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# Microwave Magnetoimpedance of Superconducting Tin*

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Measurements, using a bimodal cavity, of the temperature and magnetic field dependence of the surface impedance of a single crystal of superconducting tin at a frequency of 23.5 Gc/sec are reported. In the geometry used, the static and microwave magnetic fields were parallel over the surface of the sample. The temperature dependence of the reactance in zero field agrees well with that calculated by Miller from the BCS theory. A small unexpected knee in the temperature dependence of the resistance is observed, centered around a reduced temperature of $t=0.88$. This knee may arise from a band of $p$ electrons with a smaller energy gap whose temperature dependence differs markedly from the BCS form, as proposed by Suhl, Matthias, and Walker. The change of surface resistance with applied field is found to be negative in the temperature range of the knee with the greatest negative dependence occuring at the center of the knee. The change of resistance is found to be positive outside this temperature range. The change of reactance with field is found to be positive. The association of the negative field dependence of the surface impedance with a band of $p$ electrons is shown to give a qualitative explanation of the field dependence as observed in this and other investigations.

## INTRODUCTION

THE study of the high-frequency surface impedance and its dependence on temperature, frequency, and static magnetic field has provided much useful information about both normal[1] and superconducting metals.[2]

For most pure metals in the normal state and at low temperatures, the surface impedance at microwave frequencies is found to be nearly independent of temperature[3] but a strong function of frequency[3] and magnetic field.[1] The theory of the anomalous skin effect as developed by Reuter and Sondheimer[4] and extended by Dingle[5] gives a reasonably satisfactory explanation of the temperature and frequency dependence of the surface impedance of normal metals. The study of the magnetic field dependence has been particularly useful in analyzing the complex band structure of real metals, and has yielded valuable information about the Fermi surface and effective masses of electrons in metals in the normal state.[1]

The surface impedance of metals in the superconducting state has been found to be a strong function of temperature as well as of frequency and magnetic field.[2] The temperature and frequency dependence of the surface impedance in zero applied field has been found to be in generally satisfactory agreement with the BCS theory of superconductivity as shown by Miller.[6] What discrepancies there are have been ascribed to the complex and anisotropic band structure of real metals as compared with the isotropic theoretical model.[2] The magnetic-field dependence of the surface impedance has been studied at several frequencies by a number of investigators. Tin is the only metal that has been studied extensively and the following remarks apply to it. At relatively low frequencies, Sharvin and Gantmakher[7] (2 Mc/sec) and Connell[8] (700 kc/sec) found a

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1 M. Ya. Azbel' and I. M. Lifshitz, in *Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961) Vol. III, pp. 288-332.

2 J. Bardeen and J. R. Schrieffer, in *Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961) Vol. III, pp. 170–287.

3 A. B. Pippard, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1954), Vol. 6, pp. 1–45.

4 G. E. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).

5 R. B. Dingle, Physica **19**, 311 (1953).

6 P. B. Miller, Phys. Rev. **118**, 928 (1960).

7 Yu. V. Sharvin and V. F. Gantmakher, Zh. Eksperim. i Teor. Fiz. **39**, 1242 (1960) [English transl.: Soviet Phys.—JETP **12**, 866 (1961)].

8 R. A. Connell, Phys. Rev. **129**, 1952 (1963).

small increase in the surface reactance with applied field in reasonable agreement with the Ginzburg-Landau theory.[9] At higher frequencies, in the microwave range, more complicated effects appear. Spiewak[10,11] (1 Gc/sec) and Richards[12] (3 Gc/sec) found that near the transition temperature both the resistance and reactance decrease with applied field. This negative field dependence has been described as anomalous.[10] Richards also found that the negative field dependence becomes positive when tin is alloyed with a few tenths of a percent of indium. Pippard[13] (10 Gc/sec) and Douglass and Dresselhaus[14] (9 Gc/sec) found the resistance to decrease with applied field only in a limited range of temperatures somewhat below the transition but to increase very near the transition and at lower temperatures. They found the reactance to increase with field at all temperatures. Fawcett[15,16] (36 Gc/sec) found only a slight increase of the resistance with field. The above-mentioned high-frequency effects have been found to be highly anisotropic and to depend on the relative orientation of the static and microwave magnetic fields. The parallel orientation has been found to yield the greatest and most anomalous field dependence.[10–12]

An attempt by G. Dresselhaus and M. Spiewak Dresselhaus[17] to explain the results of Spiewak[10,11] in terms of a two-fluid model was only partially successful. This theory indicated, however, that more than one band of electrons may be important and suggested that one band might be more effective in determining the surface impedance in a magnetic field while another band might be more effective in determining the surface impedance in zero field. Alternatively, Bardeen[18] suggested that a disturbance of the equilibrium fraction of normal and superconducting electrons may be the cause of the observed effects. This idea is supported by the apparently simple behavior found at the lower frequencies.

In many cases, these magnetic effects are small so that a sensitive experimental technique is needed. Pippard,[13] Spiewak,[11] and Richards[12] all used a technique developed by Pippard[19] which enhances the sensitivity by using a very thin wire sample—of the order of 100 $\mu$ diam—as the center conductor of a coaxial line. Such a small size complicates the preparation and handling of a sample and may introduce size effects into the results. Also, the wire shape makes the study of anisotropy more difficult. Recently, Dresselhaus, Douglass, and Kyhl[20] developed a technique which utilizes a very high $Q$ dielectric resonator. This technique employs a flat bulk sample which simplifies sample preparation and the study of anisotropy and greatly reduces the possibility of size effects. The resonator, however, operates in a high-order mode so that the effect of the relative orientation of the static and microwave magnetic fields is difficult to study.

