

## Fluctuation Effects in the ac Conductivity of Thin Superconducting Lead Films at Microwave Frequencies\*

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The microwave transmission and reflection coefficients have been measured for thin ( $<150 \text{ \AA}$ ) lead films and for a lead film with thin manganese overlays (total thickness of overlay  $<5 \text{ \AA}$ ) in the temperature range 5.0–7.3 K at frequencies of 23.89, 37.2, and 69.5 GHz. Well below  $T_c$  [ $(T_c - T) \leq 0.2$  to  $0.3 \text{ K}$ ], the temperature and frequency dependence of these ratios are in good agreement with theoretical values calculated using the complex conductivities derived by Mattis and Bardeen. Best fits with the experimental results were obtained using complex conductivities corresponding to a superconducting energy gap of  $(4.5 \pm 0.2) \times k_B T_c$ . Above  $T_c$  both the microwave and dc data implied an excess conductivity for each film studied. This excess conductivity has been attributed to thermodynamic fluctuations in the Ginzburg-Landau order parameter for temperatures near the normal-to-superconducting phase transition. In agreement with the predictions of Aslamazov and Larkin for the two-dimensional limit, the dc measurements indicate a value of  $0.152 \times 10^{-4} \Omega^{-1}$  for  $\tau_0/R_n$ . Both the temperature and frequency dependence of the implied excess ac conductivity above  $T_c$  are accounted for by fluctuation-effect calculations of Schmidt. In the temperature region just below  $T_c$  [ $(T_c - T) \sim 0.1 \text{ K}$ ], the experimental results indicate an excess ac conductivity compared to the predictions of the Mattis and Bardeen (MB) theory. Recently, Schmidt has extended his theory of fluctuation effects in the ac conductivity to temperatures below  $T_c$ ; combining these fluctuation-induced conductivities with those of MB (due to quasiparticles) permits the calculation of transmission coefficients in good agreement with experiment. We believe this to be direct evidence for fluctuation effects in a two-dimensional superconductor in the presence of quasi-long-range order. The deposition of a manganese overlay of approximately  $2 \text{ \AA}$  upon a  $150\text{-\AA}$  lead film resulted in a 46% reduction in the microwave-measured energy gap. Essentially no change was observed in the dc transition temperature.

### INTRODUCTION

The electromagnetic response of a metal in the superconducting state is governed by a complex conductivity  $\tilde{\sigma}(\omega, T) = \tilde{\sigma}_1(\omega, T) + i\tilde{\sigma}_2(\omega, T)$ .<sup>1</sup> Both  $\tilde{\sigma}_1$  and  $\tilde{\sigma}_2$  are strongly dependent on the absolute temperature  $T$  and the frequency of the electromagnetic radiation  $\omega$ . Neglecting the effects due to thermodynamic fluctuations in the phase of the normal-to-superconducting transition, as  $T \rightarrow T_c$ , we find  $\tilde{\sigma}_1 \rightarrow \sigma_N$ , where  $\sigma_N$  is the conductivity in the normal state. According to the microscopic theory of superconductivity,<sup>2</sup> the temperature and frequency dependence of  $\tilde{\sigma}_1$  and  $\tilde{\sigma}_2$  are inherently related to changes in the electron density of states at the Fermi surface which accompany the phase transition. Mattis and Bardeen<sup>3</sup> (MB) derived a general theory of the anomalous skin effect in normal and superconducting metals based on the original Bardeen, Cooper, and Schrieffer<sup>2</sup> (BCS) weak-coupling theory of superconductivity. In the extreme anomalous limit, their solutions for  $\tilde{\sigma}_1/\sigma_N$  and  $\tilde{\sigma}_2/\sigma_N$  for a given  $T_c$ ,  $\omega$ , and  $T$  are uniquely determined by  $\Delta(T)/\Delta(0)$  and  $2\Delta(0)/k_B T_c$ , where  $\Delta(T)$  is the half-excitation energy gap and  $k_B$  is Boltzmann's constant. In principle, then, a direct comparison of the observed electromagnetic response in various

specimens with that implied by the weak-coupling microscopic theory should be straightforward.

Two possible sources of discrepancies are strong-coupling effects and thermodynamic fluctuations near  $T_c$ . Lead films provide a suitable system for investigating both of these effects. Since most of the experimental work reported for lead has been at dc or at frequencies in the neighborhood of the gap frequency  $\hbar\omega = 2\Delta(0)$ , and considering the current experimental and theoretical interest in strong-coupling effects, fluctuation effects, and thin films, a report of experiments at microwave frequencies on thin lead films is desirable.

Although the majority of previous experimental results (Refs. 4–10) for  $\tilde{\sigma}_1$  and  $\tilde{\sigma}_2$  are in good qualitative accord with those implied by the MB formulation, measurements at infrared frequencies [ $\hbar\omega \geq 2\Delta(0)$ ] have indicated anomalous deviations in the absorption edge from those expected.<sup>4–6,8</sup> Palmer and Tinkham,<sup>7</sup> on the basis of their infrared experiments and the theoretical work of Nam,<sup>11</sup> concluded that the discrepancies in lead are probably due to the strong-coupling character of the electron-phonon interaction in the metal. The results of more recent theoretical work<sup>12</sup> support this conclusion. However, at lower frequencies [ $\hbar\omega \ll 2\Delta(0)$ ], if the proper strong-cou-

pling value for the gap is taken into account, any further modifications in  $\bar{\sigma}_1(\omega, T)$  and  $\bar{\sigma}_2(\omega, T)$ , arising from strong-coupling effects, should be vanishingly small.<sup>11</sup> A comparison of our experimental results with those obtained from the MB theory for various values of  $2\Delta(0)/k_B T_c$  will be used to ascertain the validity of this proposition.

For superconductors in which the effective electron mean free path is small compared with the Ginzburg-Landau (GL) coherence length, thermodynamic fluctuations in the order parameter can have a considerable influence on certain superconducting properties near and above  $T_c$ .<sup>13</sup> Previous experimental studies<sup>14-17</sup> on a variety of small mean-free-path systems, mostly films, have demonstrated an excess in the dc conductivity above  $T_c$  which has been attributed to fluctuation effects. Theoretical work<sup>18-24</sup> in this area is basically in agreement with experiment. The nature of the ac conductivity in the presence of fluctuations in the GL order parameter has been theoretically investigated by Schmidt<sup>25,26</sup> for temperatures both above and below  $T_c$ . D'Aiello and Freedman<sup>27</sup> have reported microwave transmission data at 20 GHz on granular Al films which are not in agreement with Schmidt's calculations. As we have noted in preliminary communications,<sup>28,29</sup> our microwave results on thin lead films indicate excess ac conductivity both above and below  $T_c$ , which is in good agreement with Schmidt's theoretical work.

Tunneling measurements by a number of investigators<sup>30-32</sup> indicate that paramagnetic overlays deposited on superconducting films can cause a large reduction in the effective superconducting energy gap and even a gapless region below  $T_c$ . However, according to Nam,<sup>11</sup> the conductivity and surface impedance in the region of a gap should be similar to that proposed by MB in spite of the modifications in the electron density of states in the presence of such overlays. The appropriate experimental results will be compared with this prediction.

In this investigation the microwave transmission and reflection coefficients of thin ( $< 150 \text{ \AA}$ ) lead films were measured in both the normal and superconducting state as a function of temperature and at three frequencies 23.89, 37.2, and 69.5 GHz. Following the measurement of the coefficients for one of the films, several thin ( $\sim 1$  to  $2 \text{ \AA}$ ) manganese overlays were deposited and the measurements were repeated. In each case the results provide direct evidence as to the temperature and frequency dependence of the complex conductivity  $\bar{\sigma}_1 + i\bar{\sigma}_2$ . These experiments should provide useful information in three areas of recent and current interest in superconductivity: (i) the influence of the strong-coupling interaction on  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$  at frequencies much less than the gap frequency, (ii) effects of fluctuations in the GL order parameter on the

ac conductivity both above and below  $T_c$ , and (iii) modifications in  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$  in the presence of very thin paramagnetic overlays.

#### EXPERIMENTAL

The microwave cryostat, which constituted a major portion of the experimental apparatus, consisted of a large vacuum chamber incorporating entrance and exit waveguides, an evaporation assembly, a primary helium reservoir supporting the various helium shields, and a number of nitrogen reservoirs (see Fig. 1). The main features of this cryostat and the functions of the components have been described previously.<sup>10</sup>

The lead films were prepared in the vacuum chamber by slow vapor deposition ( $1 \text{ \AA}/\text{min}$ ) of high-purity lead (99.999%) on quartz substrates cooled to 77 K. The substrates were optically polished Z-cut quartz plates ( $3.15 \times 5.08 \times 0.0381 \text{ cm}$  and  $3.15 \times 5.08 \times 0.0635 \text{ cm}$ ) with the optical axis perpendicular to the large surface. The lead was evaporated from a point-source molybdenum oven. The flux of the evaporating atoms was highly collimated to assure uniformity along the large dimension of the film. Following the deposition of a given film, it was thermally annealed by allowing the sample block to warm to room temperature.

