TABLE I. Liquids for domain conversions at 0°C using plate electrodes.

c domain	Dielectric constant[a]	a domain	Dielectric constant[a]	Mixed domain	Dielectric constant[a]
Methyl sulfate[b]	48	Marcol[b,c]	2–4	Acetone[b]	20.7 (25°C)
Glycerol[d]	47.2	Carbon tetrachloride[b]	2.24 (20°C)	Isopropyl alcohol[b]	20.1 (21°C)
Furfural[b]	41.9 (20°C)	n-Butyl alcohol[d]	7.8 (19°C)	Isobutyl alcohol[b]	17.8 (20°C)
Ethylene glycol[b]	37 (25°C)	Butyl acetate[d]	5.34	Ethyl alcohol[b]	24.3 (25°C)
Methyl alcohol[d]	37.1				
20% Methyl alcohol +80% water[e]	77.6				

[a] Dielectric constants are for 0°C unless otherwise specified.
[b] *Tables of Dielectric Constants of Pure Liquids*, National Bureau of Standards Circular 514 (U. S. Government Printing Office, Washington, D. C., 1951).
[c] A white mineral oil made by Esso Standard Oil Company.
[d] *Handbook of Chemistry and Physics*, edited by C. D. Hodgman (Chemical Rubber Publishing Company, Cleveland, 1955), thirty-seventh edition.
[e] Extrapolated from J. Wyman, Jr., J. Am. Chem. Soc. **53**, 3292 (1931).

crystal is also obtained even with a liquid medium of a large dielectric constant.

In the present study, Marcol has also been used in the 120°C temperature conversion method. The resulting crystals consist mostly of a domain, but the conversion is not as complete as in 0°C case. In the process of conversion using the 120°C transition, $BaTiO_3$ is transformed from the paraelectric (zero permanent dipole) to the ferroelectric state. On the other hand, in the 0°C case, $BaTiO_3$ is transformed from one ferroelectric state with a permanent dipole orientation to another ferroelectric state with a different permanent dipole orientation. A quantitative comparison between the effectiveness of domain conversion by those two methods should provide some information on the role of permanet dipoles on the nucleation of domains.

PHYSICAL REVIEW VOLUME 108, NUMBER 2 OCTOBER 15, 1957

Conductivity of Superconducting Films for Photon Energies between 0.3 and $40kT_c$*

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(Received May 17, 1957)

Far infrared and millimeter microwave transmission experiments through thin superconducting lead and tin films are reported. The frequency range covered corresponds to photon energies from 0.3 to $40kT_c$. The measurements include the previously unexplored frequency region in which a superconductor changes from an essentially lossless conductor to a normal one. By suitable analysis the effective complex conductivity of the films is obtained from the transmission data. For thin superconducting films it is shown that $[\sigma_1(\omega)-i\sigma_2(\omega)]/\sigma_N$ is, to a good approximation, a universal function of the reduced frequency $(\hbar\omega/kT_c)$, being independent of film resistance, thickness, degree of anneal, and material (for the two metals tried). At $T=0$, σ_1 appears to be very small (or zero) for photon energies below roughly $3kT_c$. Starting at $3kT_c$, σ_1 rises rapidly and reaches its limiting value σ_N at about $20kT_c$. This behavior suggests a gap of width $\approx 3kT_c$ in the electronic excitation spectrum of the superconducting state. At $T=0$ and for photon energies considerably smaller than $3kT_c$, $\sigma_2/\sigma_N\approx\alpha kT_c/\hbar\omega$, with $\alpha=3.7\pm0.7$ for both Sn and Pb. The frequency dependence is in agreement with the London theory. This theory, however, would not predict that the results for Pb and Sn should be the same and, moreover, it would give values of $\alpha\sim100$ times too large. The Pippard nonlocal theory predicts the type of universal dependence found, but with $\alpha=6.7$. For photon energies of the order of $3kT_c$, a polarizability term $\sigma_2'(\omega)$, required by the Kramers-Kronig relations because of the cutoff of $\sigma_1(\omega)$ near $3kT_c$, becomes important and tends to cancel the $1/\omega$ term in σ_2. As a result, σ_2 is reduced to a small value for photon energies above $5kT_c$. Some information about the temperature dependence of the complex conductivity has also been obtained.

I. INTRODUCTION

PERHAPS the most striking property of a superconducting metal is the large drop in the dc resistance which takes place when it is cooled through the critical temperature T_c. Below the critical temperature a lossless flow of current can occur. It has been impossible to detect any remaining trace of resistance. At frequencies corresponding to the visible spectrum, however, the behavior is entirely different. The optical properties of a superconducting metal are unchanged when it is cooled through T_c, indicating that there is

* Supported in part by the Office of Naval Research, the Signal Corps, the Air Force Office of Scientific Research, and the National Security Agency.
† National Science Foundation Postdoctoral Fellow.

no change in the electrical properties at these frequencies. Therefore, at these high frequencies the mechanisms for energy absorption which are characterized by the electrical resistance of normal metals must be also operative in the superconducting state. It has long been thought that a detailed study of this radical change in the properties of a superconductor with frequency might lead to information about the fundamental nature of the interaction responsible for superconductivity. Recent work on both the low- and high-frequency sides has helped to narrow the range of frequencies in which this transition could be taking place.

A theoretical argument suggests that the frequencies of interest should be near $\omega = kT_c/\hbar$. (Throughout this paper we use the term "frequency" to denote $\omega = \Delta E/\hbar$ rather than $\nu = \Delta E/h$.) This is obtained by dividing the free energy decrease per unit volume in the superconducting state, $H_c^2/8\pi$, by the number of electrons per unit volume having energies within kT_c of the Fermi surface, presumably the number able to participate significantly in the phase transition. This leads to an energy of order kT_c per electron. (In the case of tin the wavelength corresponding to a photon of this energy is 3.8 mm.) This suggestion is supported by recent experimental electronic specific heat data. Accurate measurements[1] have revealed an exponential dependence $[C \sim \exp(-1.5T_c/T)]$ at low temperatures. This form suggests an energy gap $E_g \sim kT_c$ in the spectrum of electronic excitations.

Starting from the low-frequency end, the behavior of superconductors has been studied up to frequencies in the millimeter microwave range. By measuring the losses in a resonant cavity the "surface resistance," which is essentially the resistance of a layer one skin-depth thick, has been determined for bulk samples. Because of the superconducting penetration depth λ and the anomalous skin effect, however, the skin depth depends in a complicated way on both frequency and temperature. As a result, it has not yet been possible to give a quantitative interpretation of the surface resistance of superconductors. Qualitatively, the evidence indicates that for nonzero frequencies the resistance does not drop discontinuously at the critical temperature but falls off more gradually. However, at least for $\omega \leq 0.5kT_c/\hbar$, R appears[2] to extrapolate to zero at $T=0$. In the measurements[3,4] from 0.5 to 2.3 $kT_c/\hbar$, experimental difficulties have made it impossible to decide whether or not the resistance approaches 0 at absolute zero. Moreover, it appears that the temperature for which the surface resistance begins to drop is lower than T_c. This downward shift seems to increase with frequency. An interpretation of this effect in terms of a gap in the electron energy levels which increases in width from 0 at T_c to a limiting value at low temperatures has been given,[5] but it does not yet appear to be established in detail.

Starting from the high-frequency side, the optical properties of metals in the normal and superconducting states have been compared. Hirschlaff[6] measured the reflectivity of Pb and Ta mirrors in the normal and superconducting states for wavelengths from 4000 to 10 000 A. No change was detected with an accuracy of $\frac{1}{2}\%$. Hilsch[7] measured the transmission of visible radiation through thin films of Sn. Together with Schertel[8] he showed that the transmission in the normal and superconducting states were the same within 2 parts in 10^5. Going to lower frequencies, Ramanathan and others[9] have studied the absorption of infrared radiation in bulk samples. At 0.014 mm, corresponding to $275kT_c$ for Sn and $140kT_c$ for Pb, no change was detected with experimental errors of 0.3% and 5%, respectively.

In a previous publication[10] we have reported experiments on far infrared and millimeter wave transmission through thin films, in principle quite similar to the work done by Hilsch. These preliminary results were shown[11] to provide strong support for an energy-gap model. In the present paper we give detailed results and discuss improved experiments covering an extended frequency range.

In a film experiment the measured value of the transmission is related directly to the admittance per square of the film as a function of frequency. The conductivity of the metal in the film is directly proportional to this admittance since the field is uniform through the film and the thickness of the current-carrying layer is independent of frequency. The resistance may therefore be expressed in ohms per square. This situation may be contrasted with that which

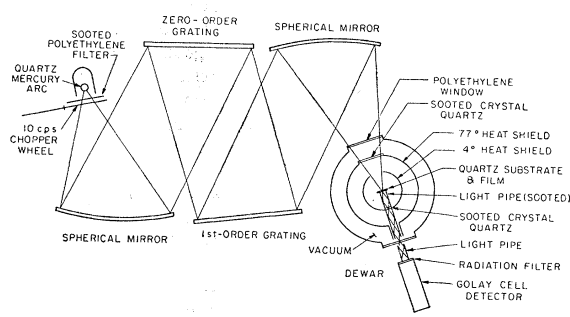

FIG. 1. Schematic diagram of the apparatus for infrared measurements.