In the present work, a bimodal cavity is employed. This cavity is a highly stable microwave bridge. In the past it has been used for the study of Faraday rotation and electron spin resonance in semiconductors and magnetic materials.[21–24] This is the first time that it has been used for the study of metals at low temperatures. The bimodal cavity was developed and analyzed in terms of an equivalent circuit by Portis and Teaney.[25] The cavity operates in the low-order $TE_{111}$ mode. It is possible to use either a flat or rod-shaped bulk sample. Thus, the difficulties inherent in the two previously discussed techniques can be largely eliminated.

In this paper, the results of an investigation of the temperature and field dependence of a high-purity single-crystal tin rod are presented. The static field was applied along the axis of the sample. In this geometry, the static and microwave magnetic fields are parallel over most of the surface of the sample and demagnetizing effects are small. Because of the rod shape, the impedance we observe is an average over certain crystal directions. These results are interpreted in terms of a multiband model of superconductivity developed by Suhl, Matthias, and Walker.[26] In this model, the BCS theory[27] is extended to include the case where two or more bands of itinerant electrons overlap. Such a situation arises in the transition elements for the $s$ and $d$ bands. They speculate that such effects may also occur in the case of superconductors such as lead and tin which have $s$–$p$ bands. They show that one can expect a separate energy gap for each band and that if interband scattering is small compared to intraband scattering, the energy gap associated with the $d$ or $p$ band may lie well below the energy gap associated with the $s$ band and

[9] V. L. Ginzburg and L. D. Landau, J. Exptl. Theoret. Phys. (USSR) **20**, 1064 (1950).
[10] M. Spiewak, Phys. Rev. Letters **1**, 136 (1958).
[11] M. Spiewak, Phys. Rev. **113**, 1479 (1959).
[12] P. L. Richards, Bull. Am. Phys. Soc. **6**, 65 (1961); Phys. Rev. **126**, 912 (1962).
[13] A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 210 (1950).
[14] D. H. Douglass, M. S. Dresselhaus, and R. L. Kyhl, Bull. Am. Phys. Soc. **8**, 78 (1963); and private communication.
[15] E. Fawcett, thesis, University of Cambridge 1955 (unpublished), as quoted by Pippard, Ref. 16 below.
[16] A. B. Pippard, in *Proceedings of the Seventh International Conference on Low Temperature Physics*, edited by F. M. Graham and A. C. Hollis Hallet (University of Toronto Press, Toronto, 1961), pp. 320–327.
[17] G. Dresselhaus and M. S. Dresselhaus, Phys. Rev. **118**, 77 (1960); Phys. Rev. Letters **4**, 401 (1960).
[18] J. Bardeen, Phys. Rev. Letters **1**, 399 (1958).
[19] A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 98 (1950).
[20] M. S. Dresselhaus, D. H. Douglass, and R. L. Kyhl, in Proceedings of the Eighth Conference on Low Temperature Physics, London 1962, edited by G. O. Jones (to be published).
[21] D. P. Snowden and A. M. Portis, Phys. Rev. **120**, 1983 (1960).
[22] D. T. Teaney, W. E. Blumberg, and A. M. Portis, Phys. Rev. **119**, 1851 (1960).
[23] A. M. Portis and D. T. Teaney, Phys. Rev. **116**, 838 (1959).
[24] A. M. Portis, Phys. Chem. Solids, **8**, 326 (1959).
[25] A. M. Portis and D. T. Teaney, J. Appl. Phys. **29**, 1692 (1958).
[26] H. Suhl, B. T. Matthias, and R. L. Walker, Phys. Rev., Letters **3**, 552 (1959).
[27] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

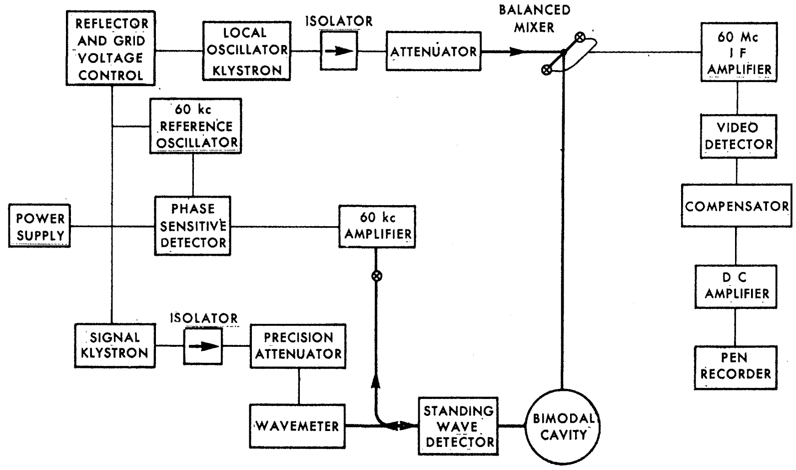


FIG. 1. Bimodal-cavity induction spectrometer.

have a temperature dependence which differs markedly from the BCS form for an isotropic model. In this paper, an association is made between the negative field dependence of the surface impedance and such a *p* band. More recently the effect of *s*-*d* bands in the transition element superconductors has been discussed by Garland.[28]

