temperatures but fail to account for the return to zero at T_c. At fixed temperature, S_d for a type-II superconductor decreases monotonically from the low-field value to zero at H_{c2}. This result is interpreted to be a consequence of increasing overlap of vortices. In type-I superconductors, S_d is also zero at the critical field H_c but in contrast with type-II superconductors, the magnitude of the Ettingshausen effect at low fixed temperatures drops abruptly at about 0.5 H_c. The sudden drop in the magnitude of the Ettingshausen effect is consistent with the previously suggested hypothesis[7] that the mechanism of resistance in a current-carrying intermediate-state slab changes from vortex flow to some other resistive mechanism, such as normal regions, which interrupt the superconducting paths.

Measurements of S_d for a barely type-II superconductor (Nb) are in progress. Experiments bearing on the question of why S_d returns to zero at T_c are planned.

ACKNOWLEDGMENTS

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Anomalies in the Magnetic Field Dependence of the Surface Impedance of Superconducting Sn†

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We have made an extensive study of the microwave surface resistance of superconducting Sn as a function of magnetic field. At reduced temperatures $t \gtrsim 0.6$ and microwave frequencies in the range of 28 to 56 Gc/sec, we find some unusual peaks in the absorption derivative. The anomalous peaks appear at the onset of a range of magnetic field where the resistance decreases with increasing field. The position in field for such a peak is found to vary with temperature approximately as $(1-t^4)^{1/3}$. The amplitude diminishes rapidly with decreasing temperature. The peak position depends linearly on the microwave frequency. The effect is anisotropic with respect to the orientation of the magnetic field in a given sample plane, as well as with the choice of sample plane for a given orientation of the field. The amplitude of the peaks depends on the polarization of the rf current relative to the magnetic field. A very light etching of the sample surface destroys the signals.

The effect is interpreted in terms of magnetic-field-induced surface bound states that correspond to classical skipping orbit trajectories. Such states are shown to have energies in the gap of the energy spectrum of the superconductor. Transitions between the bound state and the continuum above the energy gap can satisfactorily account for the experimental observations. Indeed, we believe that the experiments provide evidence for the existence of surface states in the presence of a magnetic field.

I. INTRODUCTION

MANY metals, including Sn, show an oscillatory variation of the normal-state microwave surface impedance with applied magnetic field in the range 0–100 Oe. This oscillatory effect in the weak-field regime is known to arise from transitions between quantum-mechanical surface states that correspond to classical electron trajectories skipping along the surface. Electrons in such trajectories are bound to the surface region by the magnetic field and perform a periodic motion normal to the metal surface. As Nee and Prange[1] have shown, the quantum-mechanical treatment of this periodic motion leads to a discrete-energy-level spectrum for such electron states.

The observation of some oscillatory variation in the surface impedance of metals in the normal state was first reported by Khaikin[2] and has recently been considered in a detailed study by the authors.[3,4]

The skipping electron trajectories responsible for the oscillations in the normal-state impedance penetrate the metal only to a very small depth. The ground state of the energy-level spectrum corresponds to a penetration into the metal of about 10^{-5} cm, or about one microwave skin depth δ. Successively higher energy

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[1] T. W. Nee and R. E. Prange, University of Maryland, Department of Physics and Astronomy, Technical Report No. 668 (unpublished); Phys. Letters (to be published).

[2] M. S. Khaikin, Zh. Eksperim i Teor. Fiz. 39, 212 (1960) [English transl.: Soviet Phys.—JETP 39, 152 (1961)].

[3] J. F. Koch and A. F. Kip, in *Low Temperature Physics—LT9*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1964), pp. 818–822.

[4] J. F. Koch and C. C. Kuo, Phys. Rev. 143, 470 (1966).

levels in a fixed field penetrate to increasing depths. Because the applied magnetic field in the superconducting state of a metal penetrates a comparable distance and because at a finite temperature thermally excited quasiparticle trajectories contribute to the microwave absorption, we were tempted to extend our measurements to the superconducting state.[5] Indeed, the experimental results show some structure that can readily be interpreted in terms of a bound surface state for quasiparticles closely analogous to that invoked for the explanation of the normal-state effect. Pincus[6] has recently shown that such states do exist in a type-1 superconductor and has considered their effect on the microwave absorption spectrum of Al in the presence of a magnetic field as measured by Budzinski and Garfunkel.[7] In Fig. 1 we show an example of the oscillatory signals in the normal state observed in the (100) plane of Sn, and contrast these with the variations in dR/dH observed in the same crystal at a lower temperature, where Sn is superconducting. The surface-impedance anomalies in superconducting Sn appear as peaks in the resistance derivative, and characterize the onset of a range of magnetic field where the derivative signal decreases and in fact becomes negative. The sharp rise in dR/dH at the end of the recorder trace represents the transition to the normal state at the critical field H_c.

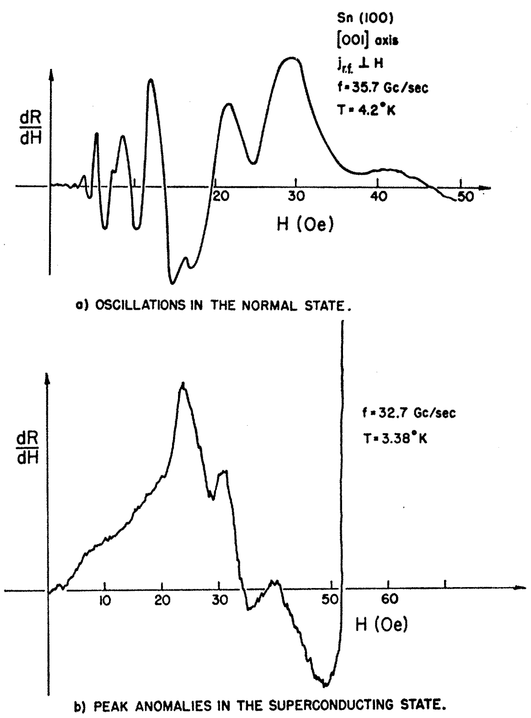


FIG. 1. Spectrum of surface-impedance variations in the normal and superconducting states of a Sn(100) sample.

