PHYSICAL REVIEW VOLUME 165, NUMBER 2 10 JANUARY 1968

Far-Infrared Absorption in Thin Superconducting Lead Films*

Leigh Hunt Palmer†
Department of Physics, University of California, Berkeley, California
AND
M. Tinkham‡
Department of Physics, University of California, Berkeley, California, and Department of Physics, Harvard University, Cambridge, Massachusetts

(Received 31 August 1967)

We describe measurements of the far-infrared conductivity $\sigma_1 - i\sigma_2$ of thin superconducting lead films with resistances of about 200 Ω/square in the normal state. The conductivity is inferred from measurements of the transmittance and reflectance of a thin film of lead which has been evaporatively deposited on a quartz crystal. We report results for the real part of the conductivity of lead over the frequency range 9 to 120 cm^{-1}. From these we infer an energy gap for lead films at $T=0$ of 22.5 ± 0.5 cm^{-1}, or $(4.5\pm0.1)kT_c$, where k is the Boltzmann constant and T_c is the superconducting transition temperature. The measurements were made at 2.0, 4.3, and 5.5°K, and the energy gap varies with temperature in the manner predicted by the Bardeen-Cooper-Schrieffer theory. The frequency dependence of the real part of the conductivity also is in good agreement with the theory. No evidence is found of the strong precursor absorption which had been previously reported in the energy gap in lead, but σ_2 is found to be anomalously low (by ~25%) near and below the gap frequency. This is believed to result from the strong-coupling anomalies discussed by Nam. This anomalously low σ_2 would also account for the anomalously steep absorption edge observed in other experiments on lead.

I. INTRODUCTION

We shall report here our far-infrared spectroscopic measurements on thin superconducting lead films. From these data we have determined the real part of the conductivity of these films as a function of photon energy in the interval corresponding to frequencies 9 to 120 cm^{-1}, and we find it to be in good agreement with that predicted theoretically by Mattis and Bardeen.[1] We find a well-defined energy gap of 22.5 ± 0.5 cm^{-1}, consistent with the tunneling measurements of Townsend and Sutton[2] after taking account of the gap averaging according to the Anderson theory[3] of dirty superconductors. The temperature dependence of this gap is found to be consistent with the prediction of Bardeen, Cooper, and Schrieffer.[4] No precursor absorption is found, but the transmission data at frequencies near and below the gap frequency are too high to be in quantitative agreement with the prediction of the Mattis-Bardeen theory. The latter discrepancy is attributed to an anomalously low value of σ_2 related to the strong-coupling anomalies predicted by Sang Boo Nam.[5] A preliminary account of this work has been given earlier.[6,7]

A previous experimental measurement, by Ginsberg and Tinkham,[8] of the transmission of thin superconducting lead films in this frequency region suggested that there are absorptive processes effective at energies *below* the energy gap which must be considered to be anomalous when compared with the theory of Mattis and Bardeen.[1] Furthermore, this apparently anomalous absorption behavior limited the precision of the gap determination to the rather crude result 20 ± 2.5 cm^{-1}, corresponding to $(4.0\pm0.5)kT_c$. The absence of the anomalous "precursor" effects in later tunneling experiments[2,9] was consistent with the idea expressed by Ginsberg and Tinkham that their origin might be in some sort of collective excitation, which, while optically active, might be weakly coupled to a tunneling process. Richards and Tinkham[10] saw evidence for the existence of precursor structure in reflectivity measurements on bulk samples of nominally pure lead. Later, Leslie and Ginsberg[11] observed corresponding structure in their measurements, which were made on bulk samples of lead alloyed with varying quantities of thallium, bismuth, and tin, using a method substantially identical with that used by Richards and Tinkham. Recently, after our experimental work was completed, Norman and Douglass[12] reported observation of precursor structure in a bulk lead foil by a direct-absorption technique, but they subsequently found this precursor absorption to be spurious.[13]

* This work was supported in part by the National Science Foundation and the Office of Naval Research.

† Present address: Physics Department, Simon Fraser University, Burnaby, B.C., Canada.
‡ Present address: Department of Physics, Harvard University, Cambridge, Mass.

[1] D. C. Mattis and J. Bardeen, Phys. Rev. **111**, 412 (1958).
[2] P. Townsend and J. Sutton, Phys. Rev. **121**, 1324 (1962).
[3] P. W. Anderson, J. Phys. Chem. Solids **11**, 26 (1959).
[4] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[5] Sang Boo Nam, Phys. Rev. **156**, 470 (1967); **156**, 487 (1967).
[6] L. H. Palmer and M. Tinkham, Bull. Am. Phys. Soc. **10**, 1206 (1965).
[7] L. H. Palmer, Ph.D. dissertation, University of California, Berkeley, 1966 (unpublished).
[8] D. M. Ginsberg and M. Tinkham, Phys. Rev. **118**, 990 (1960).
[9] I. Giaever and K. Megerle, Phys. Rev. **122**, 1101 (1961).
[10] P. L. Richards and M. Tinkham, Phys. Rev. **119**, 575 (1960).
[11] J. D. Leslie and D. M. Ginsberg, Phys. Rev. **133**, A362 (1964).
[12] S. L. Norman and D. H. Douglass, Jr., Phys. Rev. Letters **17**, 875 (1966).
[13] S. L. Norman and D. H Douglass, Jr., Phys. Rev. Letters **18**, 339 (1967).