Most of the microwave measurements were made at temperatures above 4.2 K, where the refrigeration was provided by the helium shield reservoir. A limited heat exchange between this reservoir and the primary reservoir was maintained by three No. 20 gauge copper wires. The number and size of these wires were chosen to provide an equilibrium temperature as close to helium temperature as possible and also to assure a low cooling rate. To stabilize the temperature above the equilibrium temperature, the conduction cooling of the copper wires was balanced by heat input from gaseous helium which was pumped through the primary reservoir from a large gas container. In this manner the temperature could be controlled to  $\pm 0.002 \text{ K}$  by adjusting a needle valve in the pumping line.

The temperature of the sample block was monitored by two carbon resistors. The resistors were calibrated at the superconducting critical temperature of a thick lead ( $\sim 4000 \text{ \AA}$ ) and a thick tin ( $\sim 3500 \text{ \AA}$ ) film. The critical temperatures of the films were assumed to be equal to the bulk values. A third calibration point was provided by the boiling point of helium at atmospheric pressure. All other temperatures were calculated relative to these three by the empirical relation of Clement and Quinell.<sup>33</sup>

The transmission and reflection coefficients were measured by using standard microwave techniques. The microwaves were generated by 12-, 8-, and 4-mm reflex klystrons. The frequencies were

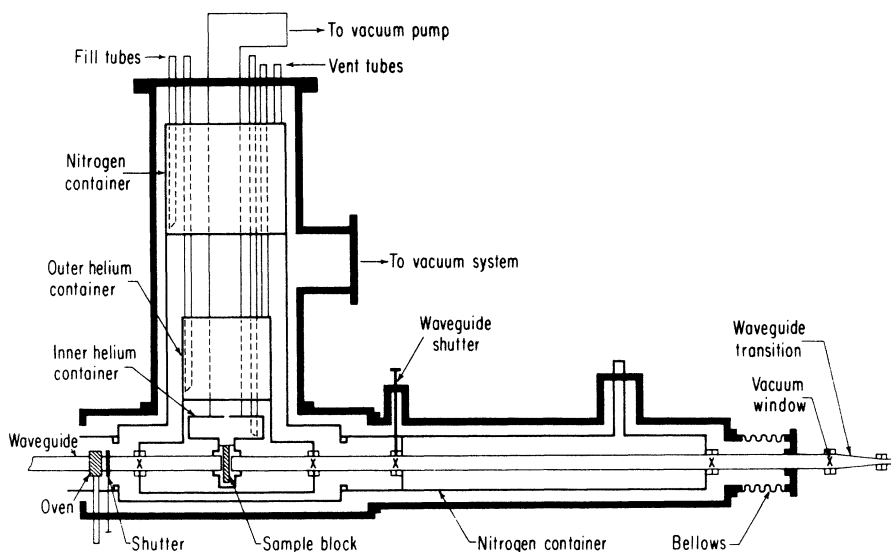


FIG. 1. Schematic drawing of the microwave cryostat. The inner and outer helium containers are referred to as the primary helium reservoir and the helium shield reservoir, respectively, in the text. A left extension arm, identical to the one illustrated, is not shown in the drawing.

measured by means of calibrated cavity wave meters. Before each experiment, the power responses of the detecting diodes were calibrated against standard precision attenuators for the complete range of power levels to be encountered. Because of the possibility of induced currents in the films exceeding critical values near  $T_c$  at high power levels, in the beginning of each experimental run the microwave power was steadily lowered until the experimental data showed no dependence upon power level. The power then was further reduced by a factor of 100 to obtain the experimental transmission and reflection coefficients for a given film.

#### SAMPLE PARAMETERS

Several sample parameters which are useful in characterizing and discussing the behavior of the various films are listed in Table I. Columns 2 and 3 list the resistances of the films at room temperature in  $\Omega/\square$ , where  $\square$  means film surface area. The values in column 2 were obtained from usual dc measurements. The values in column 3 were calculated from the transmission coefficients at 300 K. In column 4 the film resistances at 7.3 K are listed. A number of parameters which were

derived from the absolute resistance values are shown in columns 5–7. Following Chanin *et al.*<sup>34</sup> and noting that the resistivity of a given film at 7.3 K is almost entirely due to boundary and imperfection scattering, the residual resistance ratio for a dirty film can be defined as

$$\rho = \frac{R_{7.3}}{R_{300} - R_{7.3}} \approx \frac{\sigma_{300}^{\text{ideal}}}{\sigma_{7.3}} \quad (1)$$

The value of  $\sigma^{\text{ideal}}$  for lead at 273 K is  $5.06 \times 10^4 \Omega^{-1} \text{cm}^{-1}$ ,<sup>35</sup> and the average  $d(1/\sigma)/dT$  for this temperature range (273–300 K) is  $7.41 \times 10^{-8} \Omega \text{cm}/\text{K}$ <sup>36</sup>; thus, the value of  $\sigma^{\text{ideal}}$  at 300 K is approximately  $(4/59) \times 10^4 \Omega^{-1} \text{cm}^{-1}$ . Using the above value for  $\sigma_{300}^{\text{ideal}}$  and the resistance values in columns 2 and 4, the values of  $\rho$  and  $\sigma_{7.3}$  were calculated and are listed in columns 5 and 6, respectively. The film thicknesses in column 7 were estimated from  $\sigma_{7.3}$  and  $R_{7.3}$ .

The ratio of the absolute conductivity to the electron mean free path  $l_{\text{eff}}$  is independent of temperature. From the measurement of the ac surface conductivity in the limit of the anomalous skin effect, Chambers<sup>37</sup> gives a value for  $\sigma/l_{\text{eff}}$  of  $9.4 \times 10^{10} \Omega^{-1} \text{cm}^{-2}$  for lead. The values of  $l_{\text{eff}}$  were computed from Chambers's ratio and  $\sigma_{7.3}$  of column

TABLE I. Film parameters: dc resistance at 300 K,  $R_{300}$ ; resistance obtained from transmission coefficient at 300 K,  $R_{300}^{\text{MW}}$ ; residual resistance before superconducting transition,  $R_{\text{res}}$ ; residual resistance ratio,  $\rho$ ; conductivity at 7.3 K,  $\sigma_{7.3}$ ; thickness,  $d$ ; electron mean free path at 7.3 K,  $l_{\text{eff}}$ ; coherence length,  $\xi$ ; transition temperature,  $T_c$ .

Film	$R_{300}$ ( $\Omega/\square$ )	$R_{300}^{\text{MW}}$ ( $\Omega/\square$ )	$R_{\text{res}}$ ( $\Omega/\square$ )	$\rho$	$\sigma_{7.3}$ ( $10^{-4} \Omega^{-1} \text{cm}^{-1}$ )	$d$ ( $\text{\AA}$ )	$l_{\text{eff}}$ ( $\text{\AA}$ )	$\xi$ ( $\text{\AA}$ )	$T_c$ (K)
1	60.5	63.5	45.0	2.9	1.58	141.0	16.7	21.5	7.055
3	141.5	151.0	80.0	1.3	3.53	35.5	37.5	46.5	6.680
5	43.9	35.0	25.0	1.32	3.47	115.0	31.0	39.0	7.000

6 (see column 8). According to Anderson's theory of dirty superconductors,<sup>38</sup> any anisotropy in the energy gap should be washed out for  $l_{\text{eff}} \leq \xi_0$ , where  $\xi_0$  is the coherence length for the pure material. Leslie and Ginsberg<sup>6</sup> estimated  $\xi_0$  for lead to be about 780 Å. Apparently, all of the films were well within the criteria for dirty superconductors.

Pippard<sup>39</sup> has suggested that the coherence length ( $\xi$ ) can be calculated from the equation

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{\alpha l_{\text{eff}}}, \quad (2)$$

where  $\alpha$  is an empirical constant. Goodman<sup>40</sup> derived a value for  $\alpha$  from theoretical considerations, which is adequate for the calculation of  $\xi$  to better than 5%. For the theoretical value for  $\alpha$  ( $\alpha = 1.32$ ) and the  $\xi_0$  estimate of Leslie and Ginsberg,<sup>6</sup> the values of  $\xi$  for the films are tabulated in column 9.