The problem of the surface impedance of a superconductor in a magnetic field has been considered by a great many researchers. In particular, the decrease in surface resistance with increasing applied magnetic field (i.e., the negative dR/dH in the present experiments) has been analyzed in some detail both experimentally and theoretically.[8] Even so, the anomalous peak structure in the resistance derivative, as studied in the present experiments, has not been noted in earlier work, which concentrates largely on the negative magnetoresistance phenomenon. Many of the features of the dR/dH peaks agree with observations on the negative magnetoresistance region, so that we are led to conclude that there is some relation between these.

Below, we present the results of a study of these derivative peak anomalies together with some speculations as to their origin. We have examined the peak structure as a function of many of the relevant experimental parameters, such as the anisotropy with orientation of H, the dependence on microwave frequency and polarization of rf current, and temperature. We also examine the dependence of signals for a given symmetry direction on the plane in which the signal is observed and the dependence on surface roughness.

II. EXPERIMENTAL ASPECTS

The microwave spectrometer used in this work is essentially the same as that employed for the study of the surface-impedance oscillations in the normal state.[3,4]

Samples used for the superconducting impedance measurements were oriented and cut from single-crystal boules in the shape of thin disks. The diameter-to-thickness ratio for all samples used was greater than 15. The surfaces were carefully electropolished using an acetic anhydride-perchloric acid electrolyte.

The magnetic field is applied strictly parallel to the surface of the sample. Only a small central portion of the sample surface is exposed to the microwaves. The sharp transition into the normal state observed at H_c assures us that there is essentially no intermediate state and that the applied field is uniform over the region of the sample surface where the microwave currents are flowing. The earth's magnetic field has been cancelled to better than 0.05 Oe.

The radio-frequency currents are essentially linear and can be arranged to flow in a desired direction fixed relative to sample axes. The amplitudes of the dR/dH signals are in arbitrary units. Characteristically, the integrated signal amounts to a few percent of

[5] A preliminary report on this work has been given at the American Physical Society meeting in Chicago; see Bull. Am. Phys. Soc. **12**, 418 (1967).

[6] P. Pincus, Phys. Rev. **158**, 346 (1967).

[7] W. V. Budzinski and M. Garfunkel, Phys. Rev. Letters **16**, 1100 (1966); **17**, 24 (1966).

[8] A good review of such work is contained in R. Glosser, Phys. Rev. **156**, 500 (1957).

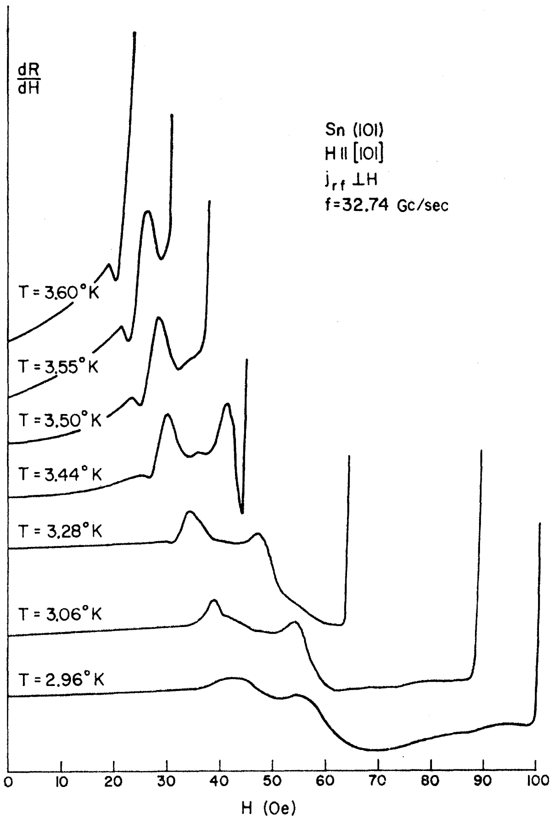


FIG. 2. Sequence of recorder tracings illustrating the dependence of the peak anomalies on temperature. (Note that dR/dH is equal to zero at $H=0$ for each of the traces. They have been displaced for clarity.)

the superconducting-state resistance. The temperatures in the experiment are determined from the vapor pressure of the liquid-helium bath. A slight amount of microwave heating of the sample was observed in the experiments so that the temperature reading had to be corrected to give the appropriate sample temperatures. The magnetic field scale in the figures is only approximate because of the time constant in the lock-in amplifier circuit. Peak positions are determined by averaging up and down sweeps of the magnetic field.

III. EXPERIMENTAL RESULTS

In the present section we seek to summarize the dependence of the dR/dH peak anomalies on various relevant experimental parameters.

Temperature

The peak position in magnetic field as well as the amplitude are functions of temperature. With decreasing temperature the peaks shift to higher magnetic field and diminish in amplitude. Figure 2 shows a set of experimental curves over a temperature range of 3.60 to 2.96°K at a fixed frequency of 32.7 Gc/sec. The critical field H_c, as indicated by the rapid rise in dR/dH at the end of each of the tracings, increases rapidly from about 20 to 100 Oe. It is evident that the peak anomalies shift to increased field much more slowly. We also note that the negative dR/dH region, that appears clearly resolved on each of the last three tracings, likewise shifts to higher fields. It seems appropriate to characterize the peaks as occurring at the onset of the negative dR/dH range of fields. The amplitude of the peaks decreases with temperature as is apparent from the figure. The peaks could not be observed below about 2.80°K. Figure 3 shows the variation of peak position with temperature for one of the two peaks in the sequence of tracings. When plotted against $(1-t^4)^{1/3}$, we find a nearly linear variation of peak position as indicated on the figure.[9] Much of the same dependence on temperature is found for other peaks in Sn, as well as for some more recent data in In crystals.