We had undertaken to do careful spectroscopy in this precursor region in order to determine details of any structure, which might enable us to infer the nature of the excitation or excitations responsible, if any. In pursuit of these data, we decided to use an essentially different method from that of the earlier workers. Ginsberg and Tinkham used an iterative data-reduction method to find real and imaginary parts of the conductivity which were consistent with the Kramers-Kronig transformations,[14] as well as with data on the far-infrared transmittance of a thin superconducting lead film. We wished to be independent from the Kramers-Kronig transformations and the somewhat questionable assumptions one has to make about extrapolated values of data at frequencies above and below the experimentally accessible region. To do this it is necessary to have two independent data of the far-infrared properties which may be chosen from among the transmittance T, reflectance R, and absorptance A, of the film. Whichever two are selected, the third can be inferred from the law of conservation of energy, i.e., $T+R+A=1$. By determining two of these parameters at any one frequency, we can calculate uniquely the complex conductivity σ at that frequency. We can then use the Kramers-Kronig relations to test the validity of our assumptions about the proper extrapolation of the behavior of σ outside our experimental region.

II. EXPERIMENT

We decided to measure transmittance and reflectance simultaneously using the Cassegrain optical configuration shown in Fig. 1. This scheme has the advantage over other possible experimental configurations that both measurements are made at near-normal incidence, which simplifies data analysis. The maximum deviation of the radiation from normal incidence is 7.2° in our apparatus, much less than the 18° maximum in the transmission measurements of Ginsberg and Tinkham.[8] Although the larger deviation has been shown to be insignificant to the earlier experiment,[15] the reduction

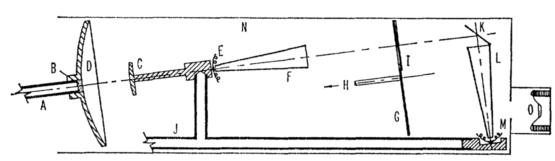

FIG. 1. Optical train: A, brass light pipe; B, sooted quartz window; C, convex primary mirror; D, concave secondary mirror; E, reflection bolometer; F, condenser cone; G, turntable; H, to rotor shaft and heat switch; I, quartz substrate; J, tube connected to helium reservoir; K, right-angle plane mirror; L, condenser cone; M, transmission bolometer; N, low-temperature radiation shield; O, molybdenum boat Pb evaporation source.

TABLE I. Film Properties. Resistances are in Ω/square. $R(T)$ is the measured dc resistance, corrected to square geometry; d is a nominal film thickness, estimated from the temperature-dependent part of the resistance, assuming Matthiessen's rule and taking $\rho(77°\text{K})=5\times10^{-6}\Omega$-cm for pure bulk lead; T_N is the measured normal-state transmittance at 22 cm^{-1} and 8°K; R_{calc} is the film resistance calculated from T_N.

Sample	$R(77°\text{K})$	$R(8°\text{K})$	d(Å)	T_N	R_{calc}
A	294	250	11	0.350	255
B	221	186	14	0.286	191
C	320	270	10	0.361	268

in the present work is a welcome consequence of the optical configuration. Most unwelcome, however, is the size increase required. The diameter of the concave secondary mirror is 14 cm, necessitating a low-temperature experimental volume 15 cm in diameter and 65 cm long. The entire optical train must be maintained at low temperature to keep the film from being heated by radiation.

The film is prepared *in situ* by vacuum deposition on a crystalline quartz substrate cooled indirectly by liquid nitrogen. The ambient background pressure is easily kept below 10^{-6} Torr during the evaporation because the liquid-nitrogen cooled walls of the chamber act as sorption pumps with a high accommodation coefficient. The evaporation takes less than two seconds, and it is quite difficult to hit a film of predetermined resistance with our present method. Optimal films for this work should have a normal-state resistance of the order of $Z_0/(n+1)=118\ \Omega$ per square, since that value gives maximum absorption of radiation by the film. $Z_0(=377\ \Omega)$ is the impedance of free space and $n(=2.10$–2.13 for these frequencies[16]) is the refractive index of the quartz substrate. As indicated in Table I, the films on which the work reported here was done had resistances between 180 and 270 Ω per square when taken to 8°K (completely normal). It was impossible to measure the normal state resistance of the film much below the transition temperature T_c by applying a magnetic field because the required critical field H_c for films so thin is impractically high. The resistance at 8°K is probably residual since it is never much less than the value measured at liquid-nitrogen temperature. The film is annealed at liquid-nitrogen temperature for a day after deposition, during which time its resistance changes typically 10–20%. Subsequently, the resistance change is less than 2% per day. (It may be significant that the films in the earlier work of Ginsberg and Tinkham were annealed at room temperature, which would allow more atomic migration and agglomeration.) The film is then taken to low temperature, and the resistance is measured through the superconducting transition region. The width of the transition is found to be between 0.2 and 0.3°K for all films, centered on (7.2 ± 0.2)°K. Film temperatures

[14] R. L. de Kronig, J. Opt. Soc. Am. **12**, 547 (1926); H. A. Kramers, Atti Congr. Intern. Fis. Como **2**, 545 (1927); for a more accessible reference see, for example, C. Kittel, *Elementary Statistical Physics* (John Wiley & Sons, Inc., New York, 1958), p. 206.

[15] D. M. Ginsberg, Ph.D. dissertation, University of California, Berkeley, 1960 (unpublished).