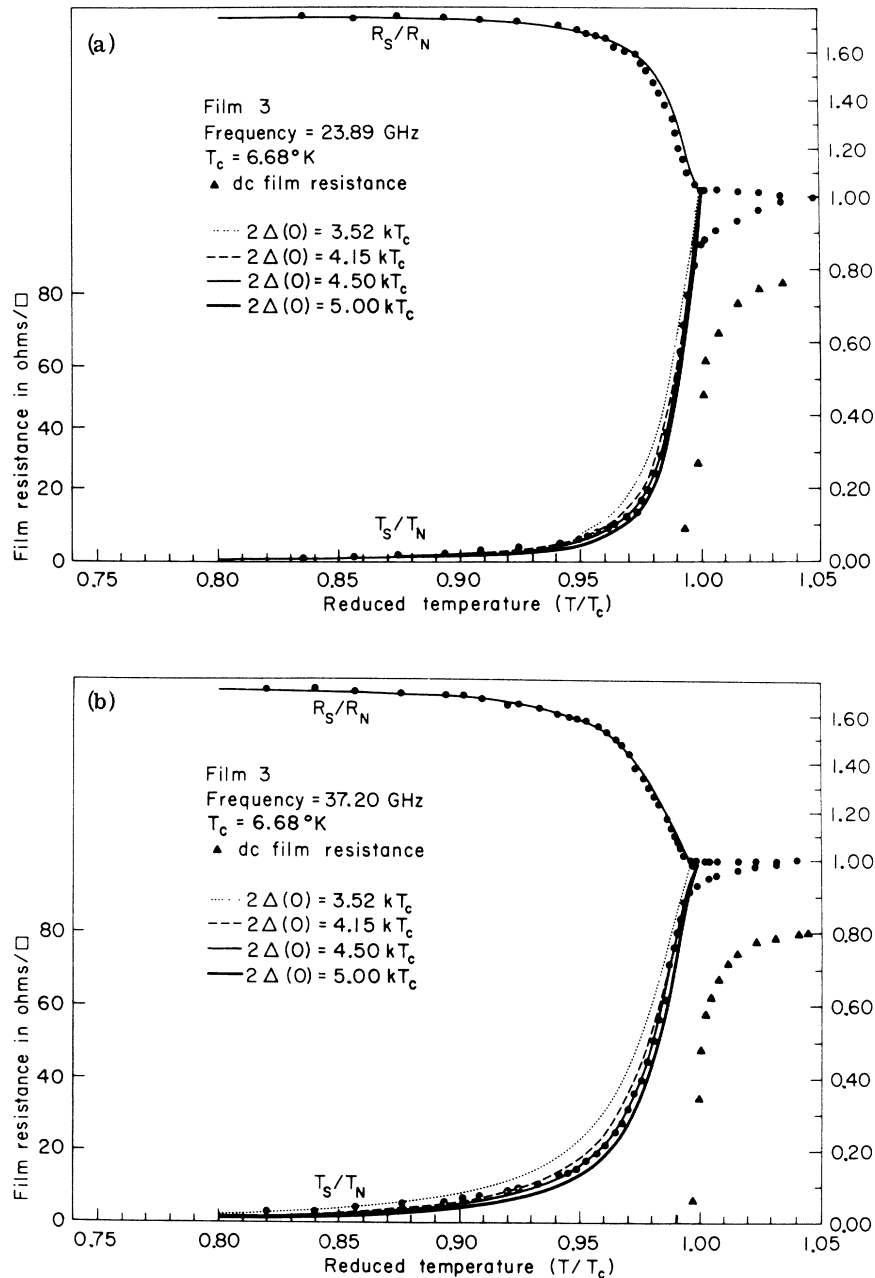


FIG. 2. Temperature dependence of the transmission and reflection coefficient ratios for film 3 at three frequencies, 23.89, 37.20, and 69.50 GHz. The dotted, dashed, and two solid lines represent  $T_S/T_N$  and  $R_S/R_N$  calculated from the conductivities of MB using the parameters given in the legend.

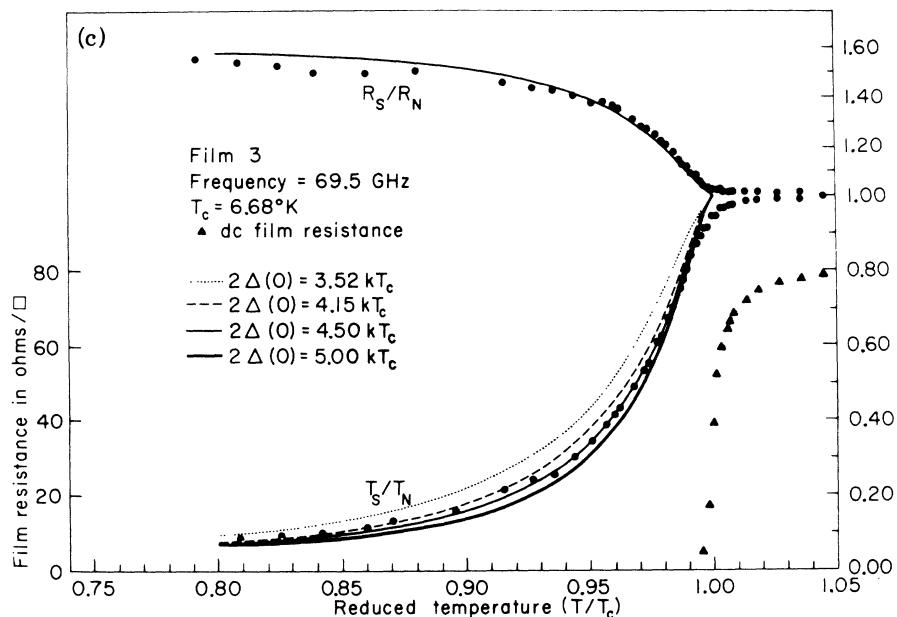


FIG. 2 (Continued).

The observed transition temperatures accurate to  $\pm 0.02$  K are listed in the last column of Table I. The transition temperature of each of the films was several tenths of a degree lower than for bulk lead. It appears from a comparison of the transition temperatures of films 1, 3, and 5 and their respective thicknesses that the reduction in  $T_c$  is a rapidly decreasing function of film thickness. At least for films 1 and 5, the values of  $T_c$ , as related to thickness, are in good agreement with the results of Vogel.<sup>41</sup> Unfortunately, his lowest film thickness was 91 Å, so a meaningful comparison for film

3 is not possible. Strongin *et al.*<sup>42</sup> have conducted an extensive investigation of the  $T_c$  of ultrathin metallic films condensed onto a variety of substrate materials. The  $T_c$ 's of our three Pb films are in reasonable agreement with their results.

#### RESULTS AND DISCUSSION

Figures 2-4 show the temperature dependence of the experimental ratios of the microwave transmission and reflection coefficients in the superconducting state to those in the normal state,  $T_S/T_N$  and  $R_S/R_N$ , for thin lead films which ranged

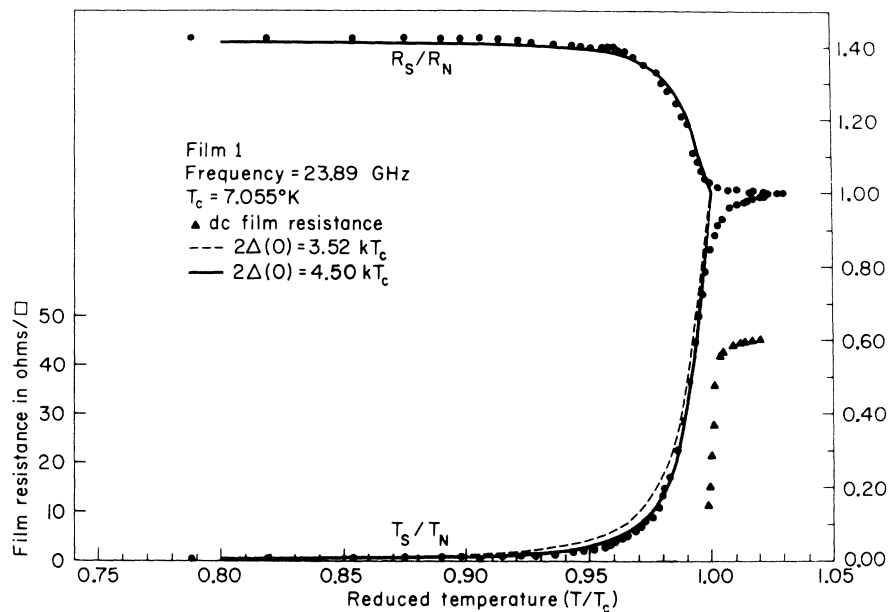


FIG. 3. Temperature dependence of the transmission and reflection coefficient ratios for film 1 at 23.89 GHz. The dashed and solid lines represent  $T_S/T_N$  and  $R_S/R_N$  calculated from the conductivities of MB using the parameters given in the legend.