Frequency

Both the region of negative dR/dH and the peak anomalies are a sensitive function of frequency. We have examined the frequency dependence at four frequencies in the range 28 to 56 Gc/sec and at several values of temperature. Figure 4 shows data at three different frequencies at a temperature of 3.2°K. The peak position is found to shift linearly to higher fields with increasing frequency as indicated in Fig. 5. It is again evident that it is appropriate to describe the peak structure as characterizing the onset of the range of magnetic field where the surface resistance decreases with increasing field. With increasing frequency the absorption derivative increases more rapidly in the region below the peak.

Polarization of rf Current

We find that the direction of the rf current relative to the magnetic field strongly influences the amplitude of the dR/dH signals. Both the anomalous peaks and the subsequent negative dR/dH region are most strongly observed with the current perpendicular to the applied field when the latter is along an axis of

[9] The point that we wish to emphasize here is that the peak position varies approximately as $1/\lambda(T)$. The functional form of $\lambda(T)$ in the nonlocal limit is rather complicated, involving the temperature dependence of both the London penetration depth and the coherence length. To the extent that the coherence length varies slowly with temperature the dominant dependence should arise from the variation of λ_L with temperature. It is for that reason that we plot the data against $(1-t^4)^{1/3}$. Even though, we would want to admit, that when displayed versus $(1-t^4)^{1/2}$ as appropriate for the local limit, one also gets a reasonably linear relation over the range of our data. We have plotted our data on peak positions directly against $1/\lambda(T)$, using measured values of $\lambda(T)$ for high-purity single-crystal specimens as given by Schawlow and Devlin [A. L. Schawlow and G. E. Devlin, Phys. Rev. **113**, 120 (1959)]. Such a plot also convincingly demonstrates $H\propto 1/\lambda(T)$.

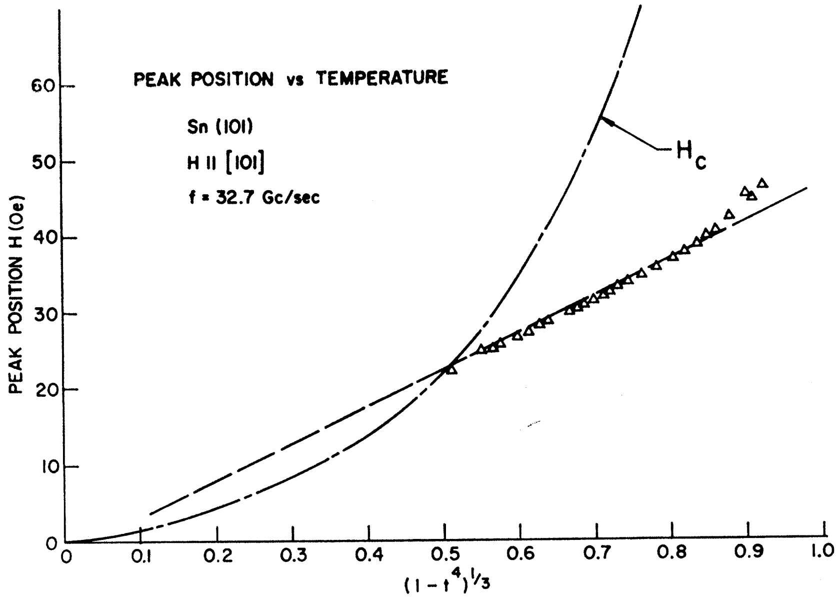


FIG. 3. Plot of peak position as a function of temperature. The points are for the first of the two peaks in the previous figure.

symmetry in the sample plane. The signal vanishes in the parallel mode of polarization as illustrated in Fig. 6. For arbitrary current directions, intermediate to these two polarizations, the signals gradually disappear with approach to the parallel configuration. There is no significant shift in the peak positions with rf-current polarization.

The polarization dependence for the situation where the magnetic field is not in a symmetry direction is not as clear cut. Good signals have been observed in the parallel-current mode.

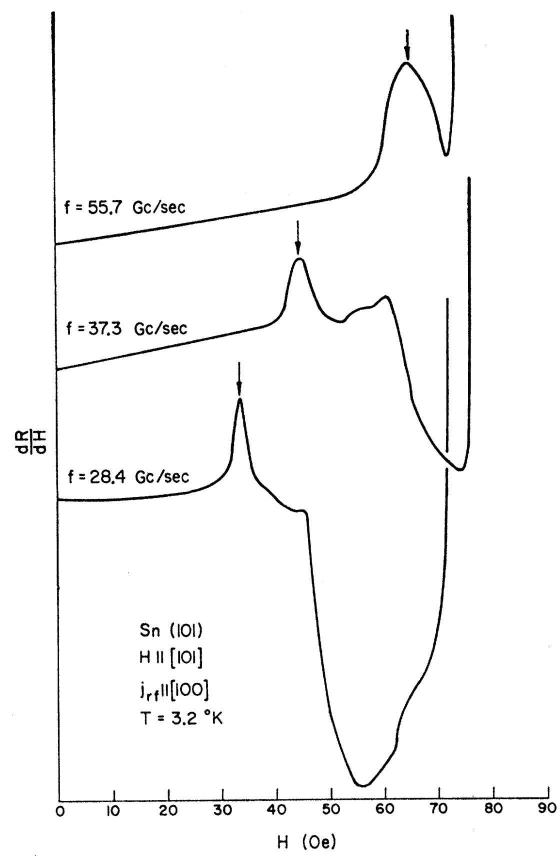


FIG. 4. Spectrum of peak anomalies at three different frequencies.

