation sources available in the far-infrared region, but it is also difficult to detect since the film is attached to a substrate of much larger heat capacity. Far-infrared radiation is ordinarily detected by measuring with a sensitive thermometer the temperature rise produced in a suitable absorber. (The thermometer used by us consists of a small chip of semiconducting germanium properly "doped" with gallium so that its electrical resistance near 1°K is a sensitive function of its temperature.) If the infrared radiation (chopped at some low frequency of the order of 10 Hz) is allowed to fall directly on the thermometer itself, and is thus partially absorbed by it, the thermometer becomes a radiation detector or "bolometer," since the resultant variations in its temperature (and thus also in its resistance) can be measured by the use of standard lock-in techniques. In order to detect directly the power absorbed in a thin metal film, the resulting temperature variations of the substrate onto which the film is deposited should, in principle, be measurable by a thermometer attached to the substrate. Such a procedure can, however, only be successful if the substrate satisfies the following three conditions:

(a) It must be nonabsorbing in the far-infrared region.

(b) It must have sufficiently large thermal conductivity so that the radiation power absorbed by the film can be transmitted to the bolometer in a time shorter than the period of the chopped radiation.

(c) Its heat capacity must be small enough so that the temperature variations produced by a given amount of absorbed power are not reduced by a prohibitive factor.

The first two conditions can be satisfied by the use of a substrate made of crystalline quartz. The third might be expected to cause difficulty since, for the given area required by the film,[20] the substrate cannot be made so thin that its heat capacity does not appreciably exceed that of the bolometer. Although a mica substrate could be made quite thin, its thermal conductivity is relatively poor and proves troublesome (particularly since the requirement of a transmission measurement necessitates attaching the thermometer to the substrate outside the region of the film). On the other hand, crystalline quartz turns out to be an adequate substrate despite the fact that, even for a minimum practicable thickness of 0.75 mm, its heat capacity exceeds that of the bolometer by a factor of 100. One favorable feature is the thin film itself, whose absorbance for infrared radiation is quite high—much larger than that of our bolometer. Hence the combination consisting of the film, substrate, and thermometer is found to have a power sensitivity which is not much less than 20% that of the bolometer by itself.[21]

The second major problem which must be solved is that of monitoring the transmitted radiation with a detector which has a uniform response as a function of frequency.[22] The detector must also look "black," i.e., it must reflect a minimal amount of radiation back to the sample. In our final design, this detector consists of a cavity which contains an absorber and into which the incident radiation is channeled by means of a cone. The absorber in the cavity consists of a relatively large crystalline-quartz substrate onto which there is deposited a semitransparent gold film and to which there is thermally connected a thermometer physically located outside the cavity.[23] The sensitivity of this

[20] Use of a film of small size is precluded, since the radiation cannot be focused down on the film (by a light cone of the type often used in conjunction with ordinary bolometers) without the introduction of errors due to the non-normal incidence of the radiation on the film.

[21] To achieve good sensitivity, it is essential to use effective filters to prevent the incidence on the sample of any thermal radiation (even that corresponding to liquid-nitrogen temperature).

[22] The need for a detector of uniform frequency response could be obviated by comparing measurements at each frequency with the sample in the superconducting and normal states. This procedure is, however, not possible in our infrared method, since the thermometer attached to the sample would lose its sensitivity at the relatively high temperatures required to make the film normal. In practice, we correct for any small frequency dependence of the detector by a calibration run, using as a sample a thin normal film such as gold (instead of a superconducting film).

[23] The cavity approximates a blackbody if the absorber has an appreciable absorptivity and an area much larger than that of the cavity entrance.

detector is comparable to that of an ordinary germanium bolometer.

The third major problem is due to the requirement that sample films of known composition must be quench-evaporated onto the back side of the substrate maintained at liquid-helium temperature. The goal of obtaining a film containing a substantially uniform distribution of impurities can be achieved[24] quite readily by successively evaporating small pellets of a physical mixture consisting of the desired relative concentrations of lead and the impurity metal. If each such pellet contributes no more than about 10 Å to the film thickness, then the differing vapor pressures of the evaporating components can only cause variations in impurity concentration within layers less than 10 Å thick; thus the film composition is substantially uniform over the total thickness of about 100 Å. The fact that the film must be quenched imposes, however, the following two conflicting requirements: The preparation of a quenched sample film necessitates that the substrate be in good thermal contact with the helium bath during the evaporation, but our infrared method demands that the substrate be thermally insulated from the bath. The problem can be solved quite effectively by using as a heat switch a 0.0025-cm-thick copper foil which connects the substrate to the helium bath. After the film has been evaporated, the thermal contact is then broken by pulling on a wire which tears through this foil.