[16] S. Roberts and D. Coon, J. Opt. Soc. Am. **52**, 1023 (1962).

were determined using an ac-bridge technique to measure the resistance of a germanium resistance thermometer. The thermometer was manufactured and calibrated by Texas Instruments. All "normal" measurements on the film were made between 8 and 9°K, and all "superconducting" measurements were made at 2.0°K, with the exception of the temperature-dependence measurements. No attempt was made to measure film thicknesses directly. Film resistances measured by a four-contact dc method and those calculated from absolute transmission measurements in the normal state (by sample in-sample out comparisons) agree to within 3% for all samples. Numerical values are given in Table I. In contrast to our excellent agreement, Ginsberg and Tinkham[8] typically found that the resistance of lead films inferred from normal transmittances was 10% less than the directly measured dc resistance. This comparison supports the notion that our films are more ideal and uniform than those used in the previous work.

The far-infrared intensity was measured at the two detectors which are gallium-doped germanium bolometers of the type invented by Low.[17] The radiation was chopped at 33 cps and coherently detected using high-gain low-noise phase-locked amplifiers connected to the bolometers. Since the films are very thin, characteristic electron scattering frequencies will be much higher than the frequencies of interest here, leading to a real and constant conductivity in the normal state. Therefore, we expect the normal-state transmittance T_N and the normal-state reflectance R_N to be frequency-independent in our spectral region. Absolute measurements made on one film at the extremes and in the middle of the accessible spectral region showed this to be a justified assumption, at least to within 5%. We used this assumption to simplify data acquisition, making our measurements relative to these constant values rather than repeatedly attempting the more difficult absolute determination. Our data were taken by recording the signals from both bolometers as the frequency was swept with the film in the superconducting state. A second sweep was then made with the film normal, and, if necessary for satisfactory data quality, alternate superconducting and normal sweeps were repeated. Transmittance ratios T_S/T_N and reflectance ratios R_S/R_N were then computed numerically from values read from the recorder charts at frequent intervals throughout the experimentally accessible spectral region.

The radiation was derived from a conventional Littrow diffraction-grating monochromator designed and built by Ohlmann and described adequately elsewhere.[18] The radiation has a relative bandwidth of about 7% throughout the experimental region.

[17] F. J. Low, J. Opt. Soc. Am. **51**, 1300 (1961).

[18] R. C. Ohlmann and M. Tinkham, Phys. Rev. **123**, 425 (1961); R. C. Ohlmann, Ph.D. dissertation, University of California, Berkeley, 1960 (unpublished).

The film temperature was maintained using a heating control loop which did not include the germanium thermometer used for measurement of the film temperature. Temperature stability was easily maintained within a few mdeg, entirely adequate for the measurements reported here. The sample assembly is linked to the helium bath through a superfluid film heat switch invented by G. J. Dick and one of us (L.H.P.).[19] The switch opens automatically when the sample is heated above the lambda temperature of helium.

III. DATA REDUCTION

We define the film conductivity σ in terms of the impedance per square of the film Z by the relation $Z=1/\sigma d$, where d is the thickness of the film. We express the conductivity σ of the film as $\sigma=\sigma_1-i\sigma_2$, where σ_1 and σ_2 are real, and we assign to the film a normalized admittance $y=Z_0/Z=y_1-iy_2$, where y_1 and y_2 are real.

In the case of radiation which is normally incident on the first surface of a lossless substrate with the sample film on its second surface, we can calculate the transmittance T and the reflectance R in terms of the index of refraction of the substrate and y_1 and y_2 in a straightforward manner[7] from simple electromagnetic theory. For this calculation, we average over interference effects due to multiple reflections within the substrate. No such effects are observed in the experiment since the substrate is quite thick and wedged (1 mm to 1.5 mm) and the relative bandwidth of the radiation is about 7%. Inverting the resulting equations for $T(y_1, y_2)$ and $R(y_1, y_2)$, we get

$$y_1=(1-T-R)/T, \tag{1}$$

$$y_2=\left[\frac{4n(1-2R_1+R_1R)}{T(1-R_1)}-(y_1+n+1)^2\right]^{1/2}, \tag{2}$$

where n is the index of refraction of the substrate and R_1 is the reflectance of the vacuum-substrate interface. Apart from the spot-check frequencies at which absolute measurements of T were made, the values of T_S and R_S required in (1) and (2) for the determination of σ_S were inferred from the measured ratios T_S/T_N and R_S/R_N under the assumption that σ_N and hence T_N and R_N were known constants, independent of frequency. For convenience, all results for σ_S are plotted as ratios to σ_N, assumed constant. It turns out to be very difficult to determine y_2 accurately above the energy gap frequency, since it is expected to be a number smaller than unity in the region above the gap, and depends sensitively on the difference between two numbers each of the order of ten. It will also depend on the imperfectly known index of refraction n in addition to experimentally determined parameters. It is also difficult to determine y_2 much below the gap frequency, since the signal to noise ratio deteriorates

[19] L. H. Palmer and G. J. Dick (to be published).

rapidly. For these reasons we were unable to infer significant values for the imaginary part of the admittance of our films from our data except in a limited frequency interval.