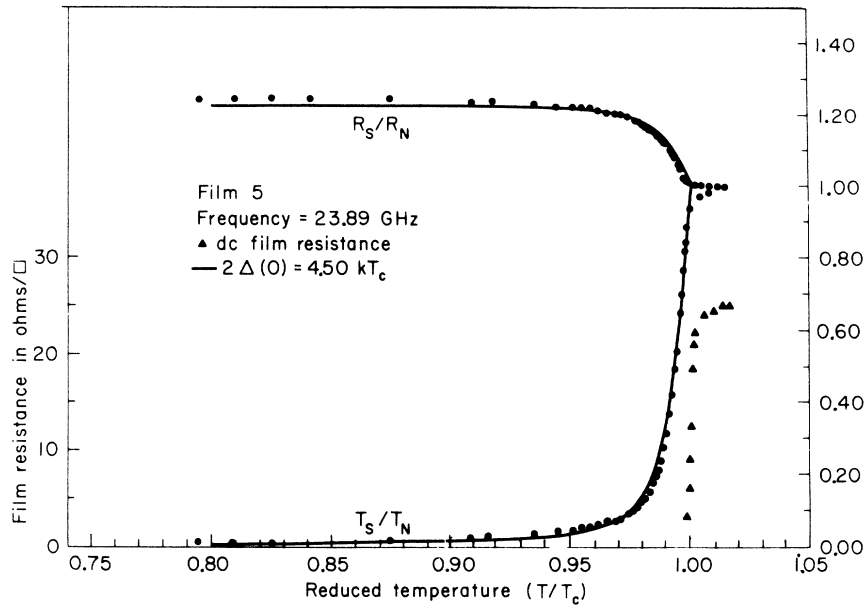


FIG. 4. Temperature dependence of the transmission and reflection coefficient ratios for film 5 at 23.89 GHz. The solid line represents  $T_S/T_N$  and  $R_S/R_N$  calculated from the conductivities of MB using the parameters given in the legend.

in thickness from about 35 to 140 Å. The reproducibility of the transmission-coefficient ratios was considerably better than is indicated by the size of the experimental points. The uncertainties in the experimental values of  $R_S/R_N$  were considerably larger than the dots indicate because of the unavoidable presence of spurious reflections in the waveguides. The following procedure was used to correct for the effects of these reflections. For temperatures and frequencies where  $T/T_c \ll 1$  and  $\hbar\omega \ll 2\Delta(T)$ , the values of  $R_S/R_N$  should be practically independent of  $\bar{\sigma}_1$  and  $\bar{\sigma}_2$  and, hence, constant of temperature. (See Figs. 2–4 and also discussion in the Appendix.) This “residual” value of  $R_S/R_N$  for a given film should depend only on the residual film resistance just above  $T_c$  and on the frequency of the microwave radiation. Thus, the correction involved the normalization of the computed and experimental values of  $R_S/R_N$  for the lowest temperatures where measurements were made. The normalization factor so obtained was then used for all the other temperatures. It is estimated that after normalization, the experimental temperature dependence of  $R_S/R_N$  is only accurate to about 5%. In the case of the transmission measurements, the influence of the spurious reflections was found to be of no significance; therefore, the majority of the quantitative conclusions presented in this paper are based on these data.

The equations which relate  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$  to the microwave coefficients are given in the Appendix. In comparing the theoretical coefficients to the respective experimental values, the only adjustable parameter used was the ratio of  $k_B T_c$  to  $2\Delta(0)$  in the conductivities of MB.<sup>3</sup> The determina-

tion of  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$ , appropriate for a given  $2\Delta(0)/k_B T_c$ , was facilitated by a table of conductivities kindly supplied by Waldram.<sup>43</sup> The residual value of the dc film resistance listed in column 4 of Table I was used for each film. It was found that for films 1 and 3 this resistance differed by less than 7% from  $R^{MW}$  (where MW means microwave), the resistance calculated from the normal-state transmission coefficient. For film 5 the difference was about 20%.

#### Nature of $T_S/T_N$ and $R_S/R_N$ Well below $T_c$ —MB Regime

A comparison of the experimental and theoretical results for three continuous films is shown in Figs. 2–4. The dotted curves were calculated from conductivities which correspond to an energy gap  $2\Delta(0) = 3.52k_B T_c$ , predicted by the microscopic theory in the weak-coupling limit.<sup>2</sup> For the entire temperature region, the theoretical ratios for this gap change much less rapidly than the observed temperature dependence for each film and frequency. Above and just below  $T_c$  ( $T > 0.975T_c$ ) the main source of the discrepancies is related to fluctuation effects, which are to be discussed in the next section. It is apparent, however, that even below these temperatures the weak-coupling theory is not adequate to describe the temperature and frequency dependences of the complex conductivities in the films.

Early measurements of the transmission properties of thin lead films at infrared frequencies by Ginsberg and Tinkham<sup>4</sup> showed that in lead the  $2\Delta(0)/k_B T_c$  ratio was considerably higher ( $\sim 4.0$ ) than predicted. More recent measurements using infrared,<sup>5–8</sup> tunneling,<sup>44–48</sup> and ultrasonic attenua-

tion<sup>49</sup> techniques indicate gaps ranging in magnitude from  $3.4k_B T_c$  to  $5.0k_B T_c$ . Wada<sup>50</sup> proposed that the physical origin of this anomalously large gap in strong-coupling superconductors, such as lead, is the result of considerable damping of the quasi-particle excitations. This damping decreases both  $\Delta(0)$  and  $T_c$ ; however, since the damping rate is much greater at higher temperatures  $T_c$  is reduced more—thereby increasing  $2\Delta(0)/k_B T_c$ . On the basis of this model, Swihart *et al.*<sup>51</sup> predicted  $2\Delta(0) = 4.4k_B T_c$  for Pb.

Theoretical curves computed for a number of gaps larger than the weak-coupling value are shown in Figs. 2–4. A detailed comparison between the experimental data and the various theoretical curves implies a gap of  $2\Delta(0) = (4.5 \pm 0.2)k_B T_c$  in the films. This value is somewhat higher than the far-infrared values of Ginsberg and Tinkham<sup>4</sup> [ $(4.0 \pm 0.5)k_B T_c$ ]; of Richards and Tinkham<sup>5</sup> [ $(4.3 \pm 0.1)k_B T_c$ ]; and of Norman<sup>8</sup> ( $4.34k_B T_c$ ). It is also about 4 to 5% higher than the tunneling values of Giaever and Megerle<sup>44</sup> [ $(4.2 \pm 0.1)k_B T_c$ ], and of Gasparovic, Taylor, and Eck<sup>46</sup> [ $(4.29 \pm 0.1)k_B T_c$ ]. Tunneling in thick lead films by Townsend and Sutton<sup>47</sup> indicated two gaps [ $(4.3 \pm 0.08)k_B T_c$  and  $(4.67 \pm 0.08)k_B T_c$ ]. Rochlin<sup>48</sup> (from tunneling) and Deaton<sup>49</sup> (from ultrasonic attenuation measurements) found gaps ranging from  $3.4k_B T_c$  to  $5.0k_B T_c$  and an average gap of about  $4.4k_B T_c$ . Palmer and Tinkham<sup>7</sup> measured the gap in thin lead films using the technique of infrared absorption. In their films, as in films 1, 3, and 5,  $l_{eff} \ll \xi_0$ . Considering the implications of Anderson's theory of dirty superconductors,<sup>38</sup> the above authors concluded that their value of  $(4.5 \pm 0.1)k_B T_c$  for thin lead films probably represented an average value of the gap over the Fermi surface. The markedly good agreement between this value and the value suggested by the present measurements supports that conclusion.

An examination of the slight discrepancies between the measured and computed transmission coefficients for  $2\Delta(0) = 4.5k_B T_c$  well below  $T_c$  shows that these are within the quoted  $\pm 5\%$  error in  $2\Delta(0)$  for each film and frequency. At least for films 1 and 3, this is probably the upper limit of the absolute error which would be expected from uncertainties in the various experimentally determined parameters, such as the effective residual film resistance. Hence, in spite of the strong-coupling nature of lead, any modifications in the conductivities of MB, other than implied by a larger gap, are not evident at the present microwave frequencies.

When studying the nature of the infrared response of superconducting lead and mercury, a definite precursor absorption at energies less than the main gap energy was observed by several investigators.<sup>4–6,52</sup> There is no indication for films 1, 3, and 5 of any structure in the temperature dependence of  $T_S/T_N$

and  $R_S/R_N$  which would imply anomalous behavior near the gap edge. In this respect, the results are in agreement with the infrared results of Palmer and Tinkham<sup>7</sup> and the latest results of Norman and Douglass.<sup>53</sup> It was pointed out by the latter investigators that the structure in the absorption edge seen by them earlier<sup>52</sup> was due to the unsuspected presence of higher-order radiation in the beam of their monochromator. Norman<sup>8</sup> suggested that this explanation might also apply to the precursor absorption seen by others, since these studies used similar infrared techniques.