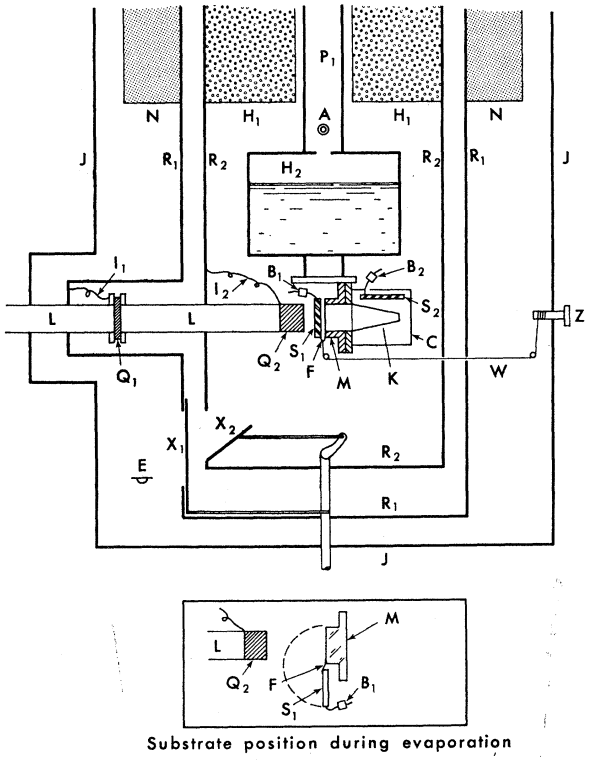

FIG. 2. Sample configuration and Dewar assembly.

B. Experimental Details

The principal features of our apparatus are shown in the schematic diagram in Fig. 1. The monochromator is of the Czerny-Turner type and uses laminar diffraction gratings.[25] Filtering is provided by crystals and zero-order reflection gratings. The monochromator is housed in a "glove box" which is flushed with dry nitrogen to avoid infrared absorption by atmospheric water vapor. To scan its useful wavelength range, the main grating is rotated by a synchronous-motor drive. The light source is chopped at 9 Hz by a rotating shutter; the thermometer outputs are then synchronously detected by standard lock-in techniques and are displayed on strip-chart recorders. The substrate supporting the sample film and the substrate supporting the gold film are both in poor thermal contact with the helium bath at 1°K and have thermal time constants of about 0.1 sec. The thermometers, which have small heat capacities, and which are attached to the substrates by good thermal links, have time constants of about 0.001 sec. Thus the thermometers can easily follow the 9-Hz temperature variations resulting from the far-infrared radiation.

Details of the cryogenic system are shown in Fig. 2. The far-infrared radiation is brought through the vacuum jacket J by a light pipe L. Thermal radiation is prevented from falling on the sample by the radiation shields R_1 and R_2, and by the filters Q_1 and Q_2.[26] The sample and its substrate S_1 are attached by a foil F to the copper block M which is in thermal contact with the helium bath. Evaporated gold electrodes on this substrate are used to monitor the film resistance.[27] Far-infrared radiation which is transmitted through the sample is channeled by the cone K into the cavity C, where it is absorbed by a gold film deposited on the substrate S_2. A thermometer (B_1 or B_2) is attached to each of the substrates S_1 and S_2 by one of its wire leads.

C. Procedures

After assembly and cooling, the sample is evaporated while the helium transfer is in progress. During this process the shutters X_1 and X_2 in the radiation shields are opened to expose the substrate (in the position shown in the inset of Fig. 2) to the tungsten "boat" E from which pellets of the sample mixture are individually evaporated until the resistance of the sample film

[24] This procedure is due to Hilsch and his co-workers (Ref. 15).
[25] R. Stolen, Ph.D. thesis, University of California, 1959 (unpublished).
[26] The filters placed in the light pipe are made of crystalline quartz. In addition, the filter Q_2, which is maintained near 4°K, is covered with a thin layer of Koh-I-Noor India ink, since this ink was found to absorb effectively radiation corresponding to liquid-nitrogen temperature.
[27] The quartz substrate is first cleaned in aqua regia and then in a hot dichromate glass-cleaning solution. The gold electrodes (about 1000 Å thick) are deposited in a bell-jar evaporator. Wire leads and the foil are then attached with indium solder. If everything is kept very clean, bonds formed in this manner are very strong.