## APPARATUS

### A. Bimodal Cavity Induction Spectrometer

A schematic diagram of the bimodal cavity induction spectrometer used in this study is shown in Fig. 1. An FXR Klystron Power Supply, Model Z815B, supplies power to two Raytheon 2K33B klystrons. An additional adjustment in the reflector and grid voltages of the local oscillator is provided by two batteries. The frequency of the signal klystron is stabilized to that of the bimodal cavity.[29] The effect of variations in the frequency of the local oscillator is minimized by sweeping its frequency from just below the pass band of the i.f. amplifier to just above by applying a 120 cps sawtooth voltage to the reflector. Microwave power transmitted through the cavity is detected in a balanced mixer by two matched and reversed 1N26A mixer diodes. The center frequency of the local oscillator is 60 Mc/sec away from that of the signal oscillator. The 60-Mc/sec component is amplified by a variable gain i.f. amplifier and detected. Most of the resulting voltage is compensated, with the unbalance amplified by a dc amplifier. The signal is finally displayed on chart paper. The magnetic field is produced by a conventional 12-in. pole-diameter iron-core electromagnet. A similar but more elaborate spectrometer has been described by Teaney, Klein, and Portis.[30]

### B. Bimodal Cavity

The bimodal cavity used in this work is based on the design of Portis and Teaney.[25] Figure 2 shows two sections through the cavity used in the present work. In order to facilitate the mounting of the sample and its thermal contact to the liquid-helium bath, one guide is coupled through the top rather than through the end of the cavity. The cavity was excited in the coaxial $TE_{111}$ mode with the sample forming the center conductor. Excitation of the *TEM* mode was prevented by the symmetry of the coupling and by having the sample of such a length that the frequency of the *TEM* mode was well away from that of the $TE_{111}$ mode. It would also be possible to study flat samples with the bimodal cavity by having the sample form one end wall. All metal parts of the cavity are made of brass.

Probes labeled $C_X$ and $C_Y$ in Fig. 2 are metallic. Insertion of these probes changes the reactive balance of the cavity modes. Probes labeled $R_X$ and $R_Y$ are lossy and are used to change the resistive balance of the cavity modes. The cavity has been analyzed in terms of a circuit of lumped elements by Portis and Teaney.[25] They find the following equations for the change in

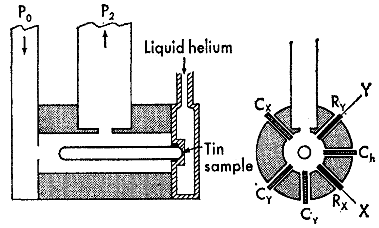


FIG. 2. Two sections through the bimodal cavity. Microwave power is coupled into the cavity through an iris in one end. Coupling into the second waveguide is through an iris in the top of the cavity. The sample is soldered to a hollow extension of the liquid-helium can which forms the other end of the cavity. Probes $C_X$ and $C_Y$ are metallic and vary the reactance of the X and Y modes. Probes $R_X$ and $R_Y$ are absorbing and are used to adjust the losses in the X and Y modes.

[28] J. W. Garland, Phys. Rev. Letters **11**, 111 and 114 (1963).
[29] A. J. George and D. T. Teaney, Rev. Sci. Instr. **31**, 997 (1960).
[30] D. T. Teaney, M. P. Klein, and A. M. Portis, Rev. Sci. Instr. **32**, 721 (1961).

transmitted power on application of a magnetic field: On reactive unbalance

$$\frac{\delta P_2}{P_2}=\frac{\cot\theta}{[(1+\beta_1)(1+\beta_2)]^{\frac{1}{2}}}\left(\frac{x_{XX}-x_{YY}}{R}+\frac{x_{XY}-x_{YX}}{R}\right)-\left(\frac{1}{1+\beta_1}+\frac{1}{1+\beta_2}\right)\left(\frac{r_{XX}+r_{YY}}{R}\right)\cos^2\theta-\left(\frac{1}{1+\beta_1}-\frac{1}{1+\beta_2}\right)\frac{r_{XY}+r_{YX}}{R}\cos^2\theta-\frac{1}{[(1+\beta_1)(1+\beta_2)]^{\frac{1}{2}}}\frac{x_{XX}-x_{YY}}{R}\sin^2\theta. \quad (1)$$

On resistive unbalance for small $\theta$

$$\frac{\delta P_2}{P_2}\cong\frac{2\csc 2\theta}{[(1+\beta_1)(1+\beta_2)]^{\frac{1}{2}}}\left(\frac{r_{XX}-r_{YY}}{R}+\frac{r_{XY}-r_{YX}}{R}\right)-\left(\frac{1}{1+\beta_1}+\frac{1}{1+\beta_2}\right)\frac{r_{XX}+r_{YY}}{R}-\left(\frac{1}{1+\beta_1}-\frac{1}{1+\beta_2}\right)\frac{r_{XY}+r_{YX}}{R}, \quad (2)$$

where $\sin^2\theta=P_2/P_{2\max}$ and $\beta_1$ and $\beta_2$ are coupling coefficients. $\mathbf{z}=\mathbf{r}+i\mathbf{x}$ is the change in impedance tensor of the sample upon application of a magnetic field. $P_{2\max}$ is obtained by splitting the cavity modes with a reactive probe, $C_X$ or $C_Y$, until the maximum transmitted power results. The first terms are rotation terms and arise either from sample anisotropy or off-diagonal elements in the impedance tensor. The reactive part of the sample impedance tensor produces the rotation on reactive unbalance while the resistive part produces the rotation on resistive unbalance. The first terms are of order $1/\theta$. The second and third terms represent the change in the level of the microwave fields in the cavity as a result of the dependence of sample losses on magnetic field. They are independent of $\theta$ for small $\theta$. The fourth term in Eq. (1) is a higher order rotation term and is only important for large $\theta$.