#### Fluctuation Effects near and above $T_c$

As can be seen in Figs. 2–4 the experimental results for each film and frequency show a monotonic decrease in  $T_S/T_N$  and a less pronounced rise in  $R_S/R_N$  in the temperature range just above the customarily defined transition temperature. In this temperature range there is also a monotonic decrease in the dc resistivity. Closer inspection of the region just below  $T_c$  [ $(T - T_c) \leq 0.2$  to  $0.3$  K] reveals that the experimental  $T_S/T_N$ 's fall below those predicted on the basis of the MB complex conductivities.<sup>3</sup> This behavior for all films and frequencies implies ac and dc conductivities near and above  $T_c$  in excess of that predicted by the BCS-type theories of superconductivity. As will be shown in the following sections, this implied that excess conductivity can be consistently accounted for by considering the effects of thermodynamic fluctuations in the phase of the normal-to-superconducting transition.

The possibility of an excess dc conductivity above  $T_c$ , due to "Curie-Weiss"-type fluctuations in the order parameter, was first theoretically investigated in some detail by Ferrel and Schmidt.<sup>18</sup> They found that in superconductors with extremely short electronic mean free paths the critical fluctuations in the phase change from normal to the superconducting state may extend over a considerable temperature region, perhaps several millidegrees. (More recent calculations<sup>54</sup> indicate that this critical region is probably much smaller.) Even above this region, however, where the fluctuations are small, the onset of the phase transition should be indicated by changes in the dc resistance given by

$$R(T) = R_n \left[ 1 + \frac{\tau_0}{T/T_c - 1} \right]^{-1}, \quad (3)$$

where  $R_n$  is the residual film resistance well above  $T_c$ , and  $\tau_0$  is a constant of the specimen. Indeed, simultaneous experiments by Glover<sup>14</sup> on amorphous bismuth films were in good agreement with this prediction. A subsequent theoretical study of the phenomenon by Aslamazov and Larkin<sup>19</sup> (AL) shows that the ratio of  $\tau_0$  to  $R_n$  for a two-dimensional system should be equal to  $0.152 \times 10^{-4} \Omega^{-1}$  regard-

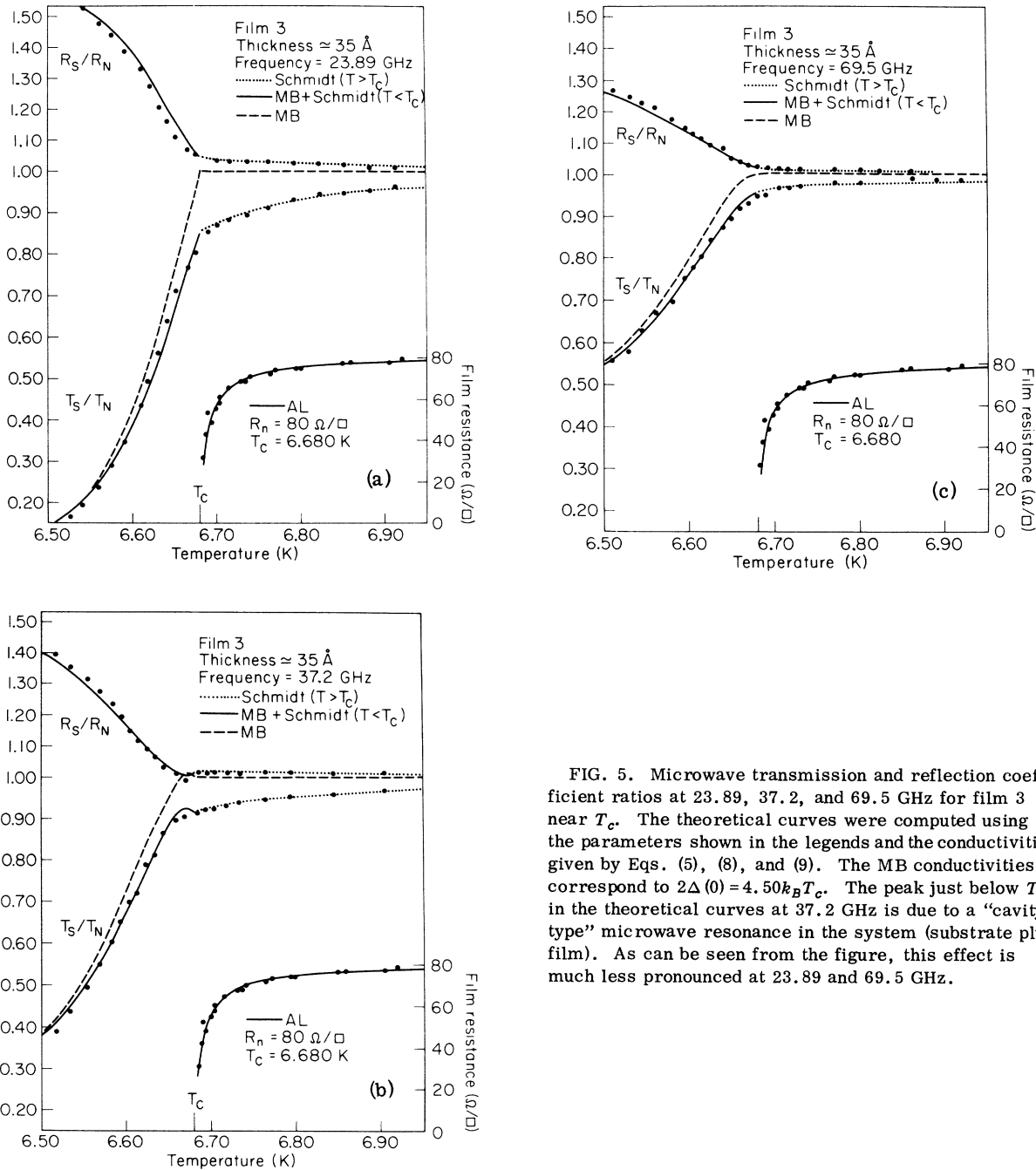


FIG. 5. Microwave transmission and reflection coefficient ratios at 23.89, 37.2, and 69.5 GHz for film 3 near  $T_C$ . The theoretical curves were computed using the parameters shown in the legends and the conductivities given by Eqs. (5), (8), and (9). The MB conductivities correspond to  $2\Delta(0) = 4.50k_B T_C$ . The peak just below  $T_C$  in the theoretical curves at 37.2 GHz is due to a "cavity-type" microwave resonance in the system (substrate plus film). As can be seen from the figure, this effect is much less pronounced at 23.89 and 69.5 GHz.

less of the origin of the specimens. More recent theoretical<sup>20-24</sup> and experimental<sup>15-17</sup> work in this area is basically in agreement with the above predictions, although there are some systems in which discrepancies between experiment and theory have been reported.<sup>17</sup> In Figs. 5 and 6 the experimental values of the dc resistance are compared with the temperature dependence implied by Eq. (3) for  $\tau_0/R_n = 0.152 \times 10^{-4} \text{ \Omega}^{-1}$ . The agreement is good for each film. In fact, the discrepancies are probably

within the experimental uncertainties which would be expected from the observed differences between the measured dc resistance and the resistance determined from the microwave transmission in the normal state. Hence the dc results indicate that we are working with a good two-dimensional fluctuation system and they tend to rule out the possibility of anomalous behavior in the ac data, which are, after all, the primary concern of these experiments.



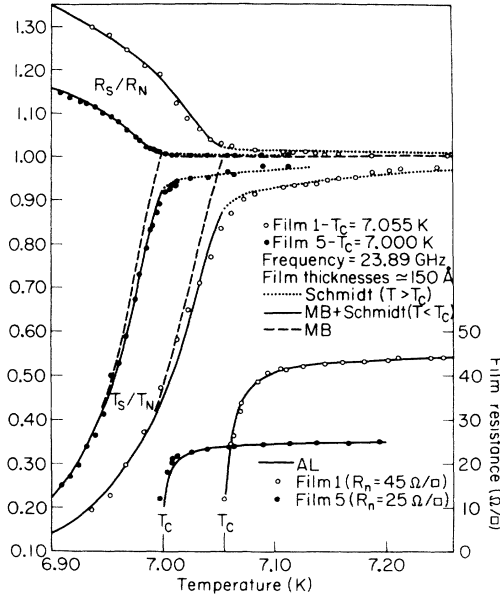


FIG. 6. Microwave transmission and reflection coefficient ratios for films 1 and 5 at 23.89 GHz near  $T_c$ . The theoretical curves were computed from the parameters given in the legend and the conductivities given by Eqs. (5), (8), and (9). The MB conductivities correspond to  $2\Delta(0) = 4.50k_B T_c$ .