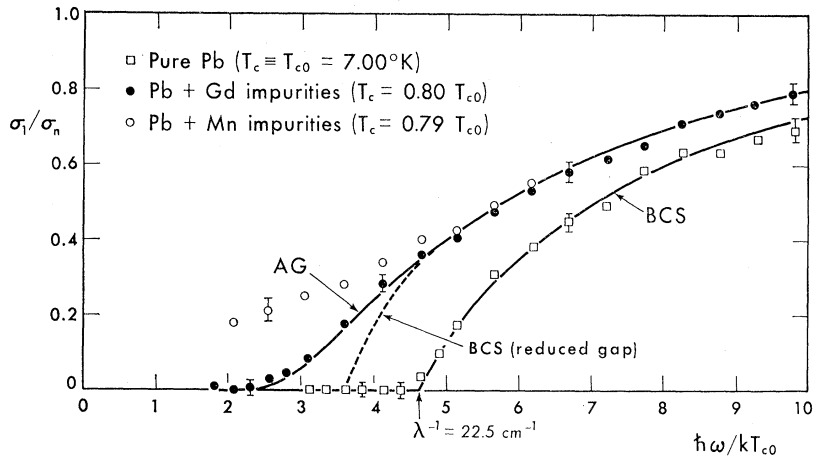

FIG. 3. Representative curves showing, as a function of the frequency ω, the real conductivity σ_1 (divided by the constant conductivity σ_n of the normal metal). The points indicate experimental data and the error bars include an allowance for possible systematic errors. The solid curves represent, respectively, predictions of the BCS theory for pure lead (with gap adjusted for best fit) and predictions of the AG theory for a magnetic impurity concentration producing a critical temperature T_c such that $T_c/T_{c0}=0.8$. For comparison, the dashed curve shows the predictions made by the BCS theory when the energy gap of the pure metal is reduced by the ratio $T_c/T_{c0}=0.8$.

reaches about 200 Ω.[28] Then the shutters are closed and the substrate is rotated into its final position (shown in Fig. 2 proper). The film is then heated so as to measure its resistance as a function of its temperature (ascertained by means of a calibrated germanium resistance thermometer), and thus to determine its critical temperature T_c.[29] After this measurement, the copper foil F is torn by pulling the manganin wire W by means of the windlass Z. The apparatus is then ready to be used for the far-infrared measurements.

The sample mixtures used in this work are the same as those used by Reif and Woolf,[8] except that some have been further diluted by the addition of more lead (followed by mechanical mixing). Small chips of the mixture are heated in a helium atmosphere to form round pellets suitable for use in the feeding mechanism designed to drop successive single pellets into the tungsten boat.

The monochromator spans the frequency range of interest by the use of three different diffraction gratings. To vary the infrared frequency, each grating is slowly rotated through its range, the exact time required (between 15 and 40 min) depending on the integration time needed to obtain satisfactory signal-to-noise ratio. The relative sensitivities of the two detectors are regularly monitored by using a reference beam available from the monochromator.[30] In addition, the output signals from the detectors are frequently checked, in the absence of radiation from the monochromator, in order to compensate for any possible dc drifts.

After a run, the output curves obtained from the strip-chart recorders are graphically smoothed. The coordinates of points taken from these curves are then punched onto cards convenient for computer processing.

[28] The temperature of the substrate does not rise above 14°K during the course of the evaporation.

[29] The temperature of the copper block and attached sample were controlled during the measurement of T_c by a closed-loop regulator which makes use of a carbon resistance thermometer and an electrical heater.

[30] In order to stabilize the sensitivities of the detectors, special precautions are taken to keep their temperatures constant.