The diagonal elements $z_{XX}$ and $z_{YY}$ are even functions of the magnetic field while the off-diagonal elements, $z_{XY}$ and $z_{YX}$ are odd functions. No difference could be detected upon reversing the field in these experiments so that the off-diagonal terms are considered negligible. The diagonal elements are seen to cancel in the first term for the isotropic case. In order to overcome this difficulty, the sample was plated with arsenic-doped copper over those portions of the sample which were predominantly in the Y mode. The copper was doped to reduce any possible change in impedance of the plated portion with magnetic field. The plating pattern is shown in Fig. 3. In this way, $z_{XX}$ is greater than $z_{YY}$ so that cancelation no longer takes place.

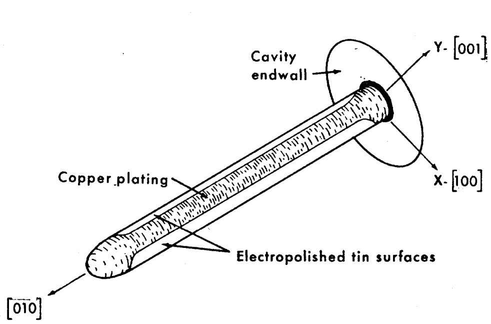


FIG. 3. Plating pattern and crystallographic orientation of the sample with respect to the cavity modes. In order to produce a first-order rotation signal, the sample was plated over those portions of the surface lying predominantly in one of the modes.

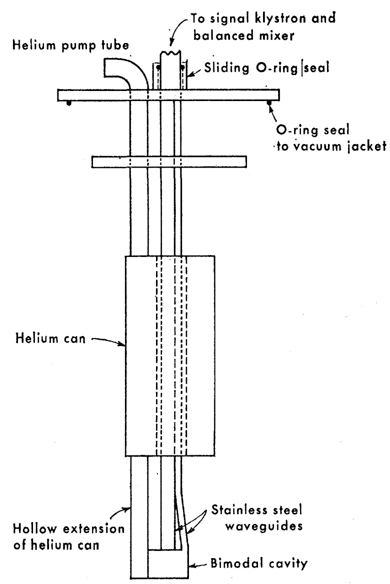


FIG. 4. Dewar assembly. Only the inner section, consisting of the helium can and bimodal cavity is shown. This section was surrounded by a nitrogen can and a vacuum jacket.

## C. Dewar Assembly

A schematic diagram of the Dewar assembly is shown in Fig. 4. Only the inner section containing the bimodal cavity and liquid helium can is shown. This inner section was immediately surrounded by a brass can containing liquid nitrogen. This composite structure was then enclosed in a brass vacuum jacket. Control of the tuning probes in the cavity was by means of fiberglas shafts which passed through "O"-ring seals in the vacuum jacket and then through holes in the nitrogen can to engage screws mounted on the cavity. Rotation of these screws results in the insertion or withdrawal of the tuning probes. The screws were lubricated with dry $MoS_2$ powder and were found to operate smoothly at liquid-helium temperatures. Both the cavity and the sample were in vacuum. Thermal contact between the sample and the liquid-helium bath was made by plating one end of the sample with copper and soldering it with gallium metal to a hollow extension of the liquid-helium can. (The transition temperature of gallium is well below the temperatures used in this work.) Care was taken to avoid other superconducting materials in the vicinity of the cavity. Even though the sample was soldered in place, its temperature, as determined from the observed critical field,[31] was always slightly greater than that determined from the vapor pressure of the liquid helium.[32] The sample temperature was taken to be that corresponding to the observed critical field.

The cavity and liquid helium can were bolted tightly together. Nonmagnetic stainless steel waveguides were used to conduct microwave power to and from the cavity. They passed freely through a hole in the helium can. Thermal contact was made at the lower ends of these guides to the liquid-helium can, and further up to the liquid-nitrogen can by flexible guide. Since the cavity and guide system were rigidly attached to the Dewar assembly in only one place, no strains were induced on cooling from room temperature. After thermal equilibrium was established, the guides were clamped to the outside of the vacuum jacket so as to reduce microphonics.

## SAMPLE PREPARATION

The tin used in this study was the "special" grade of the Vulcan Materials Company[33] and was quoted to have a purity greater than 99.9999%. A piece of this tin was melted in a small beaker on a hot plate and transferred with an eye dropper to a split graphite mold, also on the hot plate. The hot plate was permitted to cool. A single crystal was usually obtained in this manner. The orientation of this single crystal was determined by the technique of etch pits.[34] This single crystal was then used to seed another piece of molten tin placed in the same mold. The sample was brought to proper length and the ends rounded with acid. The sample was then electropolished using acetic anhydride and perchloric acid until its diameter was reduced from the mold diameter of 0.125 in. to 0.112 in. The final length of the sample was 1.115 in. The sample was then partially electroplated with arsenic-doped copper to a thickness of about 2 mils, as shown in Fig. 3.

The high quality of the sample surface was verified by the observation of several harmonics of Azbel'-Kaner type cyclotron resonance.[35] A typical recorder tracing of this resonance is shown in Fig. 5. No attempt was made to study this resonance in detail. The fractional width in field $\Delta H/H_c$ of the superconducting transition was found to be approximately 2–3% in all cases. This corresponds to that expected from demagnetizing effects for a sample of the above dimensions. No evidence for trapped flux was found.