Schmidt,<sup>25</sup> utilizing the time-dependent GL equations given by Abrahams and Tsunto,<sup>55</sup> determined the contribution of fluctuations in the GL order parameter to the response function above  $T_c$  for small wave numbers and frequencies. For the special case of thin films (the two-dimensional limit) and short electron mean free paths ( $l_{eff} < \xi_0$ ), he predicts an excess conductivity above  $T_c$  parallel to the surface of the film which is given by

$$\sigma_1^F(\omega, T) = \frac{e^2}{16\hbar\tau d} \left( \frac{\pi}{\tilde{\omega}} - \frac{2}{\tilde{\omega}} \tan^{-1} \frac{1}{\tilde{\omega}} - \frac{1}{\tilde{\omega}^2} \ln(1 + \tilde{\omega}^2) \right), \quad (4)$$

where  $\tilde{\omega} = |\pi\hbar\omega/16k_B T_c \tau|$ ,  $\tau = (T - T_c)/T_c$ , and  $d$  is the film thickness. Thus, above  $T_c$  the total conductivity is  $\sigma_1(\omega, T) = \sigma_1^F(\omega, T) + \sigma_N$  and the total normalized conductivity is

$$\frac{\sigma_1(\omega, T)}{\sigma_N} = 1 + \frac{e^2 R_n}{16\hbar\tau} \left( \frac{\pi}{\tilde{\omega}} - \frac{2}{\tilde{\omega}} \tan^{-1} \frac{1}{\tilde{\omega}} - \frac{1}{\tilde{\omega}^2} \ln(1 + \tilde{\omega}^2) \right). \quad (5)$$

As we reported previously, the conductivities implied by  $T_S/T_N$  above  $T_c$  for film 3 were in good agreement with the predictions of Eq. (5) with respect to both temperature and frequency dependence.<sup>28</sup> The dotted lines in Figs. 5 and 6 are calculated

$T_S/T_N$ 's and  $R_S/R_N$ 's corresponding to the conductivity given by Eq. (5). The experimental points for  $T_S/T_N$ 's shown in the figures have been multiplied by small normalization factors ranging in magnitude from 0.98 to 1.00. These normalization factors are essentially small corrections to the measured values of  $T_N$  and are of no consequence on the scale of Figs. 2-4. The experimental difficulties associated with the determination of  $T_N$  are discussed in some detail in Ref. 28. To allow a more direct comparison between the predictions of Eq. (5) and the experimental results, the temperature and frequency dependence of  $\sigma_1(\omega, T)/\sigma_N$  above  $T_c$ , computed from the inversion of Eq. (A3), is shown for film 3 in Fig. 7. As can be seen in Figs. 5-7, the agreement between experiment and theory is excellent for all three films.

More recently, Schmidt<sup>26</sup> has extended the fluctuation-effect calculations to include the temperature range below  $T_c$ , i. e., in the superconducting state. The results indicate fluctuation-induced ac conductivities below  $T_c$  in excess of the predictions of MB. Again, for the special case of short electron mean free paths and thin films, the real  $\tilde{\sigma}_1^F(\omega, T)$  and imaginary  $\tilde{\sigma}_2^F(\omega, T)$  parts of the fluctuation-induced conductivity for small wave numbers and frequencies are given by

$$\tilde{\sigma}_1^F(\omega, T) = \frac{-e^2}{16\hbar\tau d} \left( \frac{\tilde{\omega}}{1 + \tilde{\omega}^2} \right)$$

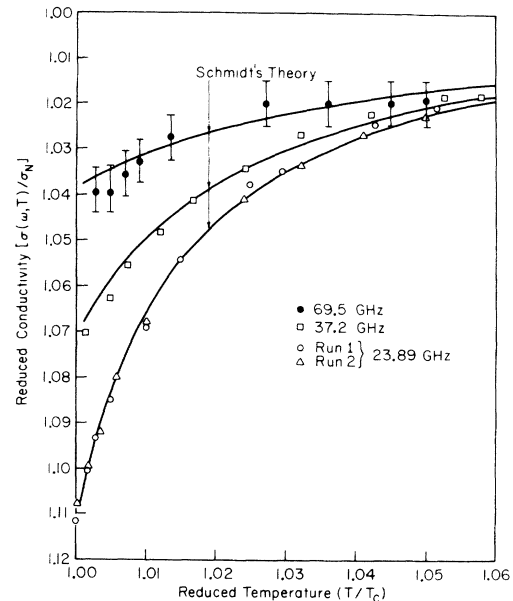


FIG. 7. A comparison of the temperature and frequency dependence of the reduced ac conductivities implied by Eq. (5) with those computed from the transmission coefficients of film 3.

$$\times \left[ \pi - 2 \tan^{-1} \frac{1}{\bar{\omega}} - \frac{1}{\bar{\omega}} \ln \left( \frac{1 + \bar{\omega}^2}{4} \right) \right] \quad (6)$$

and

$$\bar{\sigma}_2^F(\omega, T) = \frac{-e^2}{16\hbar\tau d} \left( \frac{1}{1 + \bar{\omega}^2} \right) \times \left[ \pi - 2 \tan^{-1} \frac{1}{\bar{\omega}} + \bar{\omega} \ln \left( \frac{1 + \bar{\omega}^2}{4} \right) \right]. \quad (7)$$

Combining these fluctuation-induced conductivities with those derived by MB results in the following expressions for the total normalized real and imaginary parts of the conductivity parallel to the surface of the film below  $T_c$ :

$$\frac{\bar{\sigma}_1(\omega, T)}{\sigma_N} = \frac{\bar{\sigma}_1^{\text{MB}}(\omega, T)}{\sigma_N} - \frac{e^2 R_n}{16\hbar\tau} \left( \frac{\bar{\omega}}{1 + \bar{\omega}^2} \right) \times \left[ \pi - 2 \tan^{-1} \frac{1}{\bar{\omega}} - \frac{1}{\bar{\omega}} \ln \left( \frac{1 + \bar{\omega}^2}{4} \right) \right] \quad (8)$$

and

$$\frac{\bar{\sigma}_2(\omega, T)}{\sigma_N} = \frac{\bar{\sigma}_2^{\text{MB}}(\omega, T)}{\sigma_N} - \frac{e^2 R_n}{16\hbar\tau} \left( \frac{1}{1 + \bar{\omega}^2} \right) \times \left[ \pi - 2 \tan^{-1} \frac{1}{\bar{\omega}} + \bar{\omega} \ln \left( \frac{1 + \bar{\omega}^2}{4} \right) \right], \quad (9)$$

where  $\bar{\sigma}_1^{\text{MB}}(\omega, T)$  and  $\bar{\sigma}_2^{\text{MB}}(\omega, T)$  are the real and imaginary parts of the MB conductivity, respectively. When  $T \ll T_c$ , then  $\bar{\omega}(T) \rightarrow 0$  and the proper MB results are recovered from Eqs. (8) and (9). In the limit  $T/T_c \rightarrow 1$ ,  $\bar{\omega}(T \rightarrow T_c) \rightarrow \infty$ , and

$$\frac{\bar{\sigma}_1(\omega, T \rightarrow T_c)}{\sigma_N} + i \frac{\bar{\sigma}_2(\omega, T \rightarrow T_c)}{\sigma_N} = \frac{\sigma_1(\omega, T_c - T)}{\sigma_N}.$$

Thus Eqs. (5), (8), and (9) describe the continuous evolution of the ac conductivity from  $\sigma_N$  (well above  $T_c$ ) to the MB regime [ $(T_c - T) \leq 0.2$  to  $0.3$  K]. As recently reported<sup>29</sup> the  $T_S/T_N$  data for film 3 can be accounted for over the entire temperature range, including the region just below  $T_c$ , using the conductivities given by Eqs. (5), (8), and (9).

In Fig. 5 the temperature dependence of the experimental and theoretical  $T_S/T_N$ 's and  $R_S/R_N$ 's is compared at three frequencies (23.89, 37.2, and 69.5 GHz) for a lead film of 35-Å effective thickness. In order to better illustrate the effect of fluctuations just below and above  $T_c$ , only the temperature region in the vicinity of  $T_c$  is shown. Attention is directed to temperatures below  $T_c$  [ $(T_c - T) < 0.1$  K], where the experimental  $T_S/T_N$ 's are seen to fall well below the MB prediction (dashed line). This implies that in the superconducting state some mechanism other than that con-

sidered by MB (quasiparticles) is contributing to the ac conductivity. The addition of Schmidt's fluctuation-induced ac conductivities [Eqs. (6) and (7)] to those of MB results in the  $T_S/T_N$ 's and  $R_S/R_N$ 's represented by the solid lines in Fig. 5. As can be seen, the temperature dependence of the experimental results is in good agreement with theory (solid line) at the three frequencies. Figure 6 shows data for two other films at a frequency of 23.89 GHz. The results are essentially the same as for film 3. Thus by combining fluctuation-induced and BCS-like ac conductivities we are able to account for both the temperature and frequency dependence of our microwave measurements on thin superconducting lead films.