Anisotropy with Orientation of H

The observed peak anomalies are anisotropic with the direction of the magnetic field in a given sample plane. Both the number of peaks and their position in magnetic field vary with the orientation of the field. Figure 7 shows a sequence of signals for the (101) plane of Sn as a function of the orientation of the magnetic field with respect to the [101] axis of that sample. Characteristic of the angular dependence of such signals is that they shift to increased field as the magnetic field is rotated away from the symmetry direction (Fig. 8). Because of the different angular variation of position and amplitude for each of the peaks in the (101) plane, we conclude that these represent individual peaks, rather than an oscillatory pattern.

Anisotropy of Peak Signals with Sample Plane

Characteristic of the peak anomalies is that, not only do the position and number of peaks resolved depend on the orientation of the magnetic field in a given sample plane, but for a given direction of field the spectrum depends on the sample in which that direction is observed. Data taken along the [001] axis in the (100) and (110) sample planes differ with respect to number and position of the peak anomalies observed (Fig. 9). Similar results were observed for other combinations of axes and symmetry planes.

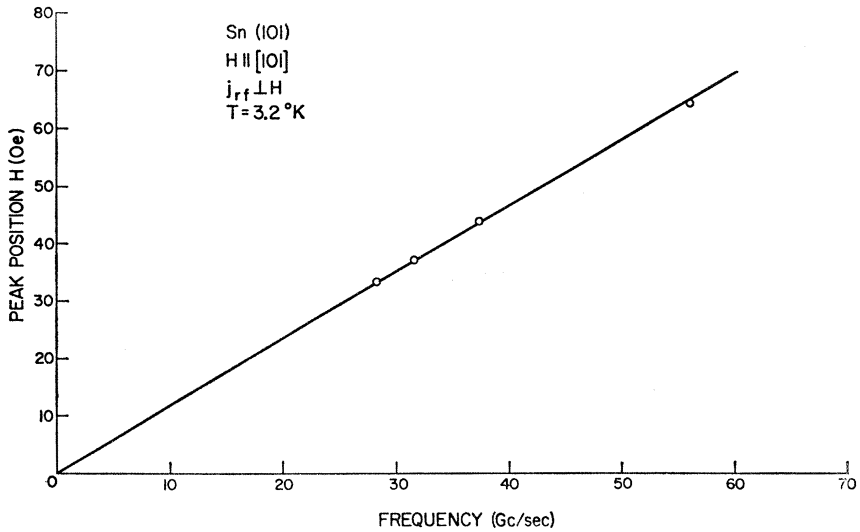


FIG. 5. Plot of peak position versus microwave frequency for four points in the range 28–56 Gc/sec.

Dependence on Surface Roughness

The peak anomalies are found to be very sensitive to the condition of the surface. As illustrated in Fig. 10, a very light etching with dilute HCl vapor causes a broadening and smearing out of the derivative peaks. With increased etching the effect disappears entirely. We conclude that a very smooth, carefully prepared surface is essential to the observation of the effect.

IV. THEORETICAL MODEL AND DISCUSSION

In the present section we engage in some theoretical speculation as to the origin of the peak anomalies. We seek to demonstrate that indeed many of our observations on the effect can reasonably be interpreted on the basis of magnetic-field-induced surface states of the type proposed by Pincus[6] for the superconducting state. We believe that the bound state considered in that work is closely related to the states considered by Nee and Prange[1] in their explanation of the normal-state impedance oscillations. Except for the details of quasiparticle dynamics and the fundamentally different energy spectrum, one can readily extend the

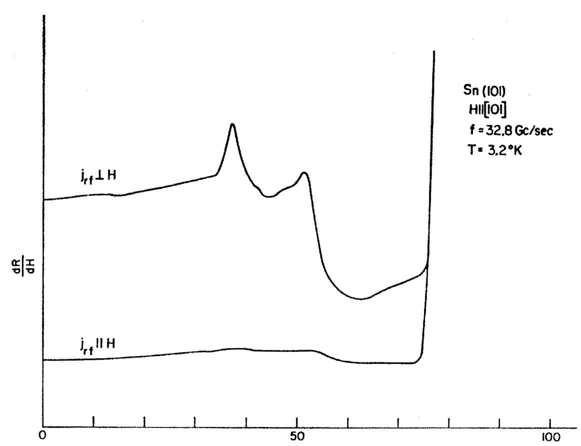


FIG. 6. dR/dH spectrum observed with rf current perpendicular and parallel to the applied magnetic field.

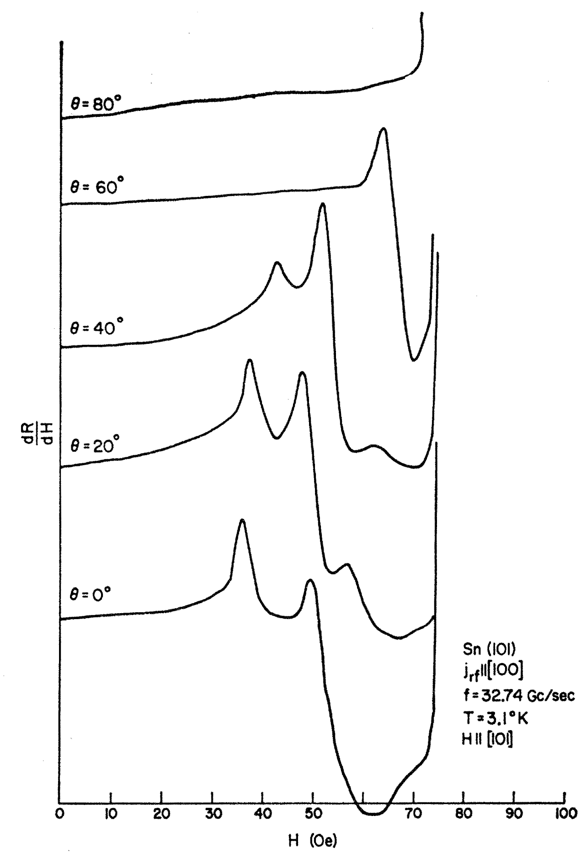


FIG. 7. Sequence of recorder tracings illustrating the anisotropy of the peak signals with the orientation of the magnetic field in the (101) sample plane. $\theta=0$ at the [101] axis.