III. RESULTS AND DISCUSSION

A. Pure Lead

There are several reasons for studying pure lead before investigating lead containing magnetic impurities. Such a study should provide a test of the usefulness of our experimental method. Furthermore, the results obtained should be of intrinsic interest since our method promises to have some distinct advantages compared to more conventional methods and since quench-evaporated films have not previously been studied by far-infrared techniques. Finally, such a study is necessary in order to interpret results obtained with lead films containing magnetic impurities. In particular, comparison with the AG theory requires a knowledge of the critical temperature T_{c0} and the gap frequency ω_{g0} of lead films free from such impurities.

The critical temperature of thick lead films (thickness $d\sim1000$ Å) has been investigated by several workers

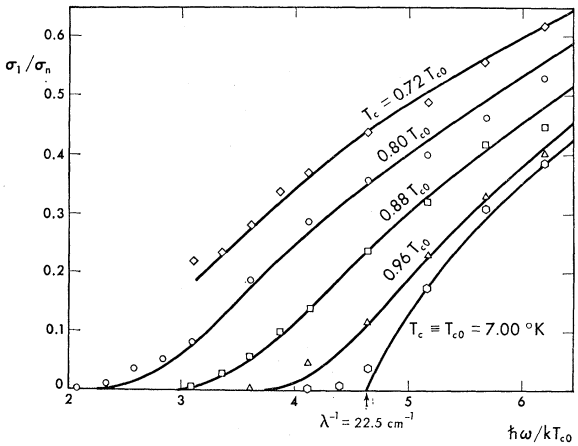

FIG. 4. Frequency dependence, near the gap edge, of the real conductivity σ_1 of lead containing various concentrations of Gd impurities. The points represent experimental data obtained from samples with the indicated critical temperatures. The solid curves indicate the predictions of the AG theory corresponding to the measured critical temperatures.

and found to be about 7.20°K for both annealed and quench-evaporated films. For the thin films ($d\sim100$ Å) used in our experiments, we observe a critical temperature of about 7.00°K, the width of the superconducting transition being about 0.1°K.[31] (As in the case of thicker films, we observe no net change in T_c after the films have been annealed at room temperature.[32]) Such a depression of the critical temperature in very thin films is in qualitative agreement with other work.[33]

Our study of the far-infrared characteristics of a number of pure lead films led to the following observations:

(a) At low frequencies ($\omega\lesssim\omega_{g0}$), our measurements of $\sigma_1(\omega)$ proved to be appreciably less subject to noise than those obtained by more conventional methods.

(b) Results obtained with quenched and annealed films were indistinguishable.

(c) In some samples, the observed values of $\sigma_1(\omega)$ did not approach zero as the frequency was lowered below the gap frequency, but approached a small, approximately constant, value.[34] The observation of this occasional behavior, whose origin is not understood, allowed us to make suitable corrections in some of our subsequent measurements on samples containing magnetic impurities.

Figure 3 shows the frequency dependence of σ_1/σ_n, the quantity of theoretical interest which compares σ_1 with the (real) constant conductivity σ_n of the normal metal at far-infrared frequencies. The data obtained from one of our pure lead samples are shown compared with the predictions derived by Mattis and Bardeen[35] on the basis of the BCS theory at zero absolute temperature. In obtaining the fit between theory and experiment, two adjustable parameters have been used. The first of these is a multiplicative normalizing parameter which is applied to the data to take into account the unknown scale factor relating the ratio of the measured detector output signals to the ratio σ_1/σ_n.[36] In principle, this normalizing parameter could be determined from measurements at very high frequencies ($\omega\gg\omega_g$) where the ratio σ_1/σ_n is known to approach unity. In practice, however, the parameter cannot be determined accurately by this procedure since experimental limitations preclude measurements at sufficiently high frequencies. At the highest frequency actually attained in a given experiment, the ratio σ_1/σ_n is, however, of the order of unity and its predicted value is insensitive to the detailed assumptions of the theory. In all our experiments we have, therefore, chosen the normalizing parameter so that the ratio σ_1/σ_n does agree with theoretical expectations at the highest frequencies of measurement.

The second parameter used in fitting the data on pure lead with the theory is the gap frequency $\omega_{g0}=2\Delta/h$ which characterizes the predictions of the BCS theory. The value of the parameter thus obtained corresponds to a wave number $\lambda^{-1}=22.5$ cm^{-1}, in agreement with the findings of other workers.[14] This is the value which was subsequently used to obtain specific predictions of the AG theory in the case of lead containing magnetic impurities.