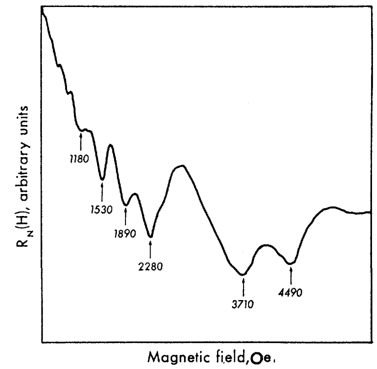


FIG. 5. Typical recorder tracing of cyclotron resonance in the normal state as seen on resistive unbalance. This resonance was not studied in detail but serves mainly to verify the high quality of the sample surface. Approximate field values of the minima are shown. A plot of these values gives evidence for two effective masses; $m_1^*=0.54\,m$ and $m_2^*=0.44\,m$. An average value of about $0.5\,m$ was used in computing the ratio of reactance to resistance in the normal state.

The orientation of the sample was determined by x-ray diffraction to an accuracy of $\pm 2°$ as shown in Fig. 3.

## EXPERIMENTAL PROCEDURE

In this work, two aspects of the surface impedance were studied. The first was the difference between the surface impedance in the normal state just above the critical field and in the superconducting state in zero applied field $Z_{NS}=Z_N(H_c^+)-Z_S(0)$. The second was the change in surface impedance in the superconducting state with applied field from zero to a field $H_c^-$ just less than the critical field, $\Delta Z_S=Z_S(H_c^-)-Z_S(0)$. This field was within 98% of the critical field as the transition to the normal state was always very sharp. This field was used as a measure of the temperature of the sample using the critical field curve of Shaw, Mapother, and Hopkins.[31]

For convenience, most of the experimental data was taken on reactive unbalance. A first-order signal proportional to $x_{XX}-x_{YY}$ and a second-order signal proportional to $r_{XX}+r_{YY}$ may be obtained in this way. Since we must compare $x_{XX}-x_{YY}$ directly with $r_{XX}-r_{YY}$, it is necessary to make a standardizing run on resistive unbalance in order to compare $r_{XX}-r_{YY}$ with $r_{XX}+r_{YY}$. From this run we find

$$r_{XX}-r_{YY}\approx 0.388(r_{XX}+r_{YY}).$$

This calibration factor was assumed to be independent of field and temperature and was applied to all the resistive data.

The quantities $(r_{XX}-r_{YY})/R$ and $(x_{XX}-x_{YY})/R$ are proportional to the reactive and resistive components of the change in surface impedance of the sample with

[31] R. W. Shaw, D. E. Mapother, and D. C. Hopkins, Phys. Rev. **120**, 88 (1960).
[32] Nat. Bur. Std. (U.S.) Monograph **10**.
[33] Vulcan Materials Company, Sewaren, New Jersey.
[34] C. S. Barrett, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1952) pp. 192–195.
[35] M. Ya. Azbel' and E. A. Kaner, Zh. Eksperim. i Teor. Fiz. **32**, 896 (1956) [English transl.: Soviet Phys.—JETP **5**, 730 (1957)]. J. Phys. Chem. Solids **6**, 113 (1958).

applied field. The constant of proportionality is the same for both the resistance and reactance and is a function of the cavity quality factor and sample filling factor. This constant could not be determined but was assumed to be independent of temperature in the liquid helium range. Since the cavity walls were brass, this assumption is reasonable.

The change in the surface impedance with field in the superconducting state is much smaller than the change that takes place when the sample goes normal. The cavity was operated near balance to measure these smaller changes. In this case only the first terms in Eqs. (1) and (2) are important.

The temperature of the sample was varied by pumping on the liquid-helium bath and stabilizing the pressure with a manostat. Measurement of the critical field showed that thermal equilibrium was quickly established in all cases.

## EXPERIMENTAL RESULTS

The contribution of the surface resistance and reactance of the sample to the losses and resonant frequency of the cavity is much smaller than the contribution from other sources. It is not possible, therefore, to determine the absolute value of the sample impedance. The change in impedance with applied field is, however, readily observed.

In order to compare the results with the surface resistance ratio $r=R_S/R_N$, and reactive skin depth $\delta_r$ calculated by Miller,[6] the following assumptions were made:

1. The surface resistance in the superconducting state is assumed to approach zero as temperature approaches 0°K so that the value of $R_{NS}$ observed can be extrapolated to $T=0$°K and used to normalize the results to the surface resistance in the normal state.

2. The values of $R_N$ and $X_N$ and their changes with field at low fields are assumed to be independent of temperature. The field dependence of $R_N$ and $X_N$ at low fields as observed at a temperature of 3.8°K are shown in Figs. 6 and 7. These changes are seen to be of the order of only 1% of $R_N$. These changes were, however, taken into account in determining the surface-resistance ratio and reactive skin depth from the observations.

The surface-resistance ratio, determined using these assumptions, is shown in Fig. 8 together with the theo-

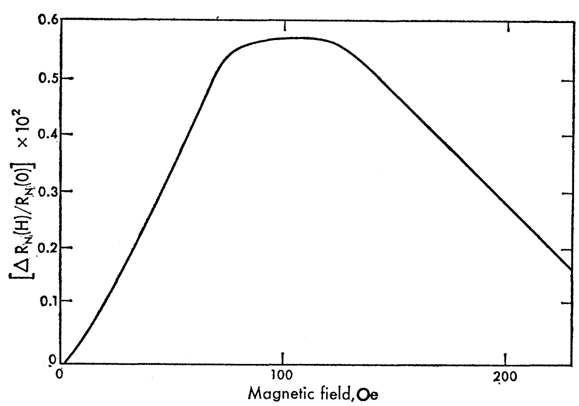


FIG. 6. Field dependence of the normal-state surface resistance for low fields at a temperature of $T=3.8$°K. The experimental error is about ±10% of the observed change.