[1] Corak, Goodman, Satterthwaite, and Wexler, Phys. Rev. **102**, 656 (1956); W. S. Corak and C. B. Satterthwaite, Phys. Rev. **102**, 662 (1956).
[2] E. Fawcett, Proc. Roy. Soc. (London) **A232**, 519 (1955).
[3] Blevins, Gordy, and Fairbank, Phys. Rev. **100**, 1215 (1955).
[4] Biondi, Garfunkel, and McCoubrey, Phys. Rev. **101**, 1427 (1956).

[5] M. J. Buckingham, Phys. Rev. **101**, 1431 (1956).
[6] E. Hirschlaff, Proc. Cambridge Phil. Soc. **33**, 140 (1937).
[7] R. Hilsch, Physik. Z. **40**, 592 (1939).
[8] R. Hilsch and A. Schertel (private communication).
[9] Daunt, Keeley, and Mendelssohn, Phil. Mag. **23**, 264 (1937); K. G. Ramanathan, Proc. Phys. Soc. (London) **A65**, 532 (1952).
[10] R. E. Glover, III, and M. Tinkham, Phys. Rev. **104**, 844 (1956).
[11] M. Tinkham, Phys. Rev. **104**, 845 (1956).

obtains with bulk metal, where variations of the skin depth may greatly complicate the interpretation of surface-resistance measurements. Film experiments have the further advantage that a moderate change in the conductivity can produce a relatively large change in transmission. The resulting intrinsic sensitivity of the method has allowed us to study the behavior of a superconductor throughout almost all of the previously unexplored and technically inconvenient frequency range in which it changes from a material having almost negligible resistance to one having the resistance of a normal metal.

II. EXPERIMENTAL METHOD

A. Procedure

The experimental setup is shown schematically in Fig. 1. Radiation from a grating monochromator passes through a film of a superconducting metal and into a detector. The film can be made either superconducting or normal, and the transmission is measured for both conditions.

B. Film and Low-Temperature Techniques

Films of lead and tin approximately 2 cm square are prepared inside the Dewar by evaporation. They are produced in place for the transmission experiments and are kept at all times under high vacuum. The metals are condensed onto a crystal quartz plate making good thermal contact with a copper block soldered to a tank which can be filled with liquid helium. A $\frac{5}{8}$-inch diameter hole in the block makes it possible to pass radiation through the film. Two radiation shields are provided, one at 4°K and the other at 77°K. Cold windows of sooted crystal quartz are inserted in these shields to reduce the radiant heating of the sample. These pass the very long-wave infrared radiation of interest but absorb the visible radiation and the infrared frequencies which predominate in room temperature radiation.

Material to form the films is evaporated from an oven placed outside the 77° radiation shield and somewhat below the plane of the section shown in Fig. 1. A shutter (not shown) is provided in the outer heat shield, making it possible to open and close the path between oven and quartz substrate.

Electrical contact with the films is made through gold electrodes coated on the quartz plate. Current and potential leads are supplied, making it possible to monitor the dc resistance continuously.

For the transmission experiments, the films are cooled until they become superconducting and the transition is followed by watching the disappearance of the dc resistance. The film can be made normally conducting at will by passing a current through it larger than a critical value. The dc resistance indicated that no appreciable heating above T_c occurred. This technique allows a direct comparison of the high-frequency energy transmitted through the film in the normal state at $T\approx T_c$ with that transmitted in the superconducting state at any accessible temperature.

The films were prepared from Johnson, Matthey Pb and Sn having a stated purity of 99.998 and 99.99%. For most of the films studied, the substrate was held at 77° during the evaporation. The low temperature was used to reduce migration of metal along the substrate and so to insure a reasonably uniform layer. The usual procedure was to anneal the film overnight at room temperature and then to cool to liquid helium temperatures for the superconductivity measurements. In order to check the effect of annealing, the substrate was in a few cases held at 4.2°K during the evaporation and the transmission measured before and after annealing.

To a good approximation the resistance of the annealed films varied linearly with temperature down to T_c. For Pb films on the order of 20 A thick, a typical value of the resistance at 20°C was 200 ohms per square and the low-temperature residual resistance was about half this value. Annealed films could be kept for periods of a week without either their low- or high-temperature resistance changing by more than a few percent.

The temperature is measured by using a carbon radio resistance cemented in a hole in the copper block which carried the quartz substrate with the film. During the transmission measurements the film temperature was usually of the order of 0.3°K above the measured temperature of the block. This temperature difference could be checked by observing the temperature dependence of the critical current when the heat-shield windows were closed. In this case the temperature of the block and the film are the same and the critical current can be calibrated against the carbon resistance thermometer to give a measure of the true film temperature.

The film thickness, though not of direct importance for the experiments, was estimated in two ways. For massive samples of a metal, lattice disorder has the effect of adding a temperature-independent contribution of resistance to the component which varies approximately linearly with temperature. To the degree that this is also true for a thin film, it is possible to calculate the thickness from the temperature-dependent part of the resistance. The values arrived at in this way agreed approximately with those calculated from the Fuchs[12] theory when one assumes random scattering of the electrons at the film surface.

The thickness of the films used for the transmission experiments was estimated to be on the order of 20 A. Preliminary experiments showed that even such thin films have well-defined superconducting properties. For a typical Pb film the transition temperature was found to be 0.1°K lower than that of bulk material. The transition region was roughly 0.1°K wide. At 0.2°K below T_c, no trace of resistance could be detected.

[12] K. Fuchs, Proc. Cambridge Phil. Soc. 34, 100 (1938).

It was down by at least a factor of 500 from the normal value. The Sn films were less well behaved, having a somewhat wider transition region. The loss of resistance, however, appeared to be complete.

In an attempt to learn something about the uniformity of the films, one of them was removed from the vacuum and examined under a microscope. In the time required for this operation, the film oxidized completely. The resulting oxide layer appeared to be uniform, and any structure must have been on a scale smaller than 1 micron. A fact speaking for the uniformity of the films is that their transmission of infrared radiation, as measured at room temperature, checked with the value predicted theoretically from the measured value of the dc resistance on the assumption of a uniform layer. This agreement held for the complete range of wavelengths used from 0.10 to 0.75 mm.

C. Infrared Techniques

The far infrared monochromator, shown in Fig. 1, was designed for use in the wavelength region between 0.10 and 0.75 mm. It is similar to ones described by McCubbin and Sinton[13] and by Genzel and Eckhardt.[14] The source is a UA3 quartz mercury arc which provides a continuous spectrum in this region. At the 0.10-mm end of the spectrum, the quartz envelope is largely opaque and emits as a body at a temperature of the order of 10^3 °K. At 0.75 mm the envelope is transparent, and one uses the direct emission from the discharge inside the tube. This has a noise temperature of the order of 10^4 °K for these frequencies, and so it provides appreciably more long-wavelength energy than any practical blackbody radiator. The radiation is chopped at the rate of 10 cps by a rotating disk, and a sooted polyethylene filter is used in front of the source to reduce the amount of stray chopped radiation in the room. A similar filter is located directly over the entrance window of the detector to reduce its response to any fluctuations of the light in the room. These filters transmit roughly 80% at these long wavelengths, but are opaque to visible and near-infrared radiation. This greatly reduces the stray energy. Additional filters of fused quartz and of rocksalt are required to suppress higher order reflection from the grating when working at wavelengths exceeding 0.2 and 0.3 mm, respectively.

Solid aluminum spherical mirrors, turned and polished on a lathe, proved adequate for our purposes. The various echelette gratings used in the experiment were ruled in the shop on a planer, and had from 12 to 50 rulings per inch. The first grating in the setup is used in zero order as a final low-pass filter to systematically scatter the shorter waves out of the beam. At frequencies where the other filters are adequate, this grating is replaced by a plane mirror. The second grating provides the dispersion, and angles from the position of the zero-order spectrum are measured using a dial on its worm-gear drive. Course gratings with low dispersion are used to allow utilization of the energy in as broad a band of frequencies as is convenient. For the same reason, no slits are provided other than the source and the film cross section.

By using 12-in. diameter optics, it is possible to obtain an aperture of $f/1.5$, even with the awkward optical arrangement necessitated by the large Dewar. To eliminate the chance that radiation which had not passed through the film might be scattered into the detector, the radiation is conveyed from the film to the detector through a brass light pipe. Since the entire cross section of the pipe is filled with radiation passing through the film, no serious loss of energy occurs from our resulting inability to focus the output onto the entrance window of the Golay detector. The signal from the detector is run through a lock-in amplifier and the result displayed on a strip-chart recorder.

Accuracy is limited by the low signal/noise ratio. A transmission ratio is measured by running in the normal and superconducting states during alternate 10-minute periods for a total of one hour. By alternating the two states, systematic drifts are cancelled. The signal from the detector is recorded continuously (through a 60-second time constant), and average values for the two transmitted signals are obtained numerically from the charts. Limits of error have been assigned on the basis of an empirical study of the system noise as it actually enters with such long-term averages.[15]

D. Microwave Techniques

In the microwave setup, the source of energy is a crystal frequency multiplier driven at ~24 000 Mc/sec by a 2K33 klystron. Constricted sections of wave guide serve as high-pass filters. They allow any harmonic to be used in the presence of only higher harmonics, whose intensity can usually be neglected. Usable power for our purposes could be obtained in the second, third, and fourth harmonics, which have wavelengths of approximately 6, 4, and 3 millimeters, respectively.