As can be seen in Fig. 3, the data agree well with theoretical predictions over the entire frequency range. The broadening of the experimental curve compared to the theoretical one can be attributed to two sources. One of these is the finite resolution of the monochromator; the other is the nonzero temperature at which the experiments were performed (about 1.5°K). The broadening is, however, fairly small and due predominantly to the limited resolution of the monochromator. Hence there is little to be gained by making comparison with the theoretical curves corrected for nonzero temperature (especially since their calculation is quite complicated in the case of the AG theory). Our results are in good agreement with those obtained by other workers.[37] In particular, we also do not find within the gap region any evidence for the "precursor" absorption which had been reported by some earlier workers.[38]

B. Lead Containing Magnetic Impurities

We have obtained far-infrared data for lead films containing various concentrations of Gd and Mn impurities. These films are evaporated from mixtures whose nominal impurity concentrations are known. Instead of specifying an exact impurity concentration, it is actually more useful to characterize each sample film in terms of its critical temperature T_c (which can

[31] The accepted value of 7.20°K for the transition temperature of thick lead films was used as a calibration point for our germanium thermometer. The original calibration provided for this thermometer by its manufacturer indicated a temperature too high by 0.05°K.

[32] However, if a quench-evaporated film is warmed to about 40°K and then cooled down again, its critical temperature T_c is found to be increased by an amount between 0.05 and 0.1°K. This increase, which was observed in both thin and thick films, disappears after annealing at room temperature. Subsequent warming of the annealed film to 40°K has then no further effect on its critical temperature.

[33] Henry Vogel, Ph.D. thesis, University of North Carolina, 1962 (unpublished); M. Strongin and O. F. Kammerer, J. Appl. Phys. **39**, 2509 (1968). Absorbed thermal radiation is insufficient to lead to discrepancies between the measured temperature and the actual film temperature. Indeed, increasing the radiation density by more than a factor of 100 (by opening shutters in the radiation shields) changes the measured critical temperature by only about 0.05°K. Hence the difference between the measured transition temperatures of thin and thick films cannot be due to the different absorptivities of these films for thermal radiation.

[34] This value is no greater than $0.05\sigma_n$, where σ_n is the conductivity of the normal metal.

[35] D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).

[36] As mentioned previously, our method provides a direct measurement of $\sigma_1 d$, where d is the thickness of the film. The desired ratio σ_1/σ_n could, in principle, be obtained by measuring the same film in its normal state. Such a measurement of the film is, however, not possible with our method, since the sensitivity of the bolometer measuring the absorption of the film is reduced by more than a factor of 100 when the film is maintained at a temperature as high as T_c.

[37] See Palmer and Tinkham (Ref. 14); also Norman (Ref. 18).

[38] D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).

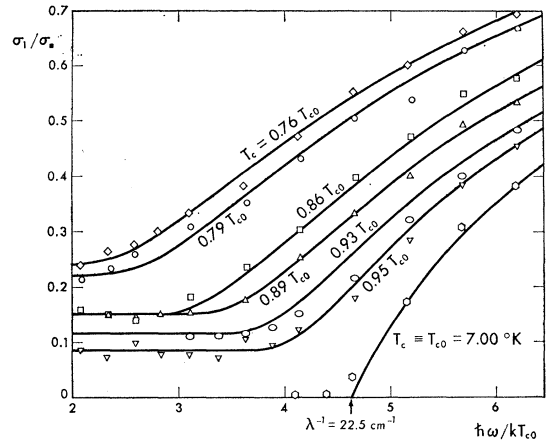

FIG. 5. Frequency dependence of the real conductivity σ_1 of lead containing various concentration of Mn impurities. The solid curves represent the predictions of the AG theory modified by adding to σ_1 a constant value chosen to obtain the best fit with each experimental curve.

be accurately measured).[39] The reason is that the critical temperature ratio T_c/T_{c0}, together with the previously determined value of the gap frequency ω_{g0} of pure lead, is sufficient to allow the value of σ_1/σ_n at any frequency to be predicted unambiguously on the basis of the AG theory. Comparison of the infrared data with the theory then involves no adjustable parameters, except for the fairly trivial normalization factor applied to the magnitude of σ_1/σ_n.