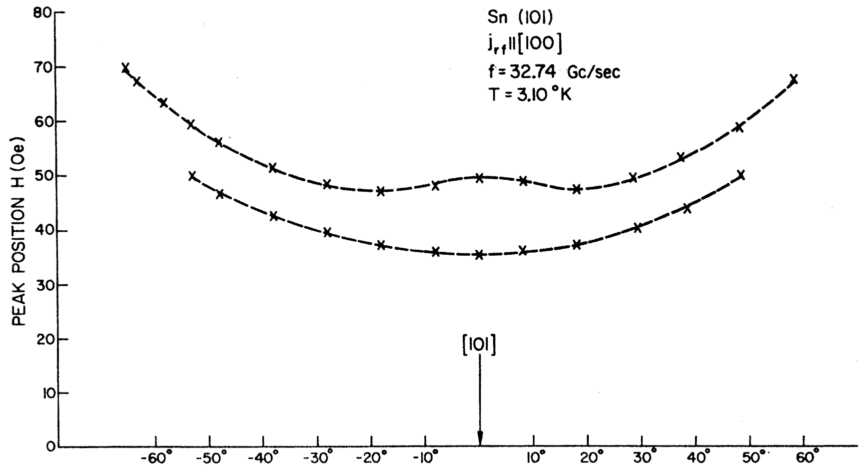


FIG. 8. Variation of peak position with orientation of the field for the two prominent peaks in the previous figure.

ideas proposed by Nee and Prange to the case of the exponentially damped magnetic field as appropriate in the superconducting state. We briefly review the explanation for the normal-state oscillations and subsequently extend the ideas to the case of the inhomogeneous magnetic field.

Consider an electron trajectory skipping along the surface of the metal by periodic specular reflection (Fig. 11). Such an electron is bound to a layer in the surface region that extends from the metal-vacuum interface to the classical turning point of the circular motion. The electron is contained in a potential well and performs a periodic motion in the z direction. With the assumption of a cylindrical Fermi surface aligned parallel to the field H, and choosing a gauge such that $A=(Hz, 0, 0)$, we have for the Hamiltonian describing such an electron state

$$\mathcal{H}=\frac{[P_x+(|e|/c)Hz]^2}{2m}+\frac{P_z^2}{2m}. \tag{1}$$

Confining our attention to the case where the $H\sim 10$ Oe and $P_x\sim P_F$ throughout the motion (i.e., very shallow trajectories), we may solve the equation for P_z

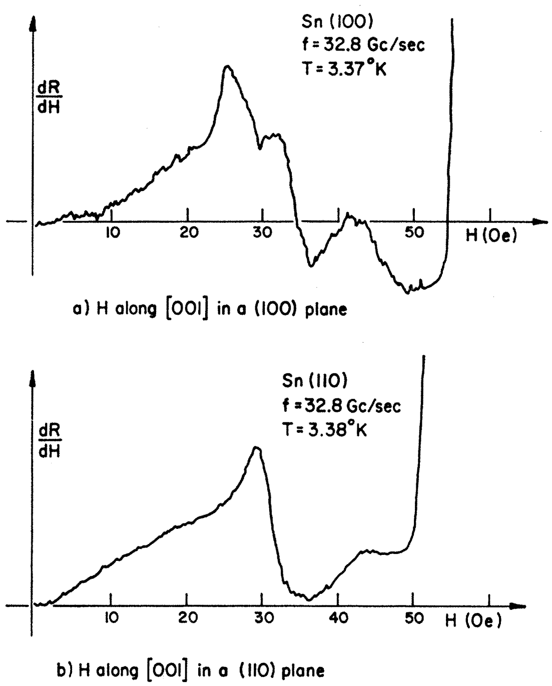


FIG. 9. Spectrum of peak anomalies for the [001] direction observed in (110) and (100) sample planes.

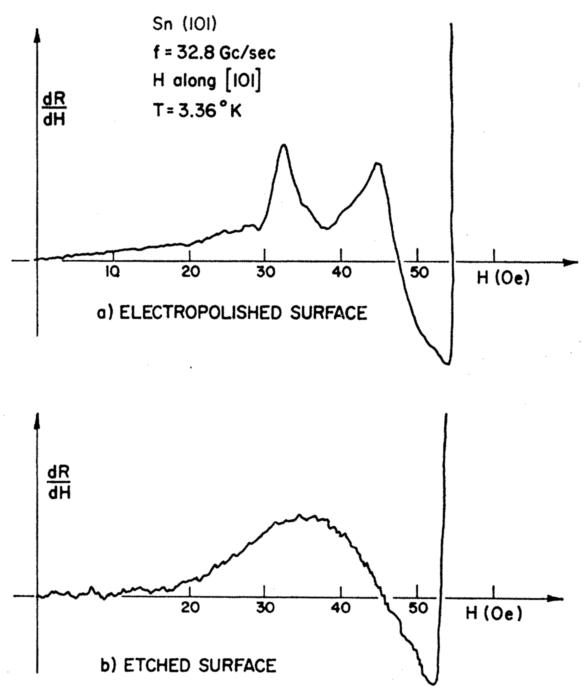
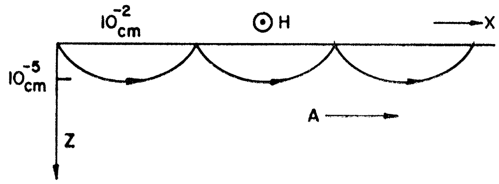
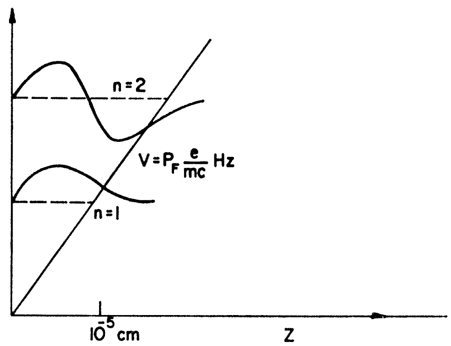