This power is brought into the Dewar through $\frac{1}{4}$-in. diameter thin-walled stainless steel tubing, with a thin polyethylene vacuum seal in the line. From the end of the tube the power is projected at the film from an adjustable distance of approximately one centimeter. Since this tube is considerably oversize for lowest-mode propagation even at 6 mm, the radiation is largely concentrated in the forward direction, and no horn is needed. The output is also of stainless steel tubing. To avoid any leakage into the pipe around the film, the pipe is attached directly to the rear of the copper block which supports the substrate and film. A Golay cell is again used as the detector. Its sensitivity is

[13] T. K. McCubbin, Jr., and W. M. Sinton, J. Opt. Soc. Am. 42, 113 (1952).

[14] L. Genzel and W. Eckhardt, Z. Physik 139, 578 (1954).

[15] This study revealed a systematic error which had lowered the apparent ratio T_S/T_N of the long-wave, low-signal/noise points in the preliminary measurements (reference 10). This error was eliminated in the present measurements.

comparable with that of a crystal detector at 3 mm and it has the advantage of having an exact power-law response.

The signal/noise ratio was satisfactory for quite rapid measurements. Standing waves, however, caused trouble and it was found impossible to reduce them to negligible proportions. The accuracy of the final results must then depend on averaging out the standing wave effects over phases. This average in principle could be performed by varying the frequency continuously over a range sufficient to insure that the number of wavelengths between each pair of reflecting surfaces would change by at least one. The behavior would then be similar to that in the infrared case where a broad band of radiation is used and standing-wave difficulties do not arise. This procedure was approximated by varying the frequency stepwise over a range of several percent. It fails to give an average, however, for surfaces which are separated by distances of only a few wavelengths. There are two such path lengths of particular importance in the apparatus: the separation of the film from the input tube which projects the microwave power, and the thickness of the quartz substrate on which the film is laid. The averaging over the first of these is approximated by mechanically varying this distance over a wavelength or so. Since there is no way to average over the second distance, a theoretical correction must be made for reflections within the quartz substrate. This essential correction is discussed in Appendix A.

III. EXPERIMENTAL RESULTS

A. Infrared Measurements

1. Frequency Dependence

The measured ratios of the transmission in the superconducting state (T_S) to that in the normal state (T_N) are plotted for a typical Pb film in the lower half of Fig. 2. The two curves correspond to different temperatures. Preliminary experiments confirmed that the transmission in the normal state is independent of frequency. We note that T_S is larger than T_N over the entire frequency range of the measurements and that it has a maximum in the frequency region between 3 and 5 $kT_c/\hbar$. At this maximum and for the lower temperature, the film is transmitting about twice as well in the superconducting as in the normal state and has approached to within 25% of complete transmission. At higher frequencies the experimental curve approaches an ordinate of 1, and for frequencies of about $20kT_c/\hbar$ the point is reached where the transmissions in the normal and superconducting states are the same within experimental accuracy. Pb films varying in residual resistance by a factor of 5 were studied and all gave curves qualitatively similar to Fig. 2. It will be shown in Sec. IV that after reduction in terms of a frequency-dependent conductivity, the data for all of the films lie close to a single curve. The curves drawn in Fig. 2 are

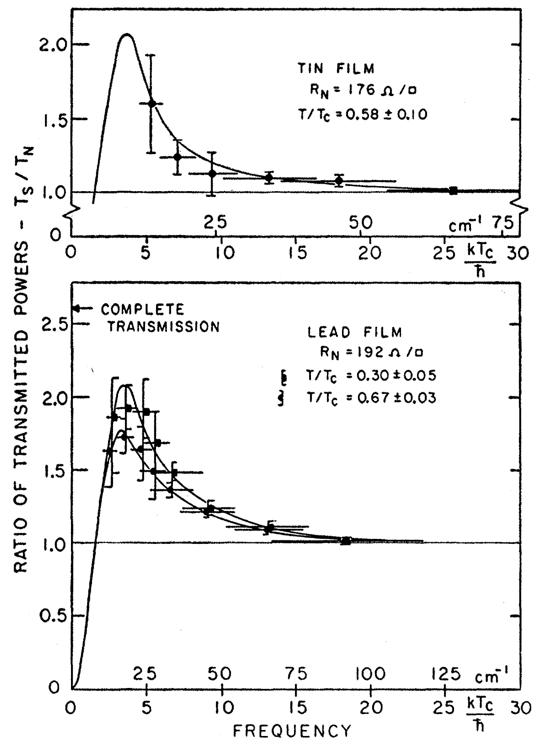

FIG. 2. Experimental ratios of power transmitted through typical lead and tin films in the superconducting and normal states, plotted against frequency. (Throughout the paper we use the term "frequency" to devote $\omega=\Delta E/\hbar$ rather than $\nu=\Delta E/h$.) The frequency uncertainty on each point is the width at half-power of the continuous spectrum used. The vertical error limits are based on the random scatter in the observed signal averaged for one hour. The curves are calculated by using the universal conductivity function for thin superconducting films discussed in Secs. IV and V.

based on these approximately universal results, and they will be discussed in Sec. IV.

2. Dependence on Material

In Fig. 2 we also show the frequency dependence of the transmission through a tin film of approximately the same resistance as the lead film shown in the same figure. Both curves are plotted on the same reduced frequency scale (reduced in terms of $kT_c/\hbar$). Accordingly, the *absolute* frequency scales differ by a factor of approximately 2 (7.2°/3.7°). Plotted in this way, the curves for Sn and Pb show a marked similarity. It is also worth noting that for the Sn film the three lowest-frequency points show a rapid systematic increase in T_S/T_N, whereas the points for Pb at the same *absolute frequencies* show a rather flat maximum. This contrast lends assurance that the maximum found with lead is not an instrumental effect associated with the unavoidably low signal/noise ratio.

3. Temperature Dependence

Transmission curves are presented in Fig. 2 for the same lead film at two different temperatures, namely

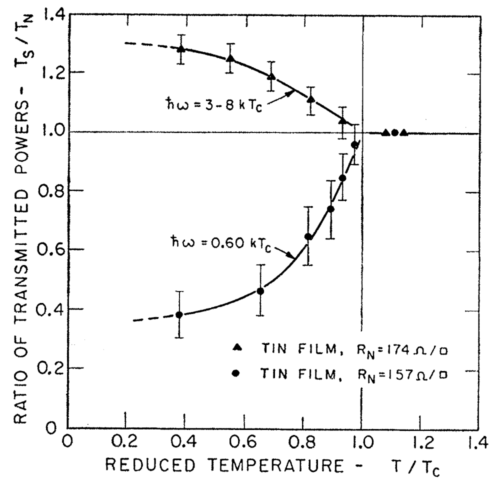

FIG. 3. Temperature dependence of the transmission ratio. The upper curve shows the increase in infrared transmission in the superconducting state over that in the normal state; the lower curve shows the decrease in microwave transmission.

0.30 and 0.67 T_c. Although the statistical errors in the data are large, the trend seems clear. The effect is more pronounced at the lower temperature, but not by a large factor. This behavior is typical of most properties of superconductors: the departure from the normal state develops rapidly near T_c, but levels off to a nearly constant value at low temperatures. We note that the deviation of the transmission ratios from unity change upon cooling from $T/T_c=0.67$ to 0.3 in roughly the same proportion (0.8 to 1) for the entire frequency range from 3 to 20 $kT_c/\hbar$. This suggests that the temperature dependence is roughly the same over the whole range of frequencies.

To check this dependence more closely, we took the data on tin plotted in the upper part of Fig. 3. Since T_c for Sn lies within the temperature range accessible by pumping on liquid helium, we were able to follow the effect nearer to the transition temperature. However, since the frequency for the transmission maximum has scaled down to a region where our source power is even less than for the transmission maximum in the case of Pb, we were forced to use a very broad band of frequencies to get a usable signal/noise ratio. This was done by eliminating the gratings and using only a rock salt transmission filter to limit the band pass. The estimated half-power points of the resulting spectrum are at 3 and 8 $kT_c/\hbar$. The errors are still very large, but again the trend seems to be clear. The effect appears to set in very near the dc value of T_c, increasing linearly with decreasing temperature at first, then leveling off at low temperatures. Unfortunately our sensitivity does not allow us to plot the behavior in the immediate vicinity of T_c with any significance.

For comparison, Fig. 3 also shows the temperature dependence of the transmission of 6-mm microwaves through a similar Sn film. At this frequency the transmission through the superconducting film is less than through the normal film, but the temperature dependence of the change is similar to that found in the infrared. (The large errors are assigned to allow for the imperfect average over standing waves.) Thus in these films there seems to be no evidence for a shifted transition temperature at any frequency, contrary to the increasingly rapid shift with increasing frequency found in the bulk metal surface-resistance measurements.[3,4]

B. Microwave Results

Transmission ratios for typical Pb and Sn films are plotted as a function of frequency in Fig. 4. All values have been corrected for the effect of standing waves in the quartz substrate, discussed in Appendix A. This correction is in some cases as large as 100% and so may not be neglected. It cannot be calculated without assumptions about the nature of the conductivity in the superconducting state. The assumption we have made here and the one used in most of the following discussion is that for frequencies up to about $3kT_c/\hbar$ and temperatures well below T_c the conduction in the films in the superconducting state is essentially lossless ($\sigma_2 \gg \sigma_1 \approx 0$). Evidence supporting this assumption will be given in Sec. IV and it will also be shown that it leads uniquely to a consistent treatment of the data over both the infrared and microwave ranges.