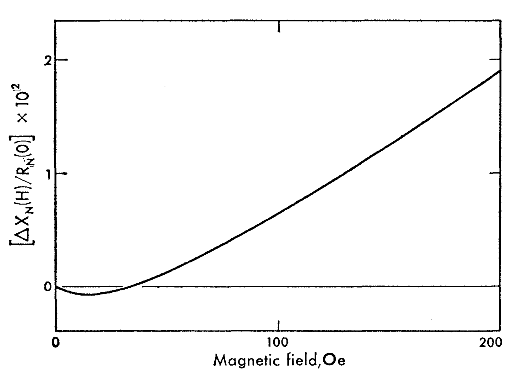


FIG. 7. Field dependence of the normal-state surface reactance for low fields at a temperature of $T=3.8$°K. The experimental error is about ±10% of the observed change.

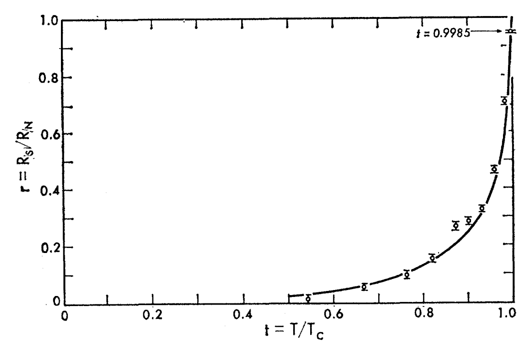


FIG. 8. Surface-resistance ratio versus reduced temperature. A small unexpected knee is observed centered around $t=0.88$. The smooth curve was obtained by extrapolating the results of Miller.[6]

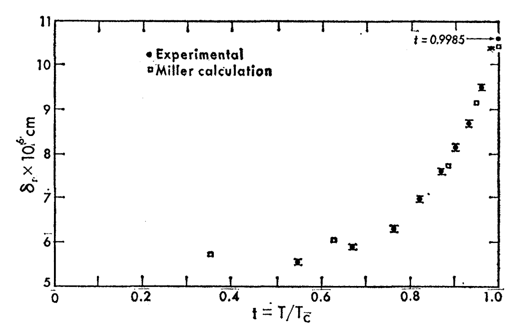


FIG. 9. Reactive skin depth in superconducting tin versus reduced temperature. The squares are from theoretical results of Miller[6] for a polycrystalline sample. The experimental points were obtained from the data, assuming a value of normal state resistance which matches our experimental values to the theoretical results at the transition.

retical curve. This latter curve was obtained by extrapolating the results of Miller[6] from his lowest reduced frequency of $\hbar\omega/kT_c=0.45$ to our value of 0.303.

In order to determine a value of the skin depth $\delta_r=cX_S/4\pi\omega$ from the observations, it is necessary to know the absolute value of the resistance and reactance in the normal state. The calculation of $X_N/R_N$ has been discussed in detail by Chambers.[36] Following Chambers' discussion, the ratio $X_N/R_N=1.78$ was calculated using

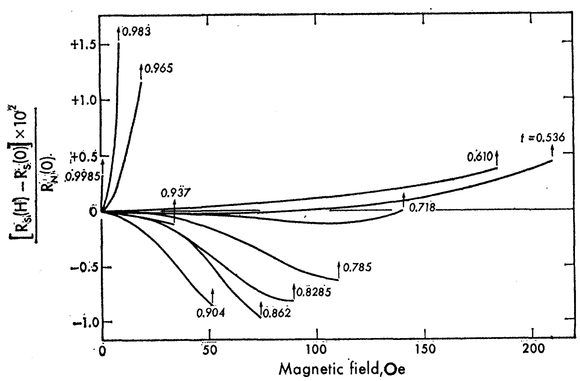


FIG. 10. Surface resistance in the superconducting state versus magnetic field at several reduced temperatures. A gradual change is seen until the critical field is reached where a sharp rise to the normal state value occurs. This break is indicated by the vertical arrow at the end of each curve. The experimental error is about ±5% of the observed change.

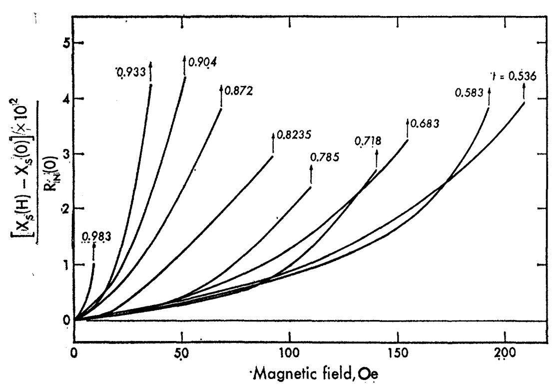


FIG. 11. Surface reactance in the superconducting state versus magnetic field. A gradual increase is seen until the critical field is reached where a sharp rise to the normal-state value occurs. This break is indicated by the vertical arrow at the end of each curve. The experimental error is about ±5% of the observed change.