The AG theory of superconductors containing magnetic impurities is based on the assumption that the conduction electrons are weakly scattered by the randomly oriented localized spins of the magnetic impurities. The theory might thus be expected to describe reasonably well the case of Gd impurities in a superconductor, since the unpaired spins of these impurities are due to the well-shielded $4f$ electrons. Figure 3 shows typical data for a lead film containing Gd impurities and indicates for this particular sample ($T_c/T_{c0}=0.80$) the predictions made by Skalski *et al.*[6] on the basis of the AG theory. As can be seen in the figure, the agreement between the data and theory is quite good. In particular, the shape of the observed curve near the gap frequency agrees well with the theoretical predictions. For comparison, we also plot in Fig. 3 the results which would be expected if *non*-magnetic impurities gave rise to the same decrease in critical temperature. In this case, the BCS theory would apply with an energy gap which, in accordance with the law of corresponding states,[3] would be reduced by the factor T_c/T_{c0} compared to that in pure lead. As is seen in Fig. 3, the predictions based on this theory are in clear disagreement with the data. Furthermore, it is apparent that the curves predicted by the BCS theory differ significantly in shape from the experimental curves (and from those based on the AG theory) and could thus never be made to fit the experimental points, irrespective of what value might be chosen for the energy gap.

Figure 4 shows in detail the extent of agreement between the AG theory and our results on lead films containing various concentrations of Gd impurities.[40] The agreement is satisfactory in all cases, and, except for the expected broadening, there appears to be no systematic discrepancy between the data and theory.

Let us now turn to the results obtained with lead films containing Mn impurities. Susceptibility measurements on lead samples containing Mn impurities indicate that the Mn atoms have well-defined local moments and do not become magnetically ordered at the temperatures and concentrations used in our far-infrared experiments.[41] Nevertheless, the results of our far-infrared measurements on lead films containing Mn impurities are quite different from those expected on the basis of the AG theory. As the representative data of Fig. 3 indicate, the deviation of the experimental points from the shape of the BCS curve is much more pronounced than would be predicted on the basis of the AG theory. This may not be overly surprising, since the Mn impurities have unpaired spins due to $3d$ electrons which can couple strongly to the conduction electrons. Hence the simple assumptions of the AG theory may be less applicable than in the case of Gd impurities.

Data obtained for a number of different Mn impurity concentrations are shown in Fig. 5. These curves are all qualitatively different from any that might be expected on the basis of the AG theory. In particular, the curves of σ_1/σ_n tend to approach at low frequencies a limiting constant value, a fact particularly apparent at small impurity concentrations. The appearance of this limiting constant value seems to be a real effect: (a) The limiting value is much larger than the nonzero constant value ($\lesssim 0.05$) occasionally observed in other samples of lead, either pure or containing Gd impurities. (b) The limiting low-frequency value does not seem to be of instrumental origin; in particular, it is independent of the sample thickness, despite the attendant large change in the relative signal levels at the two detectors. (c) The limiting low-frequency value is an increasing function of the concentration of the Mn impurities contained in

[39] The fractional impurity concentration c of a film is approximately known from the composition of the evaporated metal pellets. This concentration can also be determined more accurately from the measured transition temperature T_c by making use of the values of dT_c/dc (where $dT_c/dc=2100$°K for Mn in lead and $dT_c/dc=200$°K for Gd in lead) previously determined in the experiments of Hilsch *et al.* (see Ref. 15).

[40] The curves labeled $T_c=0.40T_{c0}$ and $T_c=0.96T_{c0}$ were obtained from particular sample films which exhibited the behavior occasionally observed in pure lead films, i.e., at the lowest frequencies σ_1/σ_n approached, instead of zero, a small constant value (0.05). Since the effect in the pure material was always positive in sign and nearly constant in frequency, and since its appearance in lead films containing Gd was not correlated with the impurity concentration, we tried to correct for the effect in these two cases by subtracting the small constant value from all the observed values of σ_1/σ_n.

[41] D. Korn, Z. Physik **187**, 463 (1965).

the sample. All these observations lead us to conclude that the limiting low-frequency values manifested by the experimental curves are characteristic of lead containing Mn impurities.