The significant thing to note here is that, when plotted on a reduced frequency scale, the Pb and Sn data fall on the same curve within the scatter of the data. The rapid rise in T_S with frequency is such as to allow a continuous joining with infrared data of the type shown in Fig. 2. The curve drawn through the

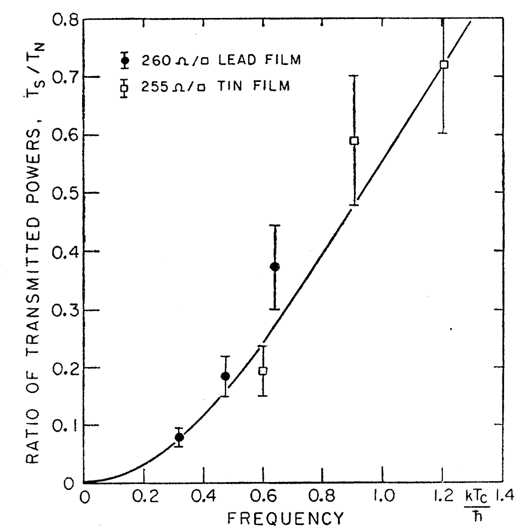

FIG. 4. Experimental ratios of microwave powers transmitted through lead and tin films in the superconducting and normal states. These experimental values have been corrected for the effects of multiple internal reflections in the quartz substrate. As in Fig. 2, the curve is calculated by using the universal conductivity function presented in Sec. IV.

data is again derived from a universal formula based on an average over many films as discussed in Sec. IV. The temperature dependence for a single frequency has been shown in the lower half of Fig. 3.

IV. DISCUSSION OF LOW-TEMPERATURE RESULTS

The optical behavior of a film is determined by the electrical properties of the material of which it is composed, as modified, of course, by the surface effects. In this section we consider the interpretation of the measured transmission ratios in terms of the effective conductivity of the material, σ. The discussion follows a suggestion previously made by one of us.[11] In general σ will be frequency-dependent and complex, allowing for currents both in and out of phase with the electric field. It will be written here in the form $\sigma=\sigma_1(\omega)-i\sigma_2(\omega)$. From the measurement of just one optical parameter, such as the transmission, it is not in general possible to determine both components. Some help is, however, offered by the Kramers-Kronig relations[16] which restrict the possible pairs of functions $\sigma_1(\omega)$ and $\sigma_2(\omega)$ (see Appendix B). Since these relations are integral transforms, any practical method of solution may involve iteration and appear to be a circular argument. However, given complete transmission data, the Kramers-Kronig restriction in principle assures a unique solution. In the case at hand, it turns out that for most frequency regions the transmission is dominated by either σ_1 or σ_2, separately, the other component being small. Namely, we can assume that for $T\ll T_c$, $\sigma_1\approx 0$ for $\hbar\omega<kT_c$ and $\sigma_2\approx 0$ for $\hbar\omega>5kT_c$. Since it will be shown that these regions can be estimated *a priori*, the analysis proceeds in a surprisingly straightforward manner. In view of the uniqueness of the solution, the fact that the pair of functions, $\sigma_1(\omega)$ and $\sigma_2(\omega)$, obtained in this way are consistent with the observed transmission data and the Kramers-Kronig relations furnishes the final validation of the assumptions.

In order to interpret the observed quantity T_S/T_N, the ratio of the power transmitted in the superconducting state to that transmitted in the normal state, in terms of conductivities, it is necessary to solve the electromagnetic problem of a plane wave incident from free space onto an infinitely extended film of thickness d($\ll$ wavelength or skin depth) laid on a substrate of index of refraction n and thickness l, backed by free space. This is an idealized version of the actual situation, and neglects edge effects. It should be a good approximation so long as the transverse dimensions of the film are large compared to a wavelength—as is true in our experiments.

A further simplification results if it is possible to neglect multiple reflections inside the quartz substrate, since l then becomes unimportant. In Appendix A it is shown that this is the case for the infrared measurements. For the microwave measurements, standing waves in the substrate do prove to be important. However, the directly observed values of the transmission ratios can be corrected for this effect by using the methods discussed in Appendix A. To simplify the present discussion, it will be assumed that this has been done.

The resulting simplified expression for the ratio of the power transmitted with a film to that with no film is

$$T=1\bigg/\left|1+\sigma d\frac{Z_0}{n+1}\right|^2, \tag{1}$$

where d is the film thickness, n is the index of refraction of the substrate, and Z_0 is the impedance of free space ($4\pi/c$, cgs; 377 ohms, mks). For the case of a metal in the normal state, the effective conductivity in a thin film, as limited by surface scattering, is independent of frequency for the frequencies of interest here. Moreover, to an excellent approximation it may be taken to have only a real part. We denote this by σ_N, and henceforth reserve σ_1 and σ_2 for description of the superconducting state. Since σ_N is a constant, Eq. (1) predicts that T_N should be a constant depending only on ($\sigma_N d$). This quantity is just the reciprocal of the dc resistance per square of the film, a quantity easily measured experimentally. In preliminary experiments the applicability of (1) to our films was checked. Upon using a series of thin Pb films, the transmission was found to be frequency-independent over the entire infrared range from 0.10 to 0.75 mm. The absolute value agreed within a few percent with that calculated from (1) using the measured value of the dc resistance per square. This suggests both that the assumptions used in deriving (1) are adequately fulfilled and that for purposes of the optical measurements the films used can be considered uniform.

By forming the ratio of two expressions of the type (1) and carrying out a simple reduction, we obtain the following expression for T_S/T_N, the ratio of the transmission in the superconducting to that in the normal state.

$$\frac{T_S}{T_N}=\frac{1}{[T_N^{\frac{1}{2}}+(1-T_N^{\frac{1}{2}})(\sigma_1/\sigma_N)]^2+[(1-T_N^{\frac{1}{2}})(\sigma_2/\sigma_N)]^2}. \tag{2}$$

The experimentally measured quantity, T_S/T_N, is given in terms of T_N [a quantity which in principle could be directly measured but was in practice usually determined from the measured dc resistance per square with the help of (1)], and the ratios σ_1/σ_N and σ_2/σ_N, which are to be determined.

A. Microwave Measurements

Microwave experiments[2] on bulk samples have shown that, for frequencies at least as high as $0.5kT_c/\hbar$, the

[16] R. de L. Kronig, J. Opt. Soc. Am. **12**, 547 (1926); H. A. Kramers, Atti congr. intern. fis. Como **2**, 545 (1927). For a recent review, see J. R. MacDonald and M. K. Brachman, Revs. Modern Phys. **28**, 393 (1956).

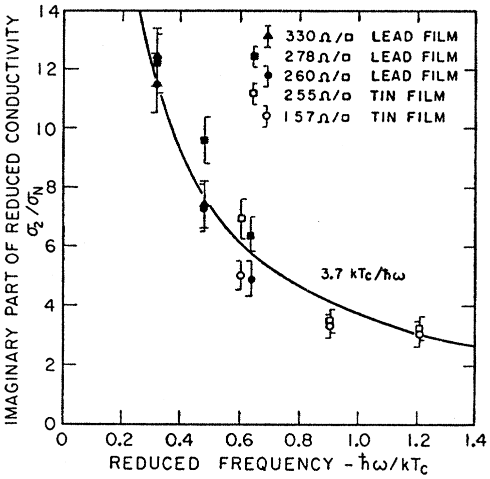

FIG. 5. Frequency dependence of the imaginary part of the reduced conductivity of five lead and tin films in the superconducting state. The values shown have been extrapolated to $T=0$ as described in the text. The indicated error limits allow only for the uncertainty in the data associated with an imperfect average over phases in the standing wave patterns. The solid curve shows the frequency dependence for a London-type conductivity with a greatly reduced coefficient.

surface resistance R approaches zero rapidly as the temperature is lowered below T_c. Since the surface resistance is directly proportional to σ_1 (if $\sigma_2 \gg \sigma_1$), this result is possible only if σ_1 approaches zero. It is worth pointing out that this property of R makes small values of σ_1 more accessible to measurement with bulk specimens than with films. Unless the properties of films and bulk metal differ in an unexpectedly fundamental way, we can then assume *a priori* that σ_1 in the films should be very small for $T \ll T_c$ and $\hbar\omega \lesssim kT_c$. Direct evidence from these film experiments that $\sigma_1 < \sigma_N$ at still higher frequencies is given by Fig. 2. If σ_1 were not reduced from its value in the normal state, no increase in transmission would be possible at all. By assuming $\sigma_2 = 0$ in (2), we can find the upper bound $\sigma_1/\sigma_N \leq 0.24$ at the transmission maximum for the film in Fig. 2. A nonzero value for σ_2 would require a still greater reduction in σ_1. In view of these considerations, we shall analyze the microwave data at $T \ll T_c$ on the assumption that σ_1/σ_N can be neglected as much smaller than σ_2/σ_N. This makes it possible to determine σ_2/σ_N directly from the observed transmission ratios by using formula (2).