the tables of Dingle.[5] We used an average value of effective mass $m^*/m\cong 0.5$ determined from the cyclotron resonance data shown in Fig. 5 and a value of $\sigma/l=9.9\times 10^{11}$ ohm$^{-1}$ cm$^{-1}$ from the experiments of Chambers.[37] The value of the surface resistance of single crystal tin has not been reported for our frequency. Furthermore, the surface resistance of tin has been

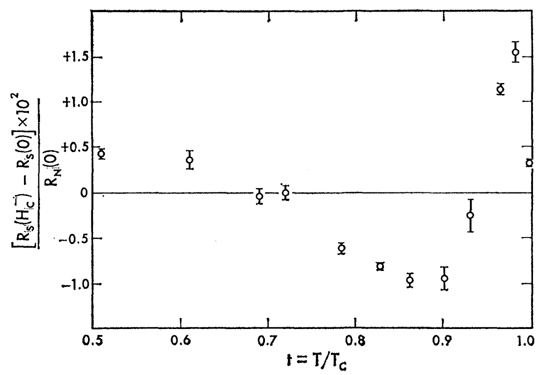


FIG. 12. The total change in surface resistance in the superconducting state with an applied field just less than the critical field versus reduced temperature. The temperature where the maximum negative change occurs coincides with the center of the knee observed in the surface-resistance ratio (Fig. 8).

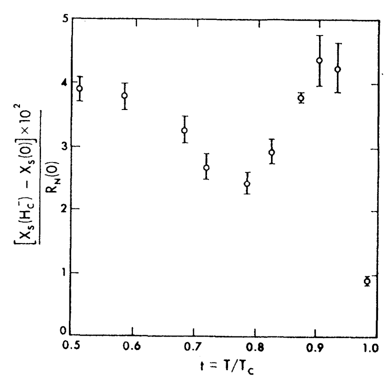


FIG. 13. Total change in surface reactance in the superconducting state with an applied field just less than the critical field versus reduced temperature.

found to be highly anisotropic[3] whereas the calculation of Miller[6] is for a polycrystalline sample. Thus, it was felt that the most reasonable comparison with Miller's[6] theory could be made by choosing a value of the normal-state surface resistance leading to his theoretical skin depth at the transition temperature. The comparison between our computed skin depth and the theoretical values calculated by Miller[6] are shown in Fig. 9.

The changes of resistance and reactance with applied field at constant temperature are shown in Figs. 10 and 11. These changes have been normalized to the surface resistance in the normal state at zero field. A gradual change was always seen up to the field $H_c^-$ where the intermediate state begins to develop. Here a sharp rise to the normal state value occurs. This is indicated by the nearly vertical line at the end of each of the curves. The total changes of resistance and reactance from zero field to $H_c^-$ are shown plotted against reduced temperature in Figs. 12 and 13. These changes are also normalized to the surface resistance in the normal state. Generally speaking the change in reactance with field was found to be more rapid and of much greater total magnitude than the corresponding change in resistance.

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## DISCUSSION OF RESULTS

### A. Initial Slopes

The value of $X_S$ just below $T_c$ was found to be slightly higher than the value in the normal state so that the slope of $X_S$ with increasing $T$ must be negative. An initial negative slope in the reactance was originally predicted by Maxwell, Marcus and Slater.[38] The observed initial slope of $R_S$ was, however, found to be positive.

Abrikosov, Gor'kov and Khalatnikov[39] have derived the following expression for the surface impedance near $T_c$ for $\hbar\omega \ll 2\epsilon_0(0)$:

$$\frac{Z_S}{R_N} = -2i\left(-i+\frac{\pi\epsilon_0^2(T)}{2T\omega}\right)^{-\frac{1}{2}}.$$

This gives for the ratio of the two slopes at the transition

$$(dR_S/dX_S)_{T_c} = -\sqrt{3} = -1.73.$$

Using the data at $t=T/T_c=0.9985$ we observe for this ratio $-1.98$. This result is in good agreement with theory considering the fact that the slope of $X_S$ is increasing rapidly toward positive values as one moves away from $T_c$.

### B. Surface Impedance in Zero Field

Previous investigators working around 25 Gc/sec have reported a smooth decrease in surface resistance with decreasing temperature[38,40–42]. In this investigation we have found in addition a small knee centered around $t=0.88$. This knee is well outside of our estimated experimental error and is reproducible from run to run.

It has been pointed out[43,44] that the onset of quantum absorption should be marked by a change in gradient in the temperature dependence of the surface resistance. The knee in the resistance that we observe may well be evidence for a second band of electrons with a smaller energy gap. The temperature dependence of this energy gap would appear to differ markedly from the BCS form, however, lying well below the BCS gap at the reduced temperature of $t=0.88$.

Suhl, Matthias, and Walker[26] have extended the BCS theory for the case of two or more interacting bands of electrons. They show that in general there is a separate energy gap for each band. They also show that, if interband scattering is much weaker than intraband scattering, the temperature dependence of some of the gaps may differ from the BCS form near the transition temperature. Their results are shown in Fig. 14. They speculate that such effects may occur in those superconductors which have $s$-$p$ bands contributing to the normal state conductivity. Tin and lead are in this category. Tunneling experiments in bulk tin by Zavaritskii[45] have given evidence at least for three distinct gaps. However, the temperature dependence of these gaps appears to have the BCS form near $T_c$. Recent tunneling experiments by Townsend and Sutton[46] have shown the presence of at least two distinct gaps in thick lead films. The temperature dependence of these gaps near $T_c$ has not yet been established.