The fluctuation-induced changes in  $T_S/T_N$  are large below  $T_c$  and well within the capabilities of microwave systems, e.g., at 23.89 GHz and 20 mK below  $T_c$ , they account for 45% of the deviation of  $T_S/T_N$  from 1 in the case of film 3. Due to their weaker dependence on  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$  [compare Eqs. (A3) and (A4) in the Appendix], the reflection coefficients are less sensitive to small changes in the conductivities. Hence, as mentioned previously, the effect of fluctuations is much less pronounced in the case of these coefficients. This, coupled with the larger experimental uncertainties in  $R_S/R_N$ , render reflection measurements at microwave frequencies less suitable for the study of fluctuation effects in thin films.

Within the framework of Schmidt's theory,<sup>25,26</sup> the dc conductivity is infinite below  $T_c$  even for a two-dimensional system such as the thin films used in our experiments. This is due to his assumption of the existence of long-range order. Hohenberg<sup>56</sup> has shown theoretically that exact long-range order cannot exist in one- and two-dimensional superconductors. However, Mikeska and Schmidt<sup>57</sup> have theoretically demonstrated that a model for a superconductor containing the vanishing of long-range order upon the transition from three to two dimensions does not automatically lead to a finite conductivity. Masker, Marčelja, and Parks<sup>58</sup> have experimentally and theoretically demonstrated that the dc resistance of two-dimensional superconducting films is not zero below  $T_c$  but decreases exponentially over a temperature interval of the same order,  $\sim \tau_0 T_c$ , as is significant in the AL and Schmidt theories. Their theoretical model of a superconductor includes the effect on the dc electrical conductivity of the fourth-order term in the GL theory. The experimental system investigated was granular Al films in which the resistance is dominated by the impedance between grains (or crystallites). Thus it would appear that both the theoretical and experimental dc conductivity below  $T_c$  for a two-dimensional superconductor needs further investigation. Also, it seems that the ap-

proximations used by Schmidt in calculating the ac conductivity below  $T_c$  are better for the ac than the dc case, as evidenced by the reasonable agreement between his theory and our experimental results. Apparently, the exact properties of long-range order are not as crucial in the ac conductivity as compared with their importance in the dc case.

#### Effects of Thin Paramagnetic Overlays

Following the measurement of the microwave coefficients of film 1, several monolayers of manganese were deposited onto the film. The modification in the properties of the film in the presence of an overlay of about 1–2 Å “thickness” is shown in Fig. 8 along with results for the host film. The slower decrease in  $T_S/T_N$  and  $R_S/R_N$ , when measured in the presence of the overlay, suggests a reduction in the energy gap. The broken curves in the figure were calculated from conductivities which correspond to  $2\Delta(0) = 2.43k_B T_c$ . In the host film the gap had a value of  $(4.5 \pm 0.2)k_B T_c$ . The presence of the overlay, therefore, caused approximately a 46% depression in  $2\Delta(0)$ . The close agreement between the measured and calculated values of  $T_S/T_N$  for the entire temperature range indicates that, in spite of the depression of the gap, the temperature dependence of  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$ , hence, of  $\Delta(T)/\Delta(0)$ , remained similar to that in the host film. This is in good accord with the predictions of Nam.<sup>11</sup>

Following the measurements for this first layer, five additional layers were deposited onto the film for a total thickness of 5 Å; however, no further changes were observed in the temperature depen-

dence of the coefficient ratios.

Reif and Woolf<sup>30</sup> studied the effects of paramagnetic impurities on the superconducting tunneling characteristics of several superconductors. They found that the nonlinear tunneling characteristics of their films became nearly straight lines in the presence of a 15-Å overlay, indicating the absence of a well-defined pure gap region. Similar gapless superconductivity induced by both magnetic and nonmagnetic metallic contacts were observed also by several other investigators.<sup>31,32</sup> A satisfactory theoretical explanation of the phenomenon was given by Fulde and Maki<sup>59</sup> and by de Gennes and Mauro.<sup>60</sup> The work of de Gennes and Mauro indicates, however, that such gapless behavior should be present only in sufficiently thick films, for which  $d > (l_{\text{eff}} \xi_0)^{1/2}$ . For the case of an overlay of “finite” thickness they predict a finite gap in the host metal for all temperatures below  $T_c$ . Since for film 1 both the thickness of the film and the overlays were relatively small, the absence of a gapless region below  $T_c$  is probably the consequence of one of the above conditions.

Reif and Woolf<sup>30</sup> found that the overlays caused a reduction in the critical temperature of their host film by as much as several tenths of a degree. In film 1 no such depression in  $T_c$  was observed. The experimental error in the measurement of the absolute magnitude of  $T_c$  was 0.02 K.

#### SUMMARY AND CONCLUSIONS

A comparison of the experimental results well below  $T_c$  for the transmission and reflection coefficient ratios in the frequency range from 24 to 70 GHz with those calculated from sets of conduc-

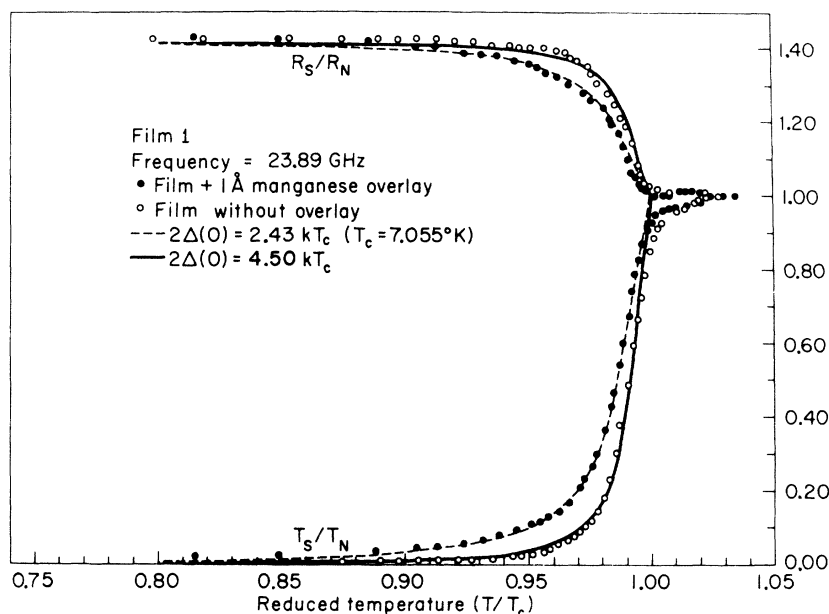


FIG. 8. The effect of a thin manganese overlay on the transmission and reflection coefficient ratios of film 1.

tivities corresponding to various values of the gap parameter  $2\Delta(0)$  in the formula of Mattis and Bardeen<sup>3</sup> indicates a gap of  $(4.5 \pm 0.2)k_B T_c$  in thin lead films. For this gap the temperature dependence of the microwave electromagnetic response is well described by the real and imaginary parts of the theoretical conductivity. Consequently, there is no indication of significant modifications in  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$  for the present microwave frequencies, other than implied by the larger gap, due to the strong-coupling character of the electron-phonon interaction in lead. Our microwave value of  $(4.5 \pm 0.2)k_B T_c$  for the magnitude of the gap is in especially good agreement with the infrared value of  $(4.5 \pm 0.1)k_B T_c$ , reported by Palmer and Tinkham<sup>7</sup> for similar thin lead films. The absence of any structure in  $T_S/T_N$  and  $R_S/R_N$  below  $T_c$  implied the absence of any precursor absorption near the gap edge, in agreement with the latest infrared results.<sup>7,53</sup>

The monotonic decrease in the dc film resistance above  $T_c$  is well described in terms of an excess conductivity due to thermodynamic fluctuations in the Ginzburg-Landau order parameter. The ratio  $\tau_0/R_n$  for each film is in remarkably good agreement with the value of  $0.152 \times 10^{-4} \Omega^{-1}$  predicted by Aslamazov and Larkin.<sup>19</sup> Also, the decrease in the microwave transmission above  $T_c$  can be accounted for using the fluctuation-induced ac conductivity theory of Schmidt.<sup>25</sup> The microwave transmission just below  $T_c$  decreases more rapidly than expected on the basis of the complex conductivities derived by Mattis and Bardeen.<sup>3</sup> This implied excess conductivity in the superconducting state is in good agreement with recent calculations of Schmidt,<sup>26</sup> in which the effects of fluctuation on the ac conductivity below  $T_c$  are considered. The relative ease of observing fluctuation effects in the transmission of microwaves through thin superconducting films should make this type of experi-

ment quite useful in further investigations, e. g., the effect of various pair-breaking mechanisms on fluctuations in the superconducting state.