The results of measurements at 6, 4, and 3 mm on three Pb and two Sn films are shown in Fig. 5.[17] All of the points fall near the single curve:

$$\sigma_2{}^L/\sigma_N = \alpha kT_c/\hbar\omega. \quad (\alpha = 3.7). \tag{3}$$

The frequency dependence has the form $1/\omega$. This is just the form to be expected for charge carriers that can be accelerated freely in an electric field and is that predicted by the London theory of superconductivity. The superscript L signifies three things: (1) this is the part of σ_2 found in low-frequency measurements, (2) the $1/\omega$ frequency dependence is that of the London theory or (3) of a lossless inductance. More precisely, the London theory predicts an imaginary conductivity

$$\sigma_2 = c^2/(4\pi\lambda^2\omega), \tag{4}$$

where λ, the "superconducting penetration depth" is a material constant. For bulk samples and temperatures well below T_c, λ^2 differs for Pb and Sn by a factor of almost two. Further, σ_2 should be independent of σ_N, the low-temperature limit of the conductivity of a particular sample. A remarkable feature of the present film results is that the measurements of $\sigma_2{}^L/\sigma_N$ for both Sn and Pb seem to fall on the same curve in terms of $\hbar\omega/kT_c$. The two sets of measurements shown for Sn were actually made on the same film. Between the two runs the film was annealed, raising σ_N by 40%. Both sets fall on the same curve with the three Pb films. This must mean that for these thin films the low-frequency ($\omega < kT_c/\hbar$) conductivity in the superconducting state is scaling directly with the normal residual conductivity in a way independent of the particular substance involved.

The value of the coefficient $3.7kT_c$ for the films turns out to be roughly equal to the width of the energy gap and is an order of magnitude smaller than (4) would predict on the basis of the measured penetration depth in bulk material. In a typical case the film value is down by a factor of roughly 100 (λ increased by a factor of 10). This major reduction of $\sigma_2{}^L$ is a necessary requirement for the surprising rise in transmission observed in the infrared experiments. If $\sigma_2{}^L$ had its bulk value, it would be large enough to prevent an increase in transmission from occurring at any frequency.

The most promising explanation presently available for these two surprising experimental results is offered by Pippard's nonlocal modification[18] of the London equations for the accelerative supercurrent. His expression for the superconducting current density in the presence of an oscillating electric field is obtained by replacing σ/l by $(i\omega\xi_0\Lambda)^{-1}$ and l by ξ in the integral expression which gives the current density in the normal state when the mean free path is comparable with other relevant dimensions and diffuse surface scattering is assumed. In these formulas, l is the mean free path in the normal state, ξ_0 is the "coherence length" for a pure sample, ξ is the coherence length in the actual sample as reduced by impurities and lattice disorder, and Λ is m/ne^2. Because of the close resemblance of the two formulas, the ratio $\sigma_2{}^L/\sigma_N = J_S/J_N$ is given simply by $(\omega\xi_0\Lambda\sigma/l)^{-1}$ provided that $\xi = l$ and that the surface scattering is diffuse. Because of the high degree of

[17] These data were reduced to $T=0$ by a small extrapolation from the values found experimentally near $T=0.4T_c$. As suggested by Fig. 3 this correction is small. The changes made were of the order of 1% and do not effect the conclusions drawn.

[18] A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

disorder present in the films, it seems reasonable to assume $\xi \approx l \ll \xi_0$ according to Pippard's theory. If ξ_0, Λ, and σ/l are expressed in terms of the Fermi velocity $\bar{v}_0$, the area of the Fermi surface, and the dimensionless constant a of Pippard's theory ($\xi = a\hbar\bar{v}_0/kT_c$), a simple reduction yields

$$\sigma_2{}^L/\sigma_N = (1/a)kT_c/\hbar\omega,$$

which is exactly the form (3) found in our experiments. Faber and Pippard[19] found $a = 0.15$ from studies of the surface reactances of wires of Al and Sn at 1200 Mc/sec. This value corresponds to $\alpha = 6.7$, which is comparable to our experimental value ($\alpha = 3.7$) obtained at frequencies 50–100 times as high, with different materials, and a radically different geometry.

When one considers that the ordinary London equations (a) would not predict the existence of a universal relation of this form, and (b) would predict coefficients α for various metals and film thicknesses which are of the order of 100 times the observed values, one sees that the Pippard nonlocal equation gives results which are immensely closer to the fact. The remaining numerical discrepancy from the Pippard result still appears to be outside the experimental errors, however. Because the dependence of the integrals on ξ or l is only logarithmic in a thin film, no more than 20% of the difference can reasonably be ascribed to a difference between ξ and l. Thus it seems likely that some other detailed form of nonlocal formulation may be required to give exact agreement with the data on macroscopic samples. Pending the availability of further data on other materials, though, the present semiquantitative agreement is not too unsatisfactory.

In contrast to the Pippard theory, it should be noted that in the absence of magnetic fields the Ginsburg-Landau theory[20] reduces to a local theory equivalent to that of F. London and H. London. Therefore it does not appear to provide a natural explanation for the observed great reduction of $\sigma_2{}^L$ in a film. As with the London theory, the only explanation is through an *ad hoc* assumption that the density of superconducting electrons, n_s or $|\Psi|^2$, decreases with decreasing film thickness.

B. Infrared Measurements

In Fig. 5, $\sigma_2{}^L/\sigma_N$, which governs the behavior of the films in the low-frequency range, is seen to drop monotonically with frequency. This results in the increase of T_S/T_N with frequency shown in Fig. 4 and at the lowest infrared frequencies in Fig. 2. Above about $3kT_c/\hbar$, however, the transmission begins to fall. This

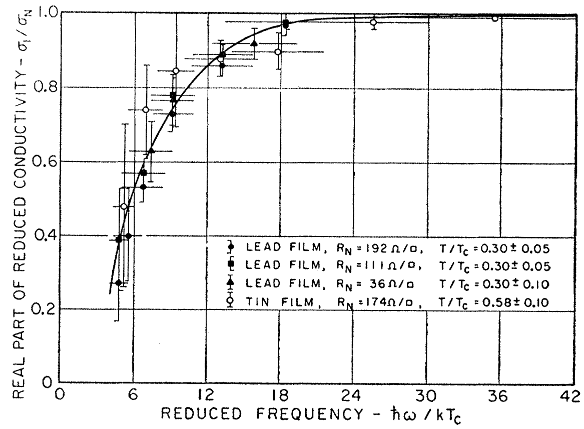

FIG. 6. Frequency dependence of σ_1/σ_N for several lead and tin films in the superconducting state.

behavior can only be explained by assuming that a new component in the complex conductivity is becoming effective. Above $20kT_c/\hbar$, Fig. 2 shows that the transmission through the film is essentially the same in the superconducting and normal states. Since the normal transmission is governed by the real (lossy) conductivity σ_N, it seems natural to assume that $\sigma_1 = \sigma_N$ for frequencies above $20kT_c/\hbar$. Since we have established in IV-A that $\sigma_1 \approx 0$ below $\hbar\omega = 3kT_c$, we are led to associate the drop in T_S/T_N above $\hbar\omega \approx 3kT_c$ with the appearance of a lossy conductivity component σ_1 in the superconducting state. For the purpose of analyzing the infrared data, we shall assume that σ_2/σ_N continues to fall rapidly with frequency, and may be neglected for $\hbar\omega > 5kT_c$. This assumption is strengthened by the fact that σ_2 enters (2) only quadratically, and it will be verified by the final self-consistency and uniqueness of the solution.

With this assumption, formula (2) allows us to determine a value of σ_1/σ_N from each measured transmission ratio for $\hbar\omega \geq 5kT_c$. The results for three lead films and one tin film are plotted in Fig. 6. As with σ_2 there is a remarkable degree of consistency among the values of σ_1 inferred for all the films, when plotted in terms of the reduced variables σ_1/σ_N and $\hbar\omega/kT_c$. This is true despite the 5:1 range of film resistances and the fact that tin and lead films are plotted together. Some of the deviations from the smooth curve drawn through the data are probably significantly outside the experimental error. None the less, to a good first approximation there seems to be a universal form for the cutoff. The behavior of σ_1/σ_N for $\omega < 5kT_c/\hbar$ cannot be inferred directly from the experimental data, since σ_2/σ_N can no longer be neglected. However, σ_1 is falling rapidly at $5kT_c$, and an extrapolation to zero at $3kT_c$ would appear to be close to the truth (at these low temperatures). With our highly disordered films, it might seem reasonable that there should be some sort of a tailing off, rather than a sharp edge. The present evidence is

[19] J. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955).

[20] V. L. Ginzburg and L. D. Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 1064 (1950); V. L. Ginsburg, J. Exptl. Theoret. Phys. (U.S.S.R.) **29**, 748 (1955) [translation: Soviet Phys. JETP **2**, 589 (1956)].