IV. RESULTS

Figure 2 shows the predictions of the Mattis-Bardeen[1] calculation for σ_1/σ_N, σ_2/σ_N and the normalized transmittance ratio T_S/T_N for a typical superconducting film. [These are calculated in the "extreme anomalous limit" and are appropriate for either high Fourier components ($q\xi_0 \gg 1$) or dirty samples ($l/\xi_0 \ll 1$), $\xi_0 = hv_F/\pi\Delta(0)$ being the usual coherence length, and l the electronic mean free path. Both of these conditions should obtain in the present case of a thin dirty film.] The curves are plotted in terms of the frequency $\tilde{\nu}$ normalized to the superconducting energy-gap frequency $\tilde{\nu}_g$.

Figure 3 shows our measurements of σ_1, the real part of the conductivity, as a function of (wave number) frequency $\tilde{\nu}$ from 8 to 60 cm^{-1}, compared with a Mattis-Bardeen theoretical curve with $\tilde{\nu}_g = 22.5$ cm^{-1}. Measurements from three samples are recorded here. The value of $\tilde{\nu}_g$ is taken as the value of $\tilde{\nu}$ at which σ_1 goes to zero with a distinct break in each curve. The agreement of experiment and theory above the gap is good. Although the plot is cut off at 60 cm^{-1} for better display of the most interesting spectral region, the fit of experiment with theory is also good from 60 to 120 cm^{-1}, our high-energy limit. Despite the generally good consistency of the data (by far-infrared standards, at least), drifts of up to $\pm 5\%$ are evident from the lack of overlap between gratings in the region around 50 cm^{-1} and the systematic divergences of runs on different films. These systematic errors result because of the difficulty of holding source intensity and detection sensitivity absolutely constant over the long periods of time (typically 30 min) between taking the superconducting and normal-state data as described above. Moreover, auxiliary heaters are required to hold bolometer temperatures and hence sensitivities the same while the film is superconducting and normal. These enabled the bolometer resistances at least to be held constant to about $\pm 0.2\%$. From these considerations of error sources, we see that systematic drifts of a few per cent are probably inevitable, and one must expect that an over-all average of the runs will give the truest result. This over-all average for σ_1/σ_N is typically 0.03 below the Mattis-Bardeen curve for frequencies above the gap out to 60 cm^{-1}. This discrepancy is of the sense and order of magnitude of the strong-coupling anomaly predicted theoretically by Nam[5] to lie in this frequency region. Our data on σ_1 are not sufficiently good to constitute a real confirmation of the theory, but at least they are not inconsistent with it. We shall return to this theory later.

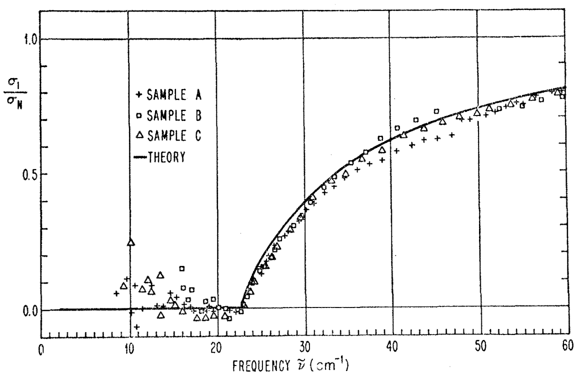

FIG. 3. Results of measurements of the real part of the normalized conductivity of three thin lead films at 2°K, compared with Mattis-Bardeen theory with gap frequency fitted to 22.5 cm^{-1}. To reduce the clutter in the figure, only about one fourth as many points are shown as were taken and recorded in Ref. 7. The points shown are selected typical points above the gap and local averages below the gap.

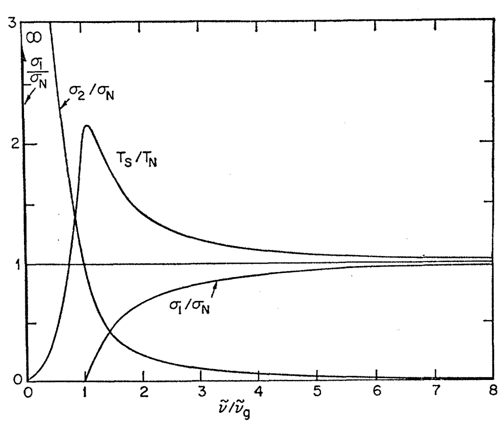

FIG. 2. Frequency dependence of normalized conductivity components σ_1/σ_N, σ_2/σ_N, and of T_S/T_N at $T=0$ according to the calculation of Mattis and Bardeen. The transmission curve is for a film resistance $377/(n+1)$ Ω per square, where n is the refractive index of the substrate.

Since the far-infrared signal power available at constant resolving power rises roughly as $\tilde{\nu}^3$, the random scatter is greatest at low frequencies, where noise is the most important. In addition to random error, sample C appears to show significant absorption below 13 cm^{-1}, but, as indicated above, this may be due to a systematic error for that particular run. The over-all preponderance of points is below $\sigma_1/\sigma_N = 0.1$ throughout the region below the gap, indicating that no "precursor" absorption process of the size of that reported by Ginsberg and Tinkham exists in our samples. It is particularly clear that there is no sizeable absorption in the upper part of the gap region.