Despite the smaller gap (54%) of film 1 in the presence of a thin ( $< 5 \text{ \AA}$ ) paramagnetic overlay, measurements indicated a well-defined gap for all temperatures below  $T_c$ . The temperature dependence of  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$  remained that of Mattis and Bardeen.<sup>3</sup> Perhaps further experiments on systems which exhibit a gapless region below  $T_c$  would be useful in establishing the behavior of  $\bar{\sigma}_1/\sigma_N$  and  $\bar{\sigma}_2/\sigma_N$  for this situation.

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#### APPENDIX

For a film of thickness  $d$  ( $\ll$  wavelength or skin depth) deposited on a substrate of thickness  $l$  and index of refraction  $n$ , the superconducting transmission and reflection coefficients have been derived previously<sup>10</sup> for the TE<sub>10</sub> mode of a rectangular waveguide. A more general result for the coefficients in a circular waveguide is given in the next paragraph.

For the case in which the radiation is incident on the film before the substrate, the coefficients in the superconducting state in a circular waveguide are

$$T_S = 4n^2 \{ n^2 [(2 + Z_{gmp} \bar{\sigma}_1 d)^2 + (Z_{gmp} \bar{\sigma}_2 d)^2] \cos^2 k_{mp} l + [(n^2 + 1 + Z_{gmp} \bar{\sigma}_1 d)^2 + (Z_{gmp} \bar{\sigma}_2 d)^2] \sin^2 k_{mp} l - n(n^2 - 1) Z_{gmp} \bar{\sigma}_2 d \sin 2k_{mp} l \}^{-1} \quad (A1)$$

and

$$R_S = \{ n^2 [(Z_{gmp} \bar{\sigma}_1 d)^2 + (Z_{gmp} \bar{\sigma}_2 d)^2] \cos^2 k_{mp} l + [(Z_{gmp} \bar{\sigma}_1 d + n^2 - 1)^2 + (Z_{gmp} \bar{\sigma}_2 d)^2] \sin^2 k_{mp} l - n(n^2 - 1) Z_{gmp} \bar{\sigma}_2 d \sin 2k_{mp} l \} \{ n^2 [(2 + Z_{gmp} \bar{\sigma}_1 d)^2 + (Z_{gmp} \bar{\sigma}_2 d)^2] \cos^2 k_{mp} l + [(n^2 + 1 + Z_{gmp} \bar{\sigma}_1 d)^2 + (Z_{gmp} \bar{\sigma}_2 d)^2] \sin^2 k_{mp} l - n(n^2 - 1) Z_{gmp} \bar{\sigma}_2 d \sin 2k_{mp} l \}^{-1}, \quad (A2)$$

where  $Z_{gmp}$  is the waveguide impedance and  $k_{mp}$  is the propagation constant in the substrate. The transmission and reflection coefficients in the

normal state  $T_N$  and  $R_N$  can be found by setting  $\bar{\sigma}_1 = \sigma_N$  and  $\bar{\sigma}_2 = 0$  in Eqs. (A1) and (A2). Since  $\sigma_N d = R_n^{-1}$ , where  $R_n$  is the normal-state resistance,

for a given frequency,  $T_S/T_N$  and  $R_S/R_N$  are uniquely determined by  $\bar{\sigma}_1/\sigma_N$ ,  $\bar{\sigma}_2/\sigma_N$ , and  $R_n$ .

For computational purposes it is convenient to express  $T_S/T_N$  and  $R_S/R_N$  by the following simplified equations:

$$T_S/T_N = A [B({}^1\sigma_1^2 + {}^1\sigma_2^2) + C{}^1\sigma_1 + D{}^1\sigma_2 + E]^{-1} \quad (A3)$$

and

$$R_S/R_N = (T_S/T_N) [B({}^1\sigma_1^2 + {}^1\sigma_2^2) + C{}^1\sigma_1 + D{}^1\sigma_2 + F] G^{-1}, \quad (A4)$$

where  ${}^1\sigma_1 = \bar{\sigma}_1/\sigma_N$ ,  ${}^1\sigma_2 = \bar{\sigma}_2/\sigma_N$ , and  $A, B, C, D, E, F$ , and  $G$  are temperature-independent constants of the experiment which can be computed from  $n, l, k_{mp}, \angle_{emp}$ , and  $R_n$ . Generally, at frequencies such that  $\hbar\omega \ll 2\Delta(0)$ ,  ${}^1\sigma_2 \gg {}^1\sigma_1$ , and  ${}^1\sigma_2^2 + {}^1\sigma_1^2 \gg {}^1\sigma_1$  and  ${}^1\sigma_2$ , when  $T \ll T_c$ . Hence, at this limit  $T_S/T_N$  should fall off approximately as  ${}^1\sigma_2^{-2}$  and  $R_S/R_N$  should tend to a constant limit.

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## Thermodynamics of Pressure Effects in V<sub>3</sub>Si and V<sub>3</sub>Ge

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The thermodynamic relationships relating the pressure dependence of the superconducting transition temperature to the changes in the elastic constants at the transition are presented and their application to the compounds V<sub>3</sub>Si and V<sub>3</sub>Ge is discussed.

In a series of recent articles<sup>1-3</sup> Testardi and co-workers have made predictions of an unusually large quadratic strain dependence of the superconducting transition temperature for the A15 superconductors V<sub>3</sub>Si and V<sub>3</sub>Ge.<sup>4</sup> Measurements<sup>5, 6</sup> of  $T_c$  as a function of pressure for these compounds fail to reveal any evidence of the quadratic dependence, with  $T_c$  increasing linearly with pressure for both compounds. Since the predicted behavior follows directly from a purely thermodynamic treatment of the elastic properties, as determined from sound velocity measurements close to  $T_c$ , and is, therefore, completely model independent, the conflict is of the most fundamental nature. It is the purpose of this paper to make a critical evaluation of the circumstances surrounding the discrepancy in an attempt to isolate its origin.

We shall begin by considering the appropriate thermodynamic relationships linking the discontinuities in the compressibility and its temperature derivative at the superconducting transition with the pressure derivatives of  $T_c$ . Starting with the difference in the Gibb's energy between the normal ( $n$ ) and superconducting states ( $s$ ),<sup>7</sup>

$$G_n(T) - G_s(T) = \frac{V}{8\pi} H_c(T)^2,$$

and successively differentiating with respect to  $T$  and  $P$  we obtain expressions for the change in specific heat  $C$ , compressibility  $\kappa$ , thermal expansion  $\alpha$ , and their various derivatives, in going from the superconducting to the normal state.

We have taken the temperature dependence of  $H_c$  to be of the general form

$$H_c(T) = B_1(T_c - T)/T_c + \frac{1}{2}B_2(T_c - T)^2/T_c^2 + \dots,$$

where the coefficients  $B_n$  are temperature independent. Although this expansion may be related to the more usual quadratic form

$$H_c(T) = H_0(1 - T^2/T_c^2)$$

by putting  $B_1 = 2H_0$  and  $B_2 = -2H_0$  we prefer to avoid this more restricted expression and obtain values for  $B_1$  and  $B_2$  from the heat-capacity data available using (1) and (2) given below. In actual practice we find that the values we obtain for  $B_1$  and  $B_2$  lead to a temperature dependence of  $H_c$  which is not very different from the quadratic form. It may be readily determined that at  $T = T_c$

$$C_n - C_s = -\frac{V}{4\pi} \left( \frac{B_1}{T_c} \right)^2, \quad (1)$$

$$\frac{\partial}{\partial T} (C_n - C_s) = -\frac{V}{4\pi} (1 + 3\alpha T_c) \left( \frac{B_1}{T_c} \right)^2 + \frac{3}{4\pi} \frac{B_1 B_2}{T_c^2}, \quad (2)$$

$$\kappa_n - \kappa_s = -\frac{1}{4\pi} \left( \frac{B_1}{T_c} \right)^2 \left( \frac{\partial T_c}{\partial P} \right)^2, \quad (3)$$

$$\begin{aligned} \frac{\partial}{\partial T} (\kappa_n - \kappa_s) = & \frac{1}{4\pi} \left( \frac{B_1}{T_c} \right)^2 \frac{\partial^2 T_c}{\partial P^2} + \frac{3}{4\pi} \frac{B_1 B_2}{T_c^3} \left( \frac{\partial T_c}{\partial P} \right)^2 \\ & + \left[ \frac{B_1}{\pi T_c} \frac{\partial}{\partial P} \left( \frac{B_1}{T_c} \right) - \frac{\kappa_s}{2\pi} \left( \frac{B_1}{T_c} \right)^2 \right] \left( \frac{\partial T_c}{\partial P} \right). \end{aligned} \quad (4)$$

On comparing (4) with the equivalent relationship derived by Testardi<sup>2</sup> we find only the first term on the right-hand side.<sup>7</sup> The loss of the term in  $(\partial T_c / \partial P)^2$  may be traced to his approximation that  $H_c(T) = 2H_0(1 - T/T_c)$ , which is equivalent to taking  $B_2 = 0$ . Since we find that  $B_2 \approx -B_1$  for both com-