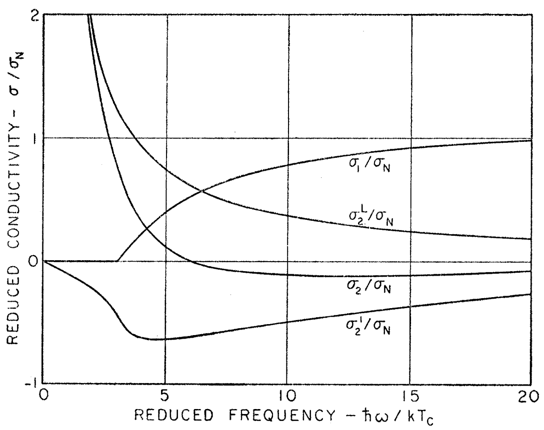

FIG. 7. Approximate universal frequency dependence of the complex conductivity of thin superconducting films at $T=0$. The curves of $\sigma_2{}^L/\sigma_N$ and $\sigma_2{}'/\sigma_N$ are shown separately to allow separate adjustment for $T>0$. The fact that σ_1 is shown going to zero at exactly $3kT_c$ is not directly measurable with our present accuracy. The data do not really exclude any projected end point between 3 and 4 kT_c.

too meager, however, to justify any more complicated assumption than a straight extrapolation to zero.[21]

A real conductivity σ_1/σ_N having the form suggested in Fig. 6 cannot be introduced without an associated imaginary conductivity, which we shall call the polarizability term $\sigma_2{}'$, required by the Kramers-Kronig equations. The exact frequency dependence of $\sigma_2{}'$ depends on the shape of the cutoff for σ_1. In any case, it is negative, it has a maximum value near the frequency at which the cutoff takes place, and it has an area $\frac{1}{2}\pi[\sigma_N-\sigma_1(\omega=0)]\approx\frac{1}{2}\pi\sigma_N$ under the curve (when plotted on a logarithmic frequency scale), independent of the form of the cutoff. The function $\sigma_2{}'(\omega)/\sigma_N$ required by the Kramers-Kronig relations as a result of the experimentally suggested form of σ_1/σ_N has been calculated by numerical integration and is plotted in Fig. 7. This is added to $\sigma_2{}^L/\sigma_N=3.7kT_c/\hbar\omega$, the component found from the low-frequency measurements, to give σ_2/σ_N, the total imaginary conductivity. Two things are to be noted from the figure. First, for frequencies smaller than about $2kT_c/\hbar$, $\sigma_2\approx\sigma_2{}^L$ showing that there is no contradiction caused by the fact that we only found a $1/\omega$ term from the microwave measurements. Second, above $5kT_c$, $\sigma_2{}^L$ and $\sigma_2{}'$ almost cancel, leaving only a small value for σ_2. This shows that the assumption used in obtaining σ_1/σ_N from the transmission ratios, namely that σ_2/σ_N could be neglected for frequencies $>5kT_c/\hbar$, is correct.

As the final test for the self-consistency of the analysis, transmission curves for films having the same resistance as those of Figs. 2 and 4 have been calculated using formula (2) and the conductivities of Fig. 7. The resulting curves are those shown in Figs. 2 and 4 together with the experimental points. (The curves for $T/T_c=0.67$ and 0.58 are based on temperature-dependent functions discussed in Sec. V.) In all cases the fit is satisfactory. Clearly each set of data could be fitted somewhat better by a suitably chosen pair of functions $\sigma_1(\omega)$ and $\sigma_2(\omega)$. However, considering that the functions chosen are averages based on films of many different resistances and of two different metals, the agreement is surprisingly good.

Actually, the crucial point in this test is the accuracy with which the calculated curves fit the peak in transmission. In this region, from about 3 to 5 kT_c, both σ_1 and σ_2 are important. Moreover, the value of σ_2 depends critically on the partial cancellation of $\sigma_2{}^L$ by $\sigma_2{}'$. Therefore, the agreement of the calculated and measured peak heights within the experimental accuracy and reproducibility from film to film completes the circle of argument. It shows that the functions plotted in Fig. 7 are the unique conductivity functions satisfying all the experimental and theoretical (Kramers-Kronig) requirements.

Of course, the accuracy of these functions is limited by the accuracy and extent of the experimental data. Unfortunately it is in precisely the most interesting region (that near $3kT_c$) that the limitations on accuracy are most severe. It is not possible to say whether σ_1 has a sharp cutoff as shown or a slightly rounded one with a tail. Neither can one locate the exact position of the effective cutoff. However, it seems that it must lie between 3 and 4 kT_c if the agreement found with the plotted functions (based on a sharp cutoff at $3kT_c$) is not to be seriously destroyed.

To explain the results of the film transmission experiments, then, the real (lossy) conductivity must to a good approximation depend on frequency as indicated in Fig. 7, being zero or at least very small up to frequencies corresponding for Pb and Sn to about $3kT_c/\hbar$. Here energy absorption by the superconductor begins to become possible, and σ_1 now increases rapidly with frequency until for $\omega\approx 20kT_c/\hbar$, or about seven times the cutoff frequency, energy is absorbed equally well by superconducting and normal material. This is suggestive of an energy gap model in which we suppose that a finite amount of energy E_g is required to produce an individual excitation from a condensed, many-electron ground state. The film experiments indicate a gap width of about $3kT_c$ for both Pb and Sn.[22] For $\hbar\omega<E_g$, the energy of the photons is insufficient to bridge the gap, and therefore no electrons can be excited. For photons having energies large compared to E_g the presence of the gap will no longer be felt and superconducting and normal metal will act alike. For

[21] It should be pointed out that the analytic approximation $\sigma_1/\sigma_N=1-\omega_g{}^2/\omega^2$, with $\hbar\omega_g=3kT_c$, which was suggested in our preliminary report, does not give an adequate fit to our improved data.

[22] While this paper was in preparation, Bardeen, Cooper, and Schrieffer [Phys. Rev. **106**, 162 (1957)], have presented a new theory of superconductivity. It predicts an energy gap $E_g\approx 3.7kT_c$ for tin, if one utilizes experimental values for H_0 and the specific heat parameter γ. The very satisfactory agreement of this value with our experimental results strongly supports their theory.

photon energies just above E_g, the shape of the "absorption edge" $\sigma_1(\omega)$ will depend on details of the density of states near the gap and the matrix elements for transitions across the gap. Therefore it should prove particularly useful in testing any proposed detailed model.

The gap widths found here for Sn and Pb on the basis of a detailed study of the conductivity as a function of frequency are consistent with recent careful specific heat measurements.[1] For V, Sn, Al, and Tl and exponential dependence $\exp(-\beta T_c/T)$ is found for the low-temperature electronic specific heat, with $\beta \approx 1.5$. This exponential form suggests an energy gap E_g in the spectrum of electronic excitations. The width of the gap would be βkT_c or $2\beta kT_c$, depending on whether the excitation produces one or two statistically independent entities. The latter situation $[C \sim \exp(E_g/2kT)]$ obtains, for example, in intrinsic semiconductors, where a hole-electron pair is created by the absorption of a single quantum of energy. If this situation may be presumed to hold for the superconductor, then the specific-heat data yield an energy gap $E_g \approx 3kT_c$ in agreement with our spectroscopic result.

V. TEMPERATURE DEPENDENCE OF CONDUCTIVITY FUNCTIONS

A. Microwave Measurements

The major departures from the low-temperature conductivity functions discussed in the previous section occur near T_c, where for all frequencies σ_2 must drop toward zero and σ_1 must approach σ_N. Under these conditions, it is clear that our assumption that σ_1/σ_N is negligibly small at microwave frequencies can no longer be justified, even if σ_2/σ_N is still much larger than 1. Some temperature dependence must be assumed to interpolate between $\sigma_1/\sigma_N = 0$ at $T=0$ and $\sigma_1/\sigma_N = 1$ at $T = T_c$. We have followed the usual assumption, namely, that $\sigma_1/\sigma_N = (T/T_c)^4 \equiv t^4$ for these low frequencies well below the energy gap, where quantum absorption should be impossible. This is the conductivity associated with the "normal electrons" in the Gorter-Casimir[23] two-fluid model. In an energy gap model it may be considered to be the conductivity of electrons thermally excited out of the condensed state into a roughly normal continuum of states.

By using this assumption the 6-mm microwave data for Sn ($\hbar\omega = 0.6kT_c$) shown in Fig. 3 were analyzed, and the results for $\sigma_2{}^L/\sigma_N$ are plotted against temperature in Fig. 8. These results are satisfactorily fitted by

$$\sigma_2{}^L(\omega,t) = (1-t^4)^{\frac{1}{2}} \sigma_2{}^L(\omega,0). \qquad (5)$$

This dependence is contrary to the $(1-t^4)$ dependence expected on the basis[24] that $\sigma_2{}^L \sim 1/\lambda^2$ and $\lambda \sim (1-t^4)^{-\frac{1}{2}}$. For comparison, a $(1-t^4)$ curve is also shown in Fig. 8,

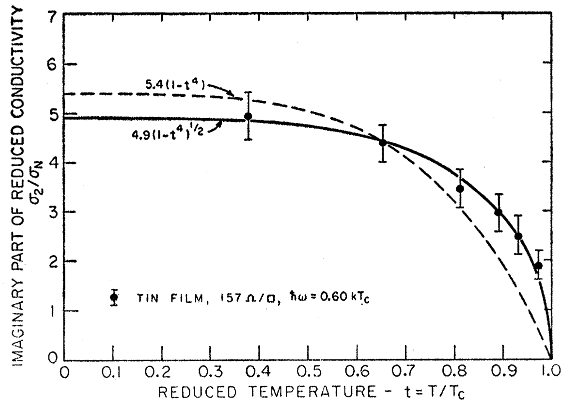

FIG. 8. Temperature dependence of the imaginary part of the conductivity of a superconducting tin film at $\hbar\omega = 0.6kT_c$. The experimental points were obtained from the observed transmission ratios by assuming $\sigma_1/\sigma_N = t^4$ at this frequency. The data are best fitted by a $(1-t^4)^{\frac{1}{2}}$ dependence, shown in the solid curve. For comparison, a $(1-t^4)$ dependence, which had been expected, is shown by the dashed curve.

but it does not give an acceptable fit to the data. The temperature dependence given by the Pippard theory is $(1-t^4)^{\frac{3}{2}}$, apart from a weak logarithmic factor. This dependence is even further from our results than the temperature dependence given by the simple London equations. This discrepancy shows that the details of the theory are still quite obscure.