The frequencies at which the various curves attain their limiting low-frequency values correspond roughly to the gap frequencies predicted from the critical temperatures of the samples on the basis of the AG theory. This observation suggests that the data on lead samples containing Mn impurities can be empirically represented as the superposition of two contributions by writing

$$\sigma_1(\omega)=\sigma_1^{(\mathrm{AG})}(\omega)+\sigma_c. \tag{5}$$

Here $\sigma_1^{(\mathrm{AG})}(\omega)$ is the real part of the conductivity as derived from the AG theory by using the measured critical temperature, while σ_c is a frequency-independent contribution which depends on impurity concentration.[42] To determine how well the functional form (5) is adequate to represent the data, the constant σ_c was chosen so as to obtain best fit with each experimental curve. Figure 5 shows then the extent to which the empirical relation (5) agrees with the experimental data over the entire frequency range. The quantity σ_c is found to be proportional to the impurity concentration c, i.e., to the measured reduction of the critical temperature. [More precisely, we found that $\sigma_c/\sigma_n=b(1-T_c/T_{c0})$, where $b=1.2\pm0.2$.[43]]

The results of our infrared experiments on superconductors containing magnetic impurities correspond well with the results of tunneling measurements performed on the same systems by Woolf and Reif.[8] In particular, the present infrared work corroborates their finding that the effect of rare-earth impurities, such as Gd, can be satisfactorily described by the AG theory. Furthermore, our work, as well as theirs, indicates that transition-metal impurities, such as Mn, have a much stronger effect on the energy-gap properties than is predicted by this theory.

C. Conclusions

We have developed a new far-infrared method for the study of thin superconducting films. The method involves the direct measurement of the radiation absorbed by a film and has the virtue of yielding immediately the real conductivity σ_1 of the film material. In addition, the method is capable of yielding data of good accuracy at low frequencies, a feature of particular value for studying the effects produced by magnetic impurities in the region of the energy gap. When applied to *pure* lead films, the method confirms the work of Palmer and Tinkham[14] and gives data in good agreement with the BCS theory.

The method has been applied to study lead films containing various concentrations of paramagnetic impurities. In contrast to the expectation for samples containing nonmagnetic impurities, the far-infrared data for films containing magnetic impurities are found to be qualitatively different from the predictions of the BCS theory. In particular, in the case where the magnetic impurities are Gd atoms (which have spins due to unpaired $4f$ electrons), the data show a significant broadening of the gap edge and are in quantitative agreement with the calculations performed on the basis of the AG theory by Skalski *et al.*[6] In the case where the magnetic impurities are Mn atoms (which have spins due to unpaired $3d$ electrons), the observed effects in the gap region are much more pronounced than in the case of Gd impurities and are not adequately described by the AG theory.

The infrared results correspond well with the results obtained in the previous investigation by Woolf and Reif[8] where the same systems were studied by means of the tunneling technique. In both types of experiment, the introduction of Gd impurities leads to data in good agreement with the predictions of the AG theory, while Mn impurities produce effects more pronounced than predicted by this theory. The tunneling measurements are subject to the possible criticism that the observed effects might be due to experimental artifacts caused by the presence of magnetic impurities within the tunnel junction itself. On the other hand, the far-infrared measurements are immune from any such objections. Hence they confirm the interpretation of the earlier tunneling experiments and show quite conclusively that all the observed effects represent intrinsic characteristics of superconductors containing magnetic impurities.

ACKNOWLEDGMENTS

We wish to thank P. L. Richards, G. I. Rochlin, C. M. Surko, and M. Tinkham for many helpful discussions. We are especially grateful for assistance by L. H. Palmer and for the use of samples provided by M. A. Woolf.

[42] An anomalous contribution to σ_1 below the gap frequency was also observed by W. S. Martin and M. Tinkham [Phys. Rev. **167**, 421 (1968)] in experiments on pure lead films in a parallel magnetic field, a situation which should also be described by the AG theory. This anomalous contribution was attributed by them to the presence of normal vortex regions induced by a small perpendicular component of the magnetic field. The anomalous contribution σ_c observed in our case seems, however, to be an intrinsic property of the Pb-Mn films.

[43] G. J. Dick, Ph.D. thesis, University of California, 1969 (unpublished).