Surface States in Superconducting Indium

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Measurements of the microwave (10–40-GHz) surface impedance of superconducting indium in a magnetic field have revealed the distinct peak structure that is associated with the excitation of quantum-mechanical surface-bound quasiparticle states. The impedance peaks are found to depend on frequency and temperature as predicted by the model. We have discovered a sensitive dependence of the peaks on the surface roughness that can be understood qualitatively in terms of Pincus's theory of the surface states. Following Garfunkel, we have carried out calculations of the surface impedance that correctly give peaks in the impedance derivative at values of magnetic field where the surface electron binding energy equals the microwave photon energy. The calculated peaks have the experimentally observed frequency-temperature scaling.

I. INTRODUCTION

WE are concerned here with the measurement and interpretation of the microwave surface impedance of a type-I superconductor in a magnetic field. Such studies have a long and venerable history dating back to experiments carried out by Pippard some 20 years ago. More recent, and more closely related to the present work, are the experiments of Glosser and Douglass,[1] Glosser,[2] Budzinski and Garfunkel,[3] and Koch and Kuo.[4]

The Koch-Kuo experiments centered on the discovery of sharp peak structure in the magnetic field dependence of the surface impedance of tin crystals. Such resonance peaks were found to shift linearly in magnetic field with applied microwave frequency. With decreasing temperature, peaks were observed to shift to higher magnetic field approximately as the reciprocal of the penetration depth $\lambda(T)$ of the magnetic field. An interesting perspective on the interpretation of this data was gained with the theoretical prediction of the existence of bound quasiparticle states in the screening current layer.[5] These magnetic-field-induced surface states, as has recently been shown,[6] can account for the important features of the data. A closely related point of view, used by Garfunkel in a calculation of surface impedance,[7] envisions the group of screening current carrying electrons as experiencing a Doppler shift of their energy spectrum relative to electrons unaffected by the magnetic field. His impedance calculation takes account of microwave transitions from the Doppler shifted surface states. As we show in a later section, such a calculation not only reproduces the sharp derivative peak structure but also gives the experimentally observed frequency-temperature scaling of the peak position.

The present experiments in indium are a sequel to the Koch-Kuo work in tin. We have increased the range of experimental frequencies by extending observations down to 10 GHz. The more extensive and accurate temperature dependence data in indium has allowed us to confirm the relation of peak position to the temperature dependent penetration depth $\lambda(T)$. We have discovered a sensitive dependence of peak position on surface preparation.[8] This aspect was not realized in the tin experiments. The surface impedance calculations presented in this paper relate our observations of the dR/dH peaks to Garfunkel's interpretation[7] of the magnetic-field dependence of the impedance.

II. SOME RELEVANT THEORY

We are interested here in presenting just enough theory to provide the necessary motivation for later discussion.

Central to the interpretation of the impedance spectra is the realization that there exist bound quasiparticle states in the screening current skin layer of a type-I superconductor in the presence of a magnetic field. These surface states have energies in the gap of the BCS[9] spectrum of electronic excitations. Starting with the Bogoliubov equation and approximating the penetration of the magnetic field as a step function, Pincus has found solutions for the bound state energies as a function of applied magnetic field strength. The kinetic energy of motion perpendicular to the surface,

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[1] R. Glosser and D. H. Douglass, in *Low Temperature Physics* (Plenum Press, Inc., New York, 1965), Vol. 9, p. 385.
[2] R. Glosser, Phys. Rev. **156**, 501 (1967).
[3] W. V. Budzinski and M. P. Garfunkel, in *Low Temperature Physics* (Plenum Press, Inc., New York, 1965), Vol. 9, p. 391; Phys. Rev. Letters **16**, 1100 (1966); **17**, 24 (1966).
[4] J. F. Koch and C. C. Kuo, Phys. Rev. **164**, 618 (1967).
[5] P. Pincus, Phys. Rev. **158**, 346 (1967).
[6] J. F. Koch and P. Pincus, Phys. Rev. Letters **19**, 1044 (1967).
[7] M. P. Garfunkel, Phys. Rev. **173**, 516 (1968).
[8] J. F. Koch and J. R. Maldonado, in *Low Temperature Physics* (St. Andrews University Press, St. Andrews, 1969), Vol. XI, p. 764.
[9] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev,. **108** 1175 (1957).

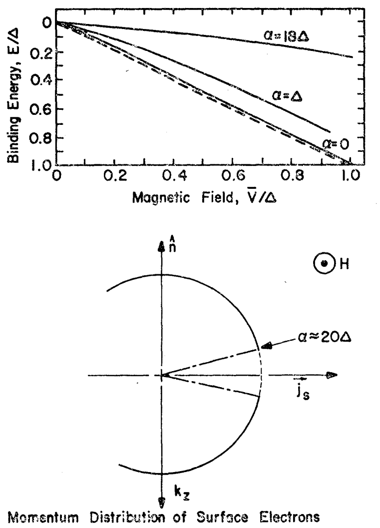

FIG. 1. Surface electrons moving parallel to the Meissner screening currents are bound in quantum-mechanical states. In the first part of the figure is shown the variation of the binding energy with normalized magnetic field for electrons with different values of the kinetic energy normal to the surface [after P. Pincus, Phys. Rev. **158**, 346 (1967)]. The lower half of the figure indicates schematically the narrow angular region on the Fermi surface, over which electron states become bound to the surface of the metal, in energy levels within the superconductor gap. Only electrons moving at a small angle to the surface are affected by the magnetic field.

α in the Pincus paper, plays the role of a parameter in that calculation.

For the cylindrical section of Fermi surface considered in Fig. 1, Pincus finds bound-state solutions for states only in the immediate neighborhood of $k_z=0$ and for which the Fermi velocity v_F is parallel to the screening current. With $\alpha=0$ (i.e., $k_z=0$) the state has a maximum binding energy as measured from the top of the gap of the BCS spectrum. As is evident from the figure, for $\alpha=0$ the energy varies linearly with applied field H and is nearly equal to the depth of the square well potential $\bar{V}$ in the Pincus theory. For this state, we write the binding energy ϵ as

$$\epsilon \approx \bar{V} \approx (ehk_F/m)\lambda H\,, \tag{1}$$

where k_F is the Fermi momentum and λ the temperature-dependent penetration depth of the magnetic field. Higher values of α yield solutions with decreased values of the binding energy, until at $\alpha \approx 20\Delta$ this energy is negligibly small. For sufficiently small values of the parameter α several different bound state solutions are possible, but have been omitted in the diagram. As the value of α increases, not only does the binding energy decrease, but also an appreciable deviation from the linear dependence on magnetic field becomes apparent. The angular region of the Fermi surface, containing electrons whose energy has been significantly affected by the presence of the field, is

$$\theta \approx \left(\frac{\alpha_{\max}}{E_F}\right)^{1/2} \approx \left(\frac{20\Delta}{E_F}\right)^{1/2} \approx 5°$$

for the case of indium.

The fact that only electron states moving nearly parallel to the surface contribute significantly to the Meissner currents is also evident from the usual consideration of nonlocal effects. When λ is much less than the coherence length ξ (for indium, $\lambda/\xi \approx 0.05$), the surface currents are due only to a narrow zone with angular width of the order of λ/ξ about the line $k_z=0$. Only these electron states experience a shift of momentum by something like mv_s, where v_s is the drift velocity associated with current flow in the surface layer.

It is essentially this picture that provides the starting point for Garfunkel's calculation.[7] All electrons contained in the penetration depth and moving at a small angle (less than λ/ξ) to the surface are considered as moving with identical velocity v_s and are shifted in energy by an amount $\hbar \mathbf{k}_F \cdot \mathbf{v}_s$ relative to the spectrum of electrons unaffected by the magnetic field. Relating v_s to the applied field, we have

$$v_s \approx (e/m)\lambda H\,, \tag{2}$$

so that [compare with Eq. (1)] all current carrying electrons experience an energy shift equal to $\bar{V}$. The fine points of how the wave functions of the surface electrons are changed, or how the energy shift varies with α, are overlooked in this approach.

The close analogy of the Prange-Nee surface quantum states[10] to those described by Pincus has been stressed by Koch and Kuo.[4] The description of the Pincus bound states in terms of skipping trajectories provides a good physical interpretation of the states, while accounting for superconductivity only as an afterthought. The skipping trajectories described by Koch and Kuo are essentially solutions to the Bogoliubov equation in the limit where the gap energy Δ that couples the equations can be ignored. In the classical terms of skipping electron trajectories, the limited range ($\alpha > 20\Delta$) of bound solutions can be understood as a limit on the electron trajectories that will be trapped at the surface in a magnetic field decaying with distance into the metal. An electron starting at a sizeable angle (large α) to the surface will not be deflected sufficiently to make a return trip to the surface and will escape from the skin layer.

In the consideration of microwave absorption the parallel-moving electrons play a central role under the conditions of long mean free path l and small skin depth δ, as is the case in these experiments. According to the description of the anomalous skin effect, only electrons moving at angles less than l/δ interact effec-

[10] R. E. Prange and T. W. Nee, Phys. Rev. **168**, 779 (1968); T. W. Nee, J. F. Koch, and R. E. Prange, *ibid.* **174**, 758 (1968).

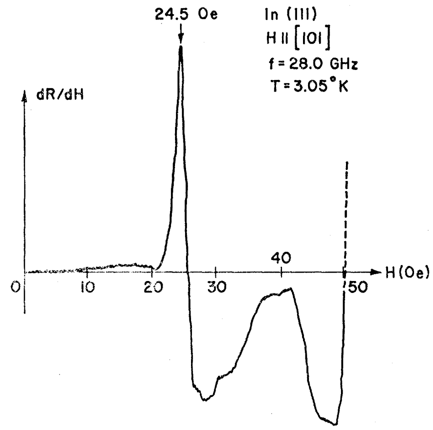

FIG. 2. Microwave absorption derivative (dR/dH) versus magnetic field applied parallel to the surface of a superconducting (111) plane indium sample. The sharp rise of the impedance at 50 Oe represents the transition to the normal state at the critical field.

tively with microwave fields in the skin layer. The experimentally observed dR/dH-versus-H curves, an example of which is shown in Fig. 2, show pronounced and sharply peaked dR/dH maxima. In Fig. 2 the 24.5-Oe peak dominates the spectrum. The structure between 30–40 Oe is comprised of several overlapping peaks that are resolved at other orientations of the field (compare Fig. 6). The theoretical model[4,6] for such peak signals envisions the absorption of photons by a surface-bound electron state, which is subsequently scattered into a state unperturbed by the magnetic field and whose energy spectrum is the usual BCS curve. The narrow lines observed in the experiment imply that of the entire spectrum of possible bound states (ranging to $\alpha\approx 20\Delta$, compare Fig. 1), those with maximal binding energy (near $\alpha=0$) contribute most effectively to the absorption. The dR/dH peak is expected to occur when the maximum binding energy [Eq. (1)] equals the microwave photon energy $\hbar w$, i.e.,

$$\hbar w=(e\hbar/m)k_F\lambda H. \tag{3}$$

The absorption of a photon also implies a momentum change of the electron state in a direction normal to the surface by an amount on the order of $2\pi/\delta\approx 10^6$ cm^{-1}. Momentum parallel to the surface is conserved. In the Pincus theory the momentum question is buried in a matrix element of the microwave electric field between the initial bound-state wave function and a final plane-wave state.

III. EXPERIMENTAL NOTES

The experiments are done using a standard microwave-absorption spectrometer. We measure the surface-resistance derivative (dR/dH) as a function of magnetic field applied parallel to the surface of a thin disk-shaped specimen.

Samples are grown from 69 grade Cominco indium, x-ray oriented, and spark-cut to the desired crystal plane. The surfaces are subsequently lapped gently on an acid-soaked cloth and electropolished in a methyl-alcohol–nitric-acid bath. The thickness of the sample never exceeded 1/20 of the diameter. To insure a uniform parallel magnetic field at the sample surface only a small central portion of the disk is exposed to the microwave radiation.

For our studies of the effect of surface roughness we worked with two different approaches. The first of these was an "etch and repolish" procedure. The sample was exposed to acid vapor and acquired a heavily, but uniformly, corroded surface. It is then electropolished for controlled time intervals to achieve various degrees of roughness. Alternatively, the surface was mechanically roughened by brushing with a camel hair brush. The stroke direction would determine the direction of the surface perturbation.

The most satisfactory method of determining sample temperature was from the observation of the discontinuous change in microwave absorption at the critical field $H_c(T)$. We independently established the relation of the critical field, as judged by a maximum in the absorption derivative, to the sample temperature. With the sample immersed in liquid helium, we measured H_c and determined T from a helium-vapor pressure reading. In subsequent runs where data is taken, the sample is linked only loosely to the helium bath with exchange gas and surface temperature is taken from the $H_c(T)$ relation. Using a calibrated carbon-resistance thermometer clamped to the back of the sample, we convinced ourselves that no significant temperature variation of the sample occurs until the critical field is reached.

The magnetic field is calibrated to an accuracy of 0.3% for the range 0–50 Oe using the resonance of diphenylpicryl hydrazil (DPPH) in an NMR apparatus. Stray magnetic fields were cancelled to better than 20 Oe.

IV. RESULTS AND DISCUSSION

In separate subsections below we consider the experimental results obtained in indium, together with a critical examination of how they fit the model involving the bound quasiparticle states in the surface layer. Where it is relevant, we compare the present results with those obtained on tin crystals.

A. Frequency Dependence

The scheme of transitions from surface states into states whose density is given by the BCS spectrum predicts a dR/dH peak at such value of the applied field where the microwave photon energy equals the binding energy [see Eq. (3)]. The nearly linear dependence of this binding energy on applied field translates into a prediction that the peaks should shift linearly to higher fields with increasing microwave frequency.

This linear dependence was observed in tin. Indium, as the present data shows, is no exception. Figure 3 gives a sequence of recorder tracings for frequencies ranging from 11.4–37.4 GHz for the case of the In(111) sample with field applied parallel to the [101] axis. An accurately linear dependence of peak position on frequency is found. Such frequency scaling was repeated at widely different temperatures, and in various different orientations in this and other samples, with no discernable deviation from the linear dependence.

According to the calculation of binding energy vs. magnetic field strength (see Fig. 1) this relationship is expected to be decidely different from linear when $\alpha\neq 0$, or for the higher energy bound states that are possible even when $\alpha=0.5$. The experimental evidence implies that the dR/dH peak involves mostly $\alpha=0$ electrons and also that observed peaks are due to the lowest bound states. The Garfunkel description of the surface electrons assigns to all of these an identical energy shift proportional to the field strength. In terms of this model the linear-frequency scaling is obvious, without any additional assumptions or qualifications.

The decrease of peak amplitude (at least relative to the background signal) with lower microwave frequency, we believe, provides the answer for why the peak structure has not been observed in other related experiments.[1,2] To make connection to such measurements as the Glosser and Douglass data on $R(H)$ in Al,[1] or other similar experiments, we examined closely the $R(H)$ curve obtained from integration of the dR/dH experimental trace. At the lowest frequency (11.44 GHz) the indium $R(H)$ curve shows only a small kink at the position of the dR/dH peak and begins to decrease more steeply. This curve looks remarkably similar to the Al data for $t=T/T_c=0.87$ and a frequency of 8.8 GHz as given by Glosser and Douglass.[1]

B. Temperature Dependence

The temperature dependence of peak position, according to our model for the dR/dH peaks, comes about through the variation of the binding energy with temperature. According to Eq. (1), this energy is directly proportional to the temperature dependent penetration length $\lambda(T)$, which in the limit of long mean free path is given by the BCS theory[9] as

$$\frac{\lambda(0)}{\lambda(T)}=\left[\frac{\Delta(T)}{\Delta(0)}\tanh\frac{\Delta(T)}{2kT}\right]^{1/3}. \tag{4}$$

$\lambda(0)$ and $\Delta(0)$ are, respectively, the penetration length and energy gap at zero temperature. With fixed microwave frequency we expect that the peak field be inversely proportional to $\lambda(T)$.

The indium data bears out this relation quite accurately. Figure 4 gives a set of recorder tracings that show the expected slow upward shift of the peak with decreasing temperature. A plot of peak position against $\lambda(0)/\lambda(T)$ as in Fig. 5 reveals the predicted straight-line relationship. This behavior is obtained in other field directions, other sample planes and at different microwave frequencies, with an equally good fit.

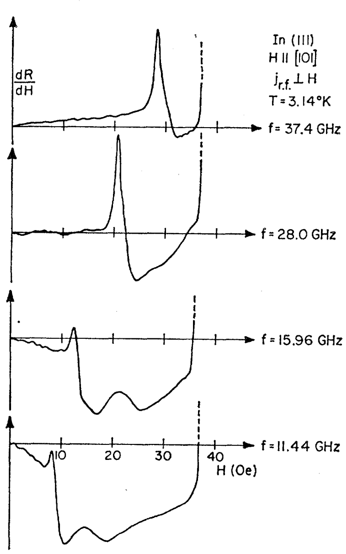

FIG. 3. Frequency dependence of the dR/dH spectrum. Peak position is found to depend linearly on the microwave frequency.