To test how strongly this conclusion rested on the particular form of the $\sigma_1/\sigma_N = t^4$ assumption, the same data were analyzed by assuming instead that $\sigma_2{}^L(t) = (1-t^4)\sigma_2{}^L(0)$, and solving for σ_1/σ_N. The resulting temperature dependence gave σ_1/σ_N rising from 0 at $t=0$ to ≈ 1.33 at $t=0.9$, then falling back to 1 at $t=1$. Since there seems to be no clear reason to expect anything but a continuous rise of σ_1/σ_N from 0 to 1,[25] it seems more likely that the former analysis is correct. At the very least, it provides a reasonable form for extrapolation of the results to $t=0$. Further experiments at other frequencies should resolve this question as to whether σ_1, σ_2, or both have rather surprising temperature dependences.

B. Infrared Measurements

Since σ_2 decreases to zero as T approaches T_c, the assumption that σ_2 is negligibly small for $\hbar\omega > 5kT_c$ is on even firmer ground than it was in the analysis of the low-temperature data. Unfortunately the only available data on the temperature dependence of transmission with monochromatized infrared radiation is that on the lead film shown in Fig. 2. If this is analyzed using (2), it is found that $[1-\sigma_1(\omega,t_1)/\sigma_N]$

[23] C. J. Gorter and H. B. G. Casimir, Physik. Z. **35**, 963 (1934).
[24] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1952).

[25] *Note added in proof.*—A counter-example is offered by the recent measurements of L. C. Hebel and C. P. Slichter [Phys. Rev. **107**, 901 (1951)], which reveal a maximum nuclear relaxation rate at an intermediate temperature near $0.8T_c$. Thus there is now much less ground for rejecting the expected $(1-t^4)$ dependence for $\sigma_2{}^L$ on the basis of the temperature dependence it would imply for σ_1.

$\cong 0.8[1-\sigma_1(\omega,t_2)/\sigma_N]$, where $t_1=0.3$ and $t_2=0.67$. Since $(1-t_1^4)=0.80$ and $(1-t_2^4)=0.99$, this suggests that we take $[1-\sigma_1(\omega,t)/\sigma_N]\approx(1-t^4)[1-\sigma_1(\omega,0)/\sigma_N]$ or

$$\sigma_1(\omega,t)/\sigma_N\approx t^4+(1-t^4)\sigma_1(\omega,0)/\sigma_N. \qquad (6)$$

This was the function used in calculating the curves for the higher temperatures shown in Fig. 2. It should be noted that (6) has the property of reducing to $\sigma_1/\sigma_N=t^4$ for frequencies below $3kT_c$. Hence it is consistent with the assumption made in V-B. Although (6) behaves correctly in various limits, it is certainly oversimplified near the energy gap, since the width of the gap presumably varies with temperature, decreasing to zero as $t\rightarrow 1$. Further experiments will be required to settle the question. In any case, to the extent that (6) holds, the polarizability term σ_2' derived from the cutoff of σ_1 will vary simply as $(1-t^4)$, keeping the same frequency dependence. Since $\sigma_2^L\sim(1-t^4)^{\frac{1}{2}}$, this makes the shape of the resulting $\sigma_2(\omega)$ curve change as $t\rightarrow 1$. This effect has been included in calculating the transmission curves for $t=0.58$ and 0.67 which are shown in Fig. 2.

VI. RELATION TO EXPERIMENTS OF BULK SAMPLES

Throughout the foregoing discussion, we have stressed the qualitative agreement between the conductivity functions which we find and those required to explain the reflection and absorption measurements on bulk samples (for the frequencies at which they are available). The only major discrepancy between the results of the two types of measurements is that we find no evidence for a shift in the apparent transition temperature at any frequency, whereas the experiments[3,4] on bulk samples indicate that the location of the sharp drop in the surface resistance curve shifts toward lower temperatures as the frequency is raised. A reasonable projection[5] of those results to a frequency of $5kT_c/\hbar$ (the midband frequency for our data of Fig. 3) would lead one to expect the break in the curve to be shifted down at least to a reduced temperature of 0.8. Such a shift is clearly incompatible with the data of Fig. 3. The fact that the curves for $T=0.3$ and 0.67 T_c in Fig. 2 have such a similar shape at all frequencies shows that even for frequencies of $15kT_c/\hbar$ the effect is well under way at $0.67T_c$. This additional evidence seems to preclude any shift which increases systematically with frequency, at least in the frequency region above $\sim 3kT_c/\hbar$.

In view of these results, the interpretation of the apparent shift of T_c with frequency found in the bulk-metal measurements becomes rather difficult. No clear contradiction is present, however, since the experiments measure two quite distinct quantities, between which no obvious relation exists. This decoupling occurs because in the film experiments the electronic mean free path is severely limited by the geometry and imperfection of the sample. This eliminates anomalous skin-effect problems and also appears to introduce a simple connection between conductivities in the superconducting and normal states which is not present in pure bulk metal. Thus, even the complete frequency and temperature dependences of the film conductivity (which are not yet available with any certainty in the critical region) would not be sufficient to allow a straightforward prediction of the result of a measurement of the surface resistance R of a bulk superconductor. For orientation purposes, however, we have made calculations along this line, neglecting the anomalous skin effect and the lack of connection between σ_2^L and σ_N in pure bulk metal. The results suggest that at temperatures just below T_c one might find either a relatively small increase *or* decrease in R for $\omega\gtrsim\omega_g$, depending on the details of the cutoff of σ_1 for $T>0$. Thus it seems quite reasonable that the change in R for these high frequencies should be small for temperatures just below T_c, if an energy gap is opening up from zero width at T_c, but it seems rather unlikely that there should be no change at all. Certainly further experimental investigation is required in this direction.

VII. CONCLUSIONS

From transmission measurements through films of lead and tin, the frequency dependence in the region from 0.3 to 40 $kT_c/\hbar$ of the complex conductivity in thin superconducting films has been determined. These measurements include most of the previously-unexplored frequency regions in which a superconductor changes from an essentially lossless conductor (for $T\ll T_c$) to a normal one. The frequency dependence (shown in Fig. 7) appears to be approximately a universal one, provided the conductivity $(\sigma_1-i\sigma_2)$ is reduced in terms of the conductivity σ_N of the film in the normal state and the frequencies are reduced in terms of $kT_c/\hbar$. This approximately universal dependence appears to be independent of film resistance, thickness, degree of anneal, and material (for the two metals tried).

At $T=0$, the real part σ_1 appears to be zero for photon energies less than roughly $3kT_c$, where it rises rapidly, reaching its limiting value σ_N at about $20kT_c$. Such behavior suggests a gap of width $\approx 3kT_c$ in the electronic-excitation spectrum of the superconducting state.

At $T=0$ and $\hbar\omega<kT_c$, σ_2 is well approximated by a term with the London-type frequency dependence $(1/\omega)$, namely $\sigma_2^L/\sigma_N=\alpha kT_c/\hbar\omega$ with $\alpha\approx 3.7$. The magnitude of this term is greatly reduced from the value expected on the basis of the London equations and the penetration depth in bulk material. The London equations also fail to predict the existence of such a universal relation. A reduction to just this universal function (but with $\alpha\approx 6.7$) would be expected on the basis of Pippard's nonlocal modification of the London equations.

Above $\hbar\omega\approx kT_c$, a polarizability term $\sigma_2'(\omega)$, which is a necessary consequence, through the Kramers-Kronig relations, of the cutoff of $\sigma_1(\omega)$ near $3kT_c$, becomes important and tends to cancel $\sigma_2{}^L$. As a result, σ_2 is reduced to a small value for frequencies above 4–5 $kT_c/\hbar$.

At temperatures $0<T<T_c$ there is some evidence that $\sigma_1(\omega,t)/\sigma_N=t^4+(1-t^4)\sigma_1(\omega,0)/\sigma_N$. For frequencies $<kT_c$ this reduces to $\sigma_1/\sigma_N=t^4$. If the data are analyzed under this assumption, the temperature dependence of $\sigma_2{}^L$ seems to be $\sigma_2{}^L(\omega,t)=(1-t^4)^{\frac{1}{2}}\sigma_2{}^L(\omega,0)$, as opposed to the $(1-t^4)$ dependence expected from penetration depth measurements as interpreted with the London equations. The temperature dependence predicted by the Pippard theory is in even worse agreement with the experiments.

VIII. ACKNOWLEDGMENT

The authors are pleased to acknowledge the assistance of Han-Ying Ku, of this laboratory, who kindly furnished the crystal harmonic generators and wave-guide filters used in the microwave experiments.