In Fig. 4 we present the result of making our measurements on a superconducting film at three different temperatures. The theoretical curves are derived from Mattis and Bardeen, using the BCS[4] temperature dependence of $\tilde{\nu}_g$, normalized by the experimentally determined value $\tilde{\nu}_g = 22.5$ cm^{-1} at 0°K. Our only approximation here is that $\tilde{\nu}_g(2°\text{K}) = \tilde{\nu}_g(0°\text{K})$, which

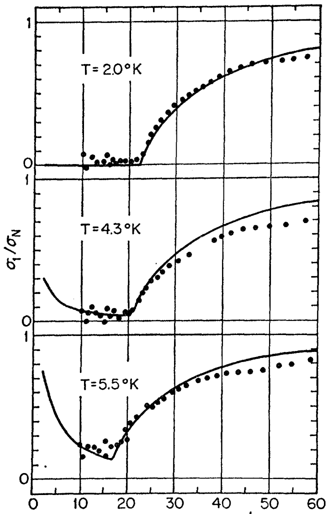

FIG. 4. Temperature and frequency dependence of normalized conductivity σ_1/σ_N in a thin superconducting lead film (sample C), compared with predictions of Mattis–Bardeen theory (calculated with the assistance of a program supplied by Harris), shown as solid curve. The gap frequency was fitted only for the low-temperature limit. The number of data points shown has been reduced as in Fig. 3.

introduces no significant error. We note that the decrease of $\tilde{\nu}_g$ with increasing temperature is in excellent accord with the theory. The increase in absorption below the gap at higher temperatures is generally consistent with theoretical expectations. The quantitative disagreement of σ_1/σ_N from the theory above the gap at the higher temperatures is probably due to systematic drifts, but since this region was of less interest, repeated runs were not made to check this point.

We tried to infer $\sigma_1(\tilde{\nu})$ from our transmittance data alone, using a method similar to that of Ginsberg[8,15] involving the Kramers-Kronig relations. We were unable to get convergent results from the application of our iterative scheme to our experimental data, although the method contained improvements on the earlier version. The scheme does yield convergent results when applied to test data generated from the theory, and the $\sigma_1(\tilde{\nu})$ generated is identical to the $\sigma_1(\tilde{\nu})$ used to produce the data. The success of this test suggests that, while the algorithm is sound, the experimental transmission data were not complete and/or accurate enough to permit analysis by this method.

We originally intended to use the Kramers-Kronig method as a check on our data, but because of the failure of convergence we shall make only qualitative observations. We have shown that $\sigma_1(\tilde{\nu})$ appears to agree well with the Mattis-Bardeen theory, but Fig. 5 shows that the transmittance does not agree with that which we would predict using the Mattis-Bardeen $\sigma_1(\tilde{\nu})$ and $\sigma_2(\tilde{\nu})$, which are appropriate Kramers-Kronig conjugate functions. The transmittance ratio at frequencies near and below the gap is systematically higher than we would predict. Thus, if we extrapolate our measured σ_1 to be zero for all frequencies between 0 and 14 cm^{-1} and to continue to approach a constant σ_N at high frequencies following the Mattis-Bardeen dependence, we shall clearly run into an inconsistency, since σ_1 will then be substantially identical with that of Mattis and Bardeen for all frequencies, implying that σ_2 must also agree with Mattis and Bardeen if dispersion theory is applied. We believe this to be a strong indication of the inapplicability of the Kramers-Kronig technique with the assumptions and extrapolation methods used in the earlier work of Ginsberg and Tinkham.[8]

The clearest indication we have that there is an anomaly in lead is the excessive peak height in the transmission ratio at the gap. Figure 5 shows that our data on sample A exceed the peak height of the Mattis-Bardeen theory by about 11%. (Similar plots for samples B and C show excess peak heights of 22% and 12%, respectively.) One might try to explain this by assuming an error in the measurement of the normal transmittance (or, equivalently, the normal resistance) of the film has been made. We tested this possibility by adjusting the film resistance used in calculating the BCS prediction to try to obtain a better fit. As an example, in Fig. 5 we show a BCS curve computed for a 200 Ω/square film as well as for the measured value of 252 Ω/square. We still have not got the peak height to agree, and the low-frequency discrepancy has been made worse, even though the assumption used to generate the adjusted curve is that the resistance we determined by measuring the normal transmittance was 25% too high, which is five times our probable error. We conclude that it is not possible to fit our data by a BCS curve for any value of film resistance.

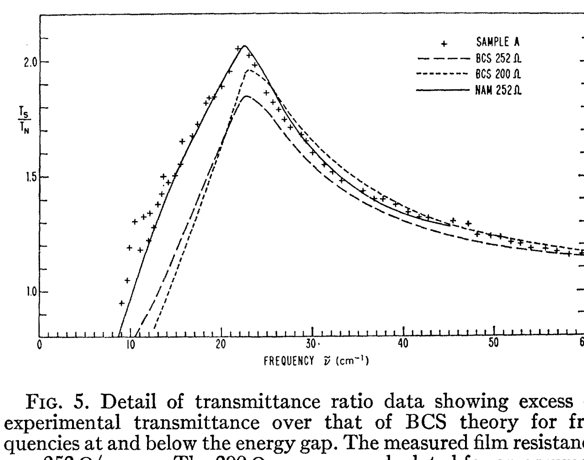

FIG. 5. Detail of transmittance ratio data showing excess of experimental transmittance over that of BCS theory for frequencies at and below the energy gap. The measured film resistance was 252 Ω/square. The 200 Ω curve was calculated for an assumed film resistance 20% lower than that determined from the absolute normal transmittance or from the dc resistance. This adjustment was chosen arbitrarily to give a better fit to the data, but the discrepancy near the peak and below the gap is not eliminated. The solid curve was computed using the strong-coupling conductivity ratios calculated by Nam. The number of data points shown has been reduced as in Fig. 3.