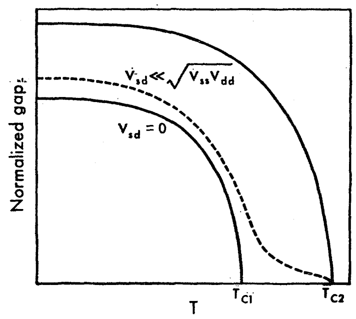


FIG. 14. Temperature dependence of the energy gaps for a multiband model as proposed by Suhl, Matthias and Walker.[26] When interband scattering $V_{sd}$ is equal to zero there are two transition temperatures. When interband scattering is finite, but much less than the geometric mean value of intraband scattering, $(V_{ss}V_{dd})^{\frac{1}{2}}$, the lower transition temperature disappears in the manner shown. One should note the similarity between the temperature dependence of the gap for $V_{sd} \ll (V_{ss}V_{dd})^{\frac{1}{2}}$ and Fig. 15.

### C. Magnetic Field Dependence

A variety of crystallographic orientations, sample shapes, and cavity geometries has been used by the many investigators studying the field dependence of the surface impedance. Since these factors have been found to be so important a comparison of results is difficult. We have limited our investigation to the case where the static and microwave magnetic fields are parallel over at least a large portion of the sample surface. This orientation has been the most extensively investigated and has usually been found to yield the most pronounced anomalous behavior.

For most crystallographic orientations, a minimum in the total change in impedance is usually found at some intermediate temperature, with the minimum in the resistance occuring at a slightly higher temperature than the minimum in the reactance. At the lower microwave frequencies the minima occur very near the transition and are deep enough to show a region in temperature

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where the resistance and reactance decrease with applied field. As frequency increases, the minima move down in temperature, broaden, and decrease in magnitude. Thus, with increasing frequency, first the reactance and then the resistance no longer show a region in temperature where the change with applied field is negative. This frequency dependence is illustrated in Fig. 15, where the temperature of the resistance minimum is plotted versus reduced frequency. The minimum in the reactance follows a similar curve. Spiewak[11] and Richards[12] did not actually locate a minimum. The points shown for Richards[12] (samples [001] and [110]) and Spiewak[11] (sample Sn1) represent the highest temperature at which they took data. Here, the total change in resistance and reactance was found to be negative and decreasing with increasing temperature. Since the total change must go to zero when the critical field goes to zero, there must be a minimum between this temperature and the transition. Data on another sample of Richards[12] ([100]), although showing a decrease in resistance with field extending to lower temperatures than with samples [001] and [110], is not included here because the data on it did not extend above a reduced temperature of $t=0.81$. The temperature dependence of the BCS energy gap is also shown in Fig. 15. The measurements of the decrease in resistance reported by Pippard[13] at 10 Gc/sec, though not detailed enough to establish the temperature of the minimum, are consistent with the dependence shown in Fig. 15. Neither Connell[8] nor Sharvin and Gantmakher[7] observed a decrease with applied field at any temperature. In both cases, however, the frequency was so much lower that the region of anomalous behavior could well be too near to the transition to have been detected.

A comparison of Figs. 8 and 12 shows that the temperature of the knee just coincides with the temperature of the minimum in $[R_S(H_c^-)-R_S(0)]/R_N$. This fact, together with the similarity between the frequency dependence of the magnetic effects (Fig. 15) and the possible temperature dependence of a smaller gap associated with a second band as proposed by Suhl, Matthias, and Walker[26] (Fig. 14) suggests that the anomalous magnetic effects may in fact be associated with this smaller gap.

The theory of Dresselhaus and Dresselhaus,[17] although only partially successful, showed that the effect of the static magnetic field on the orbits of normal electrons could lead to a decrease in resistance and

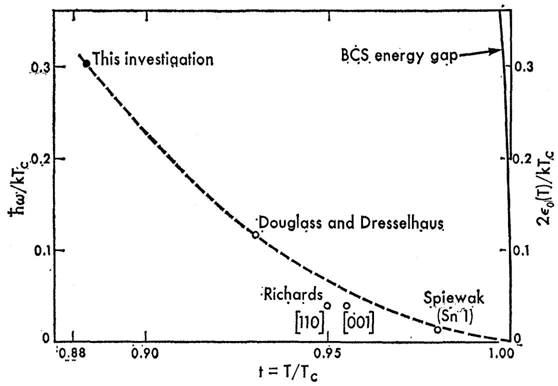


FIG. 15. The temperature of the minimum in the total change in resistance with field as found by various investigators versus frequency. Richards (Ref. 12) and Spiewak (Ref. 11) did not actually locate a minimum. Their points represent the highest temperature at which they took data.

reactance with applied field. Their attempt to fit the data of Spiewak[10,11] suggested that a band of light carriers, present only in the superconducting state, might be responsible for the anomalous magnetic effects.

The fact that the addition of indium to tin causes the disappearance of the anomalous behavior in both resistance and reactance is in contrast with the Dresselhaus theory.[12] This theory predicts that the field dependence of the resistance should become positive but that of the reactance should remain negative. The observed disappearance of the minima follows naturally from our two-gap picture. The addition of impurities will increase the interband scattering, leading to energy gaps with the temperature dependence of the isotropic BCS model.[26] In the absence of a second distinct gap we should not expect a knee in the resistivity ratio or any special behavior in the field dependence of the surface impedance in this temperature region.

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[47] Consejo Nacional de Investigaciones Cientificas y Ténicas de la RCA Argentina Fellow.