APPENDIX A. ANALYTIC METHODS FOR REDUCING TRANSMISSION MEASUREMENTS TO CONDUCTIVITIES

If we idealize the actual situation to that of a film of thickness d ($\ll$ wavelength or skin depth) laid on a substrate of thickness l and index of refraction n, we may calculate exactly the transmission of a normally incident plane wave. The result is

$$T=\frac{8n^2}{A+B\cos 2kl+C\sin 2kl}, \tag{A-1}$$

where

$$A=n^4+6n^2+1+2(3n^2+1)g+(n^2+1)(b^2+g^2),$$
$$B=2(n^2-1)g-(n^2-1)^2+(n^2-1)(b^2+g^2),$$
$$C=2(n^2-1)nb,$$
$$k=n\omega/c,$$

and $y\equiv g-ib\equiv YZ_0\equiv(G-iB)Z_0\equiv(\sigma_1-i\sigma_2)dZ_0$ is the dimensionless complex admittance per square of the film in units of the admittance $Z_0{}^{-1}$ of free space. ($Z_0=4\pi/c$, cgs; 377 ohms, mks.)

Infrared Case

In the infrared experiments we use a band of frequencies so wide that the periodic functions of $2kl$ go through at least a complete cycle within the pass band. This allows us to average over $2kl$, with the result

$$\bar{T}=\frac{8n^2}{(A^2-B^2-C^2)^{\frac{1}{2}}}\simeq\frac{8n^2}{A}\left(1+\frac{B^2+C^2}{2A^2}\right). \tag{A-2}$$

Since B and C are always less than A, and usually much less, the corrections from the multiple internal reflections are second order and very small (typically of order one percent). Moreover, since we are only interested in the ratio of transmission in two rather similar cases, these errors tend to cancel. In this way we see that we are justified in analyzing the infrared data using the simple formula quoted previously[11] for the ratio of the transmission with film to that with no film. In our present notation, it has the form

$$\bar{T}=|1+y/(n+1)|^{-2}, \tag{A-3}$$

and it is equivalent to formula (1) in the body of the article. This formula is derived by neglecting reflection within the substrate from the start, since it is clear from elementary considerations that the multiple internal reflections will not exert an important influence so long as the average over phases is justified and the reflection coefficients are reasonably small. In the normal state $y_N=g_N=Z_0/R_N$, where R_N is the dc resistance per square of the film in the normal state. Therefore $\bar{T}_N$ is independent of frequency.

By expressing y in (A-3) in terms of σ and taking the ratio of the expressions for transmission in the normal and superconducting states, one can solve for σ_1/σ_N. The result is

$$\sigma_1/\sigma_N=[1+(n+1)(R_N/Z_0)]\{(T_N/T_S)-(\sigma_2/\sigma_N)^2 \times[1+(n+1)(R_N/Z_0)]^{-2}\}^{\frac{1}{2}}-(n+1)(R_N/Z_0). \tag{A-4}$$

Note that σ_2/σ_N enters only quadratically compared to a number of order unity. Therefore, so long as σ_2/σ_N is small, as it turns out to be for $\hbar\omega\geq 5kT_c$, we can take it to be equal to zero in (A-4) without making any serious error. Inspection of (A-4) shows that the value σ_1/σ_N obtained in this way is a rigorous upper bound in any case.

Microwave Case

In the microwave region we use monochromatic radiation and the thickness of the substrate is comparable with the wavelength. This obliges us to use the complete formula (A-1) in the interpretation of the data, since the multiple internal reflections now give first-order effects. Further, the high reflectivity of the superconducting film for these microwave frequencies enhances the magnitude of these reflections. The necessity for properly including these effects is made clear by the fact that for our value of l they keep T_S/T_N roughly the same for 6-mm, 4-mm, and 3-mm radiation despite a change by a factor of 2 in the film admittance over this frequency interval.

For the purpose of analyzing the data, it is convenient to form the ratio of two expressions of the type (A-1):

$$\frac{T_S}{T_N}=\frac{g_N{}^2+\alpha g_N+\gamma}{b^2+g^2+\alpha g+\beta b+\gamma}, \tag{A-5}$$

where

$$\alpha = D^{-1}[6n^2+2+2(n^2-1)\cos 2kl],$$
$$\beta = D^{-1}[-2n(n^2-1)\sin 2kl],$$
$$\gamma = D^{-1}[n^4+6n^2+1-(n^2-1)^2\cos 2kl],$$
$$D = n^2+1+(n^2-1)\cos 2kl,$$

and where g_N and $(g-ib)$ are the dimensionless admittances of the film in the normal and superconducting states, respectively. The parameters α, β, γ may be calculated once and for all for a given n and kl, that is, for a given substrate and operating wavelength. The admittance $g_N = Z_0/R_N$ is known from the dc film resistance. Thus the observed ratio T_S/T_N is reduced to its dependence on the superconducting admittance $(g-ib)$, which is to be determined. The superconducting conductivity is then related to the normal conductivity by $(\sigma_1 - i\sigma_2)/\sigma_N = (g-ib)/g_N$.

Obviously one cannot determine both the real and imaginary parts of the conductivity at a given frequency from a single measurement of T_S/T_N at that frequency. Except near $T=T_c$, however, σ_2 is dominant in the microwave frequency region for which (A-5) is useful. Therefore it is most useful to solve (A-5) for σ_2/σ_N with σ_1/σ_N, or g, entering the formula as a correction. The desired result is

$$\sigma_2/\sigma_N = b/g_N = g_N^{-1}\{-\beta/2+[(\beta/2)^2 + (T_N/T_S)(\gamma+\alpha g_N+g_N^2)-\gamma-\alpha g-g^2]^{\frac{1}{2}}\}. \quad \text{(A-6)}$$

Since α is a positive quantity, we may always obtain an upper bound on σ_2/σ_N directly from a measured value of T_S/T_N simply by setting $g=0$ in (A-6). In the analysis referred to in Sec. V, we assumed $g/g_N = \sigma_1/\sigma_N = (T/T_c)^4$. This allows σ_2/σ_N to be determined. Knowing both σ_1/σ_N and σ_2/σ_N, we can then calculate the value that T_S/T_N would have in the absence of internal reflections by using (2).

APPENDIX B. KRAMERS-KRONIG CAUSALITY RELATION

The Kramers-Kronig integral transforms[16] relate the real and imaginary parts of any linear response function with no poles in the lower half of the complex frequency plane. This condition is equivalent to the causality requirement that no effect precede its cause. Expressed in terms of conductivities, these relations are

$$\sigma_1(\omega) = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\omega_1 \sigma_2(\omega_1) d\omega_1}{\omega_1^2-\omega^2} + C,$$
$$\sigma_2(\omega) = -\frac{\omega}{\pi}\int_{-\infty}^{\infty} \frac{\sigma_1(\omega_1) d\omega_1}{\omega_1^2-\omega^2}. \quad \text{(B-1)}$$

In obtaining these, one takes advantage of the fact that $\sigma(\omega) = \sigma^*(-\omega)$. That is, $\sigma_1(\omega)$ must be an even function, whereas $\sigma_2(\omega)$ is odd. Also, we have used the assumption that $\sigma(\omega)$ vanishes in the limit of infinite frequency, as is reasonable physically.

In the case of a superconductor, we have the lossless London-type conduction mechanism $\sigma_2{}^L = a/\omega$ in addition to terms satisfying the above restrictions. This provides a pole at the origin which must be treated separately. This separation is possible because linearity allows superposition. We gain physical insight into the situation by handling this extra term by a direct application of the causality principle. Imagine an impulsive electric field $\mathcal{E}(t) = \delta(t-0)$ is applied to a superconductor. If the current $j(t)$ which results from this pulse is calculated using $\sigma_2{}^L$ alone, the result is odd. That is, $j(-t) = -j(t)$. Therefore a current of prescribed strength would be required to have existed before the pulse of emf producing it. It would merely change sign when the pulse occurred. To obtain the physically sensible result, namely a current which starts at $t=0$ when the pulse is applied, it is easily verified that we must introduce an additional real conductivity having the form $\sigma_1(\omega) = \pi a \delta(\omega - 0)$. Therefore the London-type conductivity has no σ_1 associated with it except at zero frequency. Since σ_1 is infinite there, it could cause no energy dissipation even if σ_2 were finite.

We also note that $\sigma_1 = \sigma_N =$ constant in the region of interest would give rise to no σ_2 term through (B-1). Thus the magnitude of σ_N and $\sigma_2{}^L$ are allowed to be completely independent, and this is found to be the case in bulk samples. The fact that we find an apparent proportionality between the two in the film samples is therefore an unexpected result.

In view of the last two paragraphs, the role played by the integral relations (B-1) in our work is only to relate the cutoff of σ_1 at low frequencies, associated with the energy gap, to a polarizability term, which we denote σ_2'. (Section IV.) This term represents the high polarizability or dielectric constant $(\epsilon = -4\pi\sigma_2/\omega)$ at low frequencies which is a necessary consequence of the low-lying excited states above the gap. Classically, this high polarizability corresponds to the small restoring force $(\sim\omega_0^2)$ in an oscillator of low natural frequency. The characteristic frequency in a superconductor is of the order of 10 cm^{-1}, whereas in ordinary materials it is of the order of 1 ev or 10^4 cm^{-1}. Therefore, the dielectric constant corresponding to σ_2' (for $\hbar\omega < E_g$) is $\sim 10^6$ times as great as those (~ 1) found in ordinary materials. The existence of a large dielectric constant of this sort was predicted many years ago by Landau. As is seen in Fig. 7, even this huge value is swamped by the "inductive" polarizability, denoted by $\sigma_2{}^L$, until a frequency of order $kT_c/\hbar$ has been reached.