FIG. 10. Effect of etching the sample surface very lightly with HCl vapor.



a) SKIPPING ORBIT TRAJECTORY



b) ENERGY LEVELS AND WAVEFUNCTIONS FOR THE FIRST TWO BOUND-STATE TRAJECTORIES.

FIG. 11. Classical skipping orbit trajectory and corresponding quantum-mechanical states for the normal metal in the presence of a field. For a field of 10 Oe the separation of energy between quantum states is typically in the microwave range. Transitions between the quantum states account for the oscillations of surface impedance observed in weak magnetic fields.

to obtain

$$P_z = [2mE - P_F^2 - 2P_F(|e|/c)Hz]^{1/2}. \qquad (2)$$

Quantizing the periodic motion away from and towards the metal surface according to the Bohr-Sommerfeld prescription, we may write

$$\int_{z=0}^{z=\text{classical turning point}} P_z dz = (n-\tfrac{1}{4})\hbar\pi, \qquad n=1, 2, 3, \text{etc.} \qquad (3)$$

The phase factor $\frac{1}{4}$ occurs in this expression because of the single linear turning point in this problem. The integration can be performed immediately to yield a set of energy levels

$$E_n - E_F = [(3\pi/2\sqrt{2})(\hbar e/c)]^{2/3}(P_F/m)^{2/3}(n-\tfrac{1}{4})^{2/3}H^{2/3}. \qquad (4)$$

Transitions between the energy levels readily account for the observed oscillations in the normal-state surface impedance. The depth of penetration of the ground-state trajectory ($n=1$) into the metal is on the order of 10^{-5} cm in the range of magnetic field where the low-field oscillations have been observed. This can readily be seen by equating the ground-state energy to the potential at the turning point (see Fig. 11). Higher-order states penetrate into the metal to increasing depth as $n^{2/3}$.[10]

In the superconducting state of the metal the situation is fundamentally different. For the Sn specimens used in the experiments we have mean free path $l \sim 10^{-1}$ cm, coherence length $\xi \sim 10^{-4}$ cm, and the London penetration depth $\lambda_L \sim 10^{-6}$ cm. Accordingly, we are dealing with a pure, type-I superconductor in the nonlocal or Pippard limit. The depth of penetration of the magnetic field into the material will be $\lambda \sim \lambda_L^{2/3}\xi^{1/3} \sim 10^{-5}$ cm. We may approximate the dependence of H on z as an exponential decay in the distance λ, and consequently take $A = (-H\lambda e^{-z/\lambda}, 0, 0)$. The choice of gauge here is such as to satisfy the London equation linking the vector potential with the screening current.

If we ignore the theoretical niceties of quasiparticle dynamics and treat our excited states in the superconductor as electrons, we can write in analogy with the normal-state case

$$\mathcal{H} = \left(\frac{P_x - (|e|/c)H\lambda e^{-z/\lambda}}{2m}\right)^2 + \frac{P_z^2}{2m}$$
$$\approx [(P_x^2 + P_z^2)/2m] - 2P_x(|e|/c)H\lambda e^{-z/\lambda}. \qquad (5)$$

The second term in the expression for the energy appears as a velocity- and position-dependent potential that can be positive or negative, depending on the direction of P_x relative to the vector potential, or alternatively relative to the direction of the screening current. We see that the application of the magnetic field parallel to the surface of the superconductor results in a change of the energy of the quasiparticle states in the surface layer. In particular, let us examine those states travelling essentially parallel to the surface such that $P_x \sim P_F$, and in a direction such that they are parallel to the screening current in the surface layer. As is obvious from Fig. 12, these electron states have their energy lowered by the field, and moreover are exactly those states whose trajectories will be bent toward the surface so as to give rise to a skipping orbit bound state in the surface layer.

In the lower portion of Fig. 12, we plot the potential energy of the group of electrons considered above as a function of distance into the metal. By comparison with the situation in the normal state we see that the scale of distances is such that we would expect to find a lowest-energy bound state in the superconductor analogous to the ground state ($n=1$) in the normal metal. The lowest-energy bound state would represent a particle trapped within a distance λ of the surface and with an energy approximately equal to the depth of the potential well. Successively higher energy levels

[10] An alternate "back of an envelope" type derivation of the energy-level scheme and other parameters of this problem can be obtained by quantizing the flux enclosed by the skipping orbit trajectory [i.e., $\phi_n = (n-\frac{1}{4})2\pi\hbar c/e$].

in the exponential potential well would fall very close to the energy continuum that represents states not trapped by the field because their initial momentum in the direction normal to the surface exceeds a critical value. We note, however, that the first bound state will contribute most significantly to the microwave absorption because it represents an electron that stays in the rf skin layer throughout its motion. Consequently, we shall confine our discussion to this lowest bound state, even though we recognize that additional states can exist.

The bound state represents an energy below that of the unbound quasiparticle states and hence a state in the gap of the energy spectrum. Since the state represents a particle confined to the surface region, the depression of energy should be some suitable average of the potential that exists in the surface. We should expect that the energy separation of the bound state from the continuum is on the order of $E \sim (P_F e/mc) H\lambda$ as suggested by Eq. (5). A rigorous calculation gives

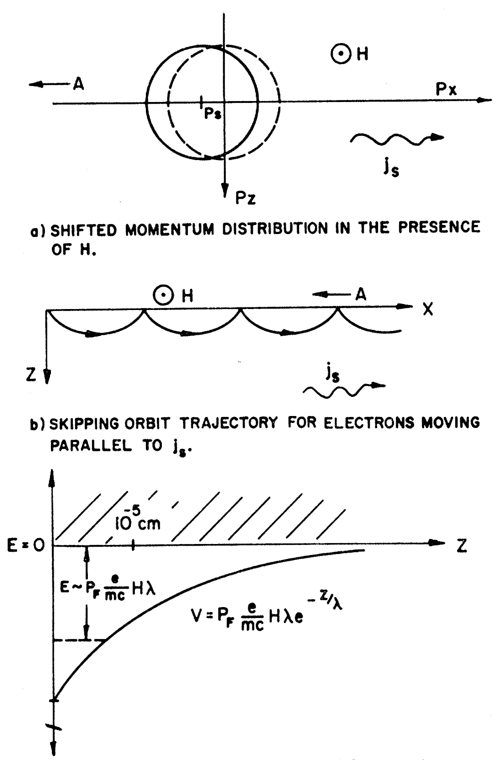


FIG. 12. In the superconducting state quasiparticles with momentum P_F parallel to the screening current have a lower energy than those antiparallel to j_s. Part (a) shows the relative direction of **H**, $\mathbf{j_s}$, **A** and the resultant displacement of the Fermi sphere in momentum space. Exactly those electron trajectories parallel to the screening current have the appropriate curvature to form a bound surface state as indicated in part (b). The last portion of the figure is a plot of the potential of the parallel electrons as a function of distance into the metal. The lowest-energy bound state has been indicated schematically.

for the first bound state in the exponential well[11]

$$E = (e/mc) P_F \lambda H - 3.72(\hbar^2/2m)(eP_F/\hbar^2 c)^{2/3} H^{2/3}. \quad (6)$$

To the extent that the second term is small, i.e., the bound-state energy falls close to the bottom of the potential well, the energy will be proportional to applied magnetic field. The detailed calculations of energy levels given by Pincus are substantially in agreement with our very much simplified treatment.

It appears to us that the picture of skipping orbit trajectories as sketched in the present arguments is largely equivalent to the more detailed and consequently less obvious derivation that Pincus gives. It would seem to us, however, that a choice of potential, as in Fig. 12, more nearly corresponds to the physical situation, and is preferable to the potential considered by Pincus. The correct choice of boundary conditions for our model should be $\psi(0) = 0$ and would correspond to the antisymmetric solution for the potential considered by Pincus. The calculations in that paper are based on the symmetric wave functions. Nevertheless, the physically significant results are much the same.

We turn next to a consideration and explanation of the various experimental observations in terms of the surface-state model. In Fig. 13 we consider schematically the density-of-states function dn/dE appropriate for a superconductor. We include an additional level in the gap that represents the surface bound state of lower energy. At finite temperature $T \sim 0.8T_c$, we have a significant population of quasiparticles in the continuum as well as in the bound-state level in the gap. The microwave energy $\hbar\omega_{rf}$ corresponds to a small fraction of the gap energy Δ. In the absence of the magnetic field the surface state merges with the continuum and absorption results from excitations of quasiparticles in the continuum. With the application of H, the surface state moves down into the gap. Scattering of the occupied bound states into the continuum gives rise to a new magnetic-field-dependent increase of the absorption as manifested by the increasing dR/dH in the experiment. As H increases, we find a peak in the absorption spectrum as $\hbar\omega \sim E$, because of the large density of final states into which we can scatter. A further increase in H, however, increases E, such that no further scattering is possible and consequently we expect a decrease in the absorption as manifested by the negative magnetoresistance region of the experimental curve. The detailed line shape for the microwave absorption curves will depend on the density-of-states curve for the superconductor as well as on the width of the bound-state level. It is important here to point out the importance of the contribution of the bound-state trajectory to the rf surface current.

[11] See, for example, P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. 2, p. 1671.

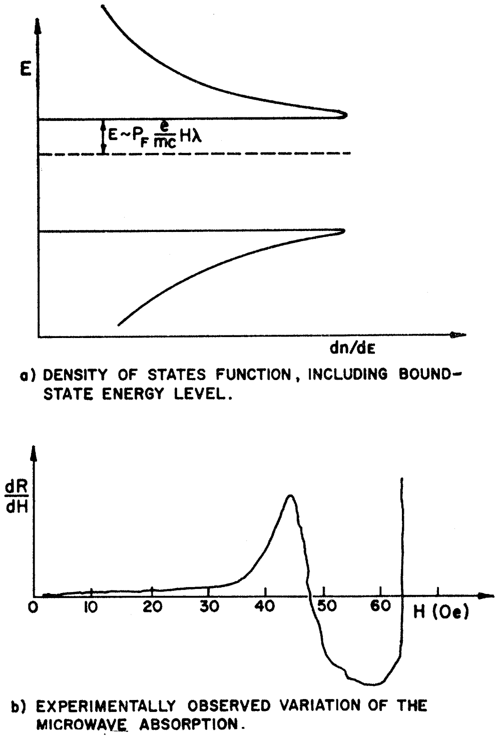


FIG. 13. Density of states as a function of energy for the type-1 superconductor in a magnetic field. The bound surface states are indicated by the additional state in the energy gap. The lower portion shows the characteristic microwave-absorption changes observed in the experiments and attributed to transitions between the bound state and the continuum. (The experimental trace shown is actually due to indium for an orientation where there is only a single peak anomaly.)

We note that microwave surface currents are confined to a layer of thickness 10^{-5} cm and only carriers that spend a significant portion of their mean free path in this layer will effectively carry current. This is the case for the skipping orbit trajectories.

With this model in mind, one may also expect to see an absorption due to breaking of the superconducting pairs. The minimum energy required for such a process to occur in a field H is $2\Delta - E$, because breaking of a pair implies the simultaneous creation of two particles moving in opposite direction. Only one of these can occupy the bound-state level. An estimate of energy and frequencies involved for this process, however, shows that we should not expect to see it in the present experiments.

We can readily show that the peak anomalies occur at the right values of field H and frequency. Using the first term of Eq. (6), with $P_F/m \sim 10^8$ cm/sec, $\lambda \sim 10^{-5}$ cm, and $H \sim 10$ Oe, we get a value of $E \sim 10^{-16}$ erg, substantially in agreement with the experimental microwave energy.

As a function of temperature we have found a shift of the peak anomalies to increasing fields (Fig. 2). Qualitatively, we may argue that since the energy of the bound state should be of the form $E \propto H\lambda$, a decrease in λ with decreasing temperature requires a corresponding increase in H to give rise to the same transition at constant frequency. In the nonlocal limit, where $\xi \gg \lambda_L$, we would expect the effective depth of penetration λ to be proportional to $\lambda_L^{2/3}\xi^{1/3}$. We have plotted $H(T)$ versus $(1-t^4)^{1/3}$ in Fig. 3 and find a reasonably good linear dependence.[9] The observed decrease in the amplitude of the effect with decreasing temperature we attribute to a decrease in the population of the quasiparticle states.

The linear dependence of the peak anomalies on experimental frequency is immediately apparent from the foregoing discussions. The peak occurs with $\hbar\omega \sim E \propto H$. We note here that the calculations by Pincus and Eq. (6) in the present work show that E is only approximately linear with H and that one may possibly expect to get deviations in the frequency scaling law when examined over a wider range of frequency.

An absorption maximum is expected when the radio-frequency surface current flows parallel to the direction of the skipping orbit trajectory. Consequently, if H is along the axis of a cylindrical section of the Fermi surface, the maximum signal is expected for current perpendicular to H.

The angular variation of the peak positions in the (101) sample plane is that expected for a cylindrical section of Fermi surface aligned along the [101] axis. The increase in peak position away from the axis results because for a cylindrical section only the component of H along the axis of the cylinder is effective in determining the curvature of orbits. A contribution to the angular variation is also expected if the depth of penetration of the field λ should depend on the direction of $\mathbf{H}$. The particular dependence of the two peaks in the (101) plane on the orientation suggests that these two must originate from two different cylindrical portions of the Fermi surface. It should also be possible to observe multiple peaks from a single section of the Fermi surface when there are several bound states in the energy gap. No such case has as yet been positively identified.

We note that the orientation dependence of the oscillatory signals in the normal state shows much the same characteristic variation of peak position with angle away from a symmetry direction. Even so, it has not proved possible in the (101) plane to make a detailed comparison of normal-state signals with the superconducting anomalies. We find along the [100] axis in that plane well-resolved normal-state oscillations. No corresponding peak anomalies in the superconducting state have been identified. It is not unreasonable to suppose that the values of P_F and λ for this orientation are such as not to give a bound state confined to the rf skin layer. More detailed work is necessary to make an exact correlation of normal- and superconducting-state signals.

The observed dependence on the sample plane of signals for a fixed direction of the field is much the same as in the normal state[3,4] and is expected for cylindrical sections of the Fermi surface with noncircular cross-section. The dependence of the peak anomalies on both the direction of the field and the sample plane identifies the effect as arising from only a point or small region of the Fermi surface.

The broadening and washing out of the peak anomalies with light etching of the surface we attribute to a lifetime effect of the skipping orbit surface states. We expect that a slight perturbation of the surface is sufficient to greatly reduce the chance of specular reflection and consequently reduce the lifetime of the state. The broadening of the corresponding energy level will result in the disappearance of the peak anomalies. We have found that the etching destroys the normal-state oscillations along with the peak anomalies.

V. CONCLUSION

In summary, we find that all the various experimental observations on the peak anomalies in the superconducting state can readily be explained in terms of the magnetic-field–induced bound states as discussed in the previous section. We believe that the experiments provide a good demonstration of the existence of such states. It appears to us that experiments of this type can provide information on the dynamical parameters of the quasiparticle states, as well as on the temperature and orientation dependence of the magnetic field penetration λ into the superconductor. The line shape observed for the peak anomalies seems to be closely linked to the density-of-states function for the quasiparticle states. It should prove possible to study quasiparticle scattering from surface roughness or possibly impurities.

We also find that the mechanism proposed for the variation of the absorption with applied magnetic field can account in a most reasonable manner for the negative magnetoresistance that has been observed in many experiments on the surface impedance of type-1 superconductors.[8] It appears reasonable that the surface bound states in the regime of fields above the peak anomaly can contribute significantly to the rf surface current, without being able to absorb energy. This mechanism should indeed reduce the surface resistance to a value less than the zero-field resistance.

While it seems surprising to us that no note has been taken of the existence of the peak structure in earlier work, we nevertheless can cite several reasons for this. To a large extent measurements have been made on $R(H)$ rather than its derivative. The peaks are expected to show up more strongly in the derivative. The somewhat lower frequencies used in earlier experiments may not show the peak structure as strongly. With reference to Fig. 4, we see that the integrated signal associated with the peak decreases with lower frequency. The peak signals would not be expected to show up distinctly where cylindrical specimens have been used, because the effect is anisotropic with the orientation of the sample surface. Another possible reason could be the surface preparation; we find that even a light tarnish broadens and washes out the peak structure.

We realize the shortcomings of many of our hand-waving arguments and recognize the need for exacting calculations of surface impedance along the lines proposed by Pincus. Even so, we feel that the physical model outlined in the discussion is a good approximation to the true state of affairs.

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