An anomalously high transmittance can be explained by an anomalously low σ_1 or σ_2. In the Mattis-Bardeen theory for $T \ll T_c$, σ_1 is near zero at the peak and at lower frequencies, and so could hardly be anomalously low. Rather, we calculate that σ_2/σ_N is about 40% below its theoretical value of unity at $\tilde{\nu}_g$, becoming about 25% low at lower frequencies. These same reduced values also give excellent agreement with the peak heights for samples B and C, although the discrepancy in peak height was twice as large in sample B because it had substantially lower resistance. This systematic agreement supports the notion that this is an intrinsic effect and not an experimental artifact. Note that impurity radiation (radiation of other frequencies, a common problem in far-infrared spectroscopy[13]) cannot account for a peak height increase, since the transmittance ratio for all other frequencies is lower than that for the peak. Another manifestation of the internal consistency of the data, but of the inconsistency with BCS, is shown in Fig. 6. This figure shows the values of σ_2/σ_N inferred using both transmission and reflection data, as outlined above.

In seeking to understand this anomaly we first recall that the constancy of T_N and hence of σ_N has been verified to a precision of only 5% even in the region in which data were taken. Any significant variation of σ_N would undermine the assumptions on which the analysis is based. Such a variation would not be completely unexpected[20] since the frequencies involved span the range of typical phonon frequencies in lead. Still the variation of σ_N should be small even in a strong-coupling superconductor, since in our thin dirty films we are dealing with the response for high-q Fourier components and rapid scattering. Hence, we do not think that this effect causes any serious error.

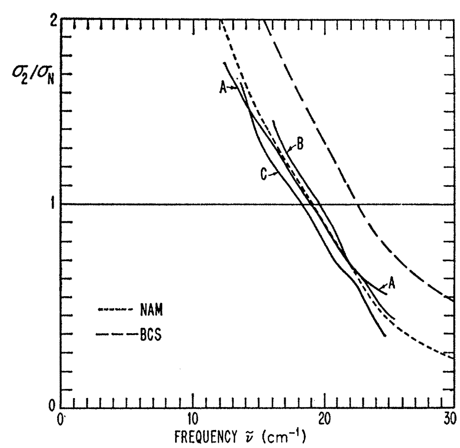

FIG. 6. Smoothed results of measurements of the imaginary part of the normalized conductivity of three lead films (A, B, and C) at 2°K. Curve labeled BCS is the weak-coupling result of Mattis and Bardeen, while that labeled Nam presents a revised version of a curve shown in Ref. 5. In both cases, the gap frequency was taken to be 22.5 cm^{-1}.

Using the Kramers-Kronig transformations and a sum rule,[21,22] it can be shown that any anomalous increase in $\sigma_1(\tilde{\nu})$ above $\tilde{\nu}_g$ would be accompanied by anomalously low $\sigma_2(\tilde{\nu})$ for $\tilde{\nu} \leq \tilde{\nu}_g$. Thus, some anomaly in $\sigma_1(\tilde{\nu})$ above 120 cm^{-1} (our high-frequency limit) could account for the peak height excess. The possibility of the existence of such an anomaly associated with strong phonon coupling has been suggested by Sang Boo Nam.[5] From his plot of the strong-coupling-induced change in σ_1/σ_N from the Mattis-Bardeen form, one can show by an approximate numerical integration (including an extrapolated tail at high frequencies) that

$$\int_0^\infty \Delta(\sigma_1/\sigma_N)\, d\tilde{\nu} \approx 0.3\tilde{\nu}_g.$$

By the sum-rule argument,[21,22] this implies a change in the strength of the superfluid response in σ_2 by a term $\Delta(\sigma_2/\sigma_N) = -(2/\pi)0.3\tilde{\nu}_g/\tilde{\nu} \approx -0.2\tilde{\nu}_g/\tilde{\nu}$. This is to be compared with the Mattis-Bardeen value $\sigma_2/\sigma_N \to (\pi/2)(\tilde{\nu}_g/\tilde{\nu})$ as $\tilde{\nu} \to 0$. Thus we expect a reduction in the low-frequency σ_2/σ_N by some 12%, and the expected reduction at $\tilde{\nu}_g$ itself turns out to be about 18%. These reductions would account for about one-half of the discrepancy mentioned above for $\tilde{\nu} \lesssim \tilde{\nu}_g$. Of course there are other changes in σ_2/σ_N depending on the distribution of $\Delta(\sigma_1/\sigma_N)$ in frequency rather than simply on its unweighted integral, but for $\tilde{\nu} \lesssim \tilde{\nu}_g$ these are generally considerably smaller than the effect just mentioned.

Such reductions in σ_2 at low frequencies are not shown in the graphs published by Nam.[5] However, in more recent unpublished calculations, Nam has found that, with the appropriate choice of branch cut, the $1/\tilde{\nu}$ term in σ_2 should be reduced by 26% in lead compared to the weak-coupling BCS result. This is in remarkable agreement with our prior experimentally estimated 25% reduction, well within our experimental uncertainty. (The discrepancy of the 26% with the 12% estimated above is surprisingly large and not understood at present.) Nam has recalculated not only the low-frequency limit of σ_2 but also its frequency dependence up to twice the gap frequency. This allows a more detailed comparison with our results, as shown in Figs. 5 and 6. Figure 5 shows that Nam's corrected σ_2/σ_N results (together with his published σ_1/σ_N results) lead to quantitative agreement with the measured transmittance ratio over the entire frequency range. Note that there is no need to "adjust" the value of film resistance, whereas the weak-coupling BCS curve failed to fit even with adjustment of R_N. Figure 6 shows that, in the range of frequency in which σ_2/σ_N could be directly inferred from the experimental data, the strong-coupling curve fits the measured data on

[20] T. Holstein, Ann. Phys. (N.Y.) **29**, 410 (1964); H. Scher and T. Holstein, Phys. Rev. **148**, 598 (1966).

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

[22] M. Tinkham and R. A. Ferrell, Phys. Rev. Letters **2**, 331 (1959).

all three films to within their scatter, whereas the weak-coupling BCS curve is much too high.

The quantitative agreement displayed above may be fortuitous. At the very least, however, the above discussion provides a plausible model explanation for the peak-height anomaly, present in all our data and (in the earlier data of Ginsberg and Tinkham on the film Pb 3) which seemed initially to violate dispersion theory. The point is that changes of only a few per cent in σ_1 over wide ranges of frequency many times (in this specific case $\sim$10 times) the gap frequency upset the sum-rule determination of the superfluid response strength from optical measurements extending to even five times the gap frequency.

V. CONCLUSIONS

As is shown in Fig. 3, there is a striking similarity between our data on σ_1/σ_N, the normalized real part of the conductivity of lead (in the thin-film limit) and the BCS-model prediction of Mattis and Bardeen. Despite the known strong-coupling nature of lead, the agreement is essentially quantitative (within our accuracy of $\sim$3%) up to five times the energy-gap frequency. This agreement is better than that found in previous work[8] even on the more ideal weak-coupling superconductors tin and indium, but this difference may well only reflect improved techniques of measurement and analysis. The good agreement is, to be sure, less clear below the gap frequency. In transferring many points to Fig. 3, there is much overlapping near zero conductivity, so points scattered away from zero look relatively more important. However, there is a preponderance of points around zero conductivity between 14 and 22.5 cm^{-1}.

In analyzing these data, we find no precursor absorption as large as one-third the size of that reported by Ginsberg and Tinkam[8] in the top third of the energy gap. Although a precursor has been detected also in diverse far-infrared experiments by Richards and Tinkham,[10] Leslie and Ginsberg,[11] and Norman and Douglass,[12] our experiment shows that, in thin films at least, it cannot be as large an effect as was previously supposed. This conclusion is in agreement with that of Norman and Douglass,[13] who suggest that radiation impurity may account for the appearance of a precursor in some experiments.

We measured an energy gap of 22.5 ± 0.5 cm^{-1} for lead at 2.0°K. Our method of determining the gap involves noting not only where σ_1 goes to zero, but also noting where the break in the σ_1 curve occurs. The reported value is a compromise between the values determined by these two criteria, which actually agree well with each other. According to the BCS[4] theoretical temperature dependence of the gap, this value should still hold true within the stated confidence limits at 0°K. Reduced to units of the critical temperature of bulk lead T_c, we get a value of $(4.5\pm0.1)kT_c$. (The T_c of our films agrees with the bulk value to within $\pm2\%$.) This compares with the far-infrared values of Ginsberg and Tinkham,[8] $(4.0\pm0.5)kT_c$, of Richards and Tinkham,[10] $(4.1\pm0.2)kT_c$, and of Norman and Douglass,[13] $\sim4.3kT_c$. By the simpler and probably more precise technique of electron tunneling, Giaever and Megerle[9] report an observed gap of $(4.3\pm0.1)kT_c$. Townsend and Sutton[2] report two gaps in tunneling measurements on thick, well-annealed lead films: $(4.30\pm0.08)kT_c$ and $(4.67\pm0.08)kT_c$. Our gap seems to be the average of these two as Anderson's theory of dirty superconductors[3] predicts. In still more refined tunneling measurements, Rochlin[23] has shown that pure unstrained lead has a spectrum of energy gaps extending from 3.4 to $4.8kT_c$, with an average over the Fermi surface of about $4.4kT_c$, again in satisfactory agreement with our results. Thus we conclude that the average gap is the same within about 2% in our very thin dirty lead films, (nominally $\sim$10–15 Å thick) as in pure, essentially bulk samples.

The temperature dependence of the gap appears to agree quite well with theory[4] and with other infrared[10] and tunneling[9] experiments, but our accuracy is limited by the higher noise level of the intermediate-temperature data. The theoretical curves in Fig. 4, with no adjustable parameters except the measured 2°K energy gap, give a good account of the absorption by thermally excited quasiparticles at frequencies below the gap as well as of the shift of the gap edge with temperature.

Although our results for σ_1/σ_N agree within our accuracy of a few per cent with the Mattis-Bardeen curves, the transmittance of our films at frequencies near and below the gap frequency lies well above that predicted assuming both σ_1/σ_N and σ_2/σ_N follow the Mattis-Bardeen curves. This implies that σ_2/σ_N is substantially ($\sim$25%) less than the Mattis-Bardeen predicted values for these frequencies. Sum-rule arguments suggested that the strong-phonon-coupling anomalies discussed by Nam might offer an explanation of this effect, although his published curves did not predict it. Subsequent unpublished calculations of Nam show a reduction of σ_2/σ_N in excellent agreement with our experiment.

Note that if this reduction of σ_2/σ_N is truly characteristic of strong-coupling effects in lead, it should also be manifest in other data on lead, but not in data on weak-coupling materials. We have already noted that the film Pb3 of Ginsberg and Tinkham showed the peak-height enhancement effect.[24] On the other hand, their data on an indium film showed a peak height in good agreement with BCS, as expected. Their

[23] G. I. Rochlin, Phys. Rev. **153**, 513 (1967).

[24] Their other lead film, Pb2, does not show the peak-height enhancement, the peak height actually being below the BCS value. This points to a lower degree of reproducibility and self-consistency of the earlier data. We recall, however, that a *low* value of peak height can have many spurious causes, such as radiation impurity, low resolution, and film inhomogeneity. Such effects can not cause the peak to be too high.

data on tin films could not be carried to frequencies low enough to clearly determine a peak height, but the data suggest a peak height *below* the BCS value, as might be expected because of radiation impurity at this very low frequency ($\sim 9\ \text{cm}^{-1}$). Thus the earlier film work is consistent with our present view in that excess peak height is found only in lead, not in tin or indium.

Finally, we note that the reduction of σ_2/σ_N would also explain an anomalous steepness of the absorption edge in bulk and film samples of lead as observed experimentally.[10,11,25] One of us has already pointed out[25] that a considerable steepening can be accounted for within the BCS framework by noting that the strong-coupling of lead causes T_c and $\tilde{\nu}_g$ to be large, and hence $\xi_0 = v_F/\pi^2\nu_g(0) \sim \lambda_L$ rather than $\xi_0 \gg \lambda_L$ as in weak-coupling superconductors. As λ and ξ become comparable, Fourier components far from the extreme anomalous limit are important in calculating an appropriate absorption edge shape, and these have a steeper absorption edge.[25] More recently, Ginsberg[26] has carried through detailed machine computations of this effect, and reached the conclusion that the theoretical absorption edge in bulk lead is still less steep than the experimentally determined one, although it is much closer than if the oversimplified limiting expressions are used. Because our present results are only for the extreme anomalous limit values of σ, we can not give a quantitative discussion of the effect on the steepness of the absorption edge, which involves all Fourier components. However, some idea of the order of magnitude of the effect can still be gained by noting that, if we retain the Mattis-Bardeen value

$$\left.\frac{d(\sigma_1/\sigma_N)}{d(\nu/\nu_g)}\right|_{\nu_g} = \pi/2$$

(as is suggested by our data); then[25] we have

$$\left.\frac{d(R_S/R_N)}{d(\nu/\nu_g)}\right|_{\nu_g} = \frac{\pi/3}{[\sigma_2(\nu_g)/\sigma_N]^{4/3}}$$

in the extreme anomalous limit,

$$\left.\frac{d(R_S/R_N)}{d(\nu/\nu_g)}\right|_{\nu_g} = \frac{\pi/(2^{3/2})}{[\sigma_2(\nu_g)/\sigma_N]^{3/2}}$$

in the extreme dirty or local limit, and

$$\left.\frac{d(A_S/A_N)}{d(\nu/\nu_g)}\right|_{\nu_g} = \frac{\pi/2}{[\sigma_2(\nu_g)/\sigma_N]^2}$$

for a thin but highly reflective film. Thus a reduction of $\sigma_2(\nu_g)/\sigma_N$ to ~ 0.6, as found here for the thin-film limit, would lead to increases of steepness by factors of 1.9–2.7, depending on the case. After taking into account the effect of a wide range of Fourier components, as discussed above, it is likely that the additional steepness enhancement due to this reduction of σ_2 would be less than these estimates, but still of the necessary order of magnitude to explain the residual discrepancy. Apart from lead, the only superconductor on which extensive quantitative absorption-edge measurements have been made[27] is aluminum, a very weak-coupling material. In this case, there is good agreement with the simple BCS result without the strong-coupling corrections, as would be expected according to our model. Very recently, Norman[28] has measured the steepness of the absorption edge in *thick* films of a number of superconductors, finding that it increases with increasing T_c/Θ_D, i.e., with increasing electron-phonon coupling strength. Such a correlation would be expected from the considerations presented here as well as from the arguments presented in Ref. 25 and mentioned briefly above.

ACKNOWLEDGMENTS

We wish to thank G. J. Dick, Dr. N. Kurti, F.R.S., and Professor F. Reif for their valuable consultation in the performance of this experiment. We also thank Dr. S. B. Nam for sending us his unpublished numerical results for σ_2/σ_N in lead. This work was partly conducted during the tenure of a National Science Foundation graduate fellowship held by L. H. Palmer.

[25] M. Tinkham, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abeles (North-Holland Publishing Co., Amsterdam, 1966), p. 431.

[26] D. M. Ginsberg, Phys. Rev. **151**, 241 (1966).

[27] M. A. Biondi and M. P. Garfunkel, Phys. Rev. **116**, 853 (1959); M. A. Biondi, M. P. Garfunkel, and W. A. Thompson, *ibid.* **136**, A1471 (1964).

[28] S. L. Norman, Phys. Rev. (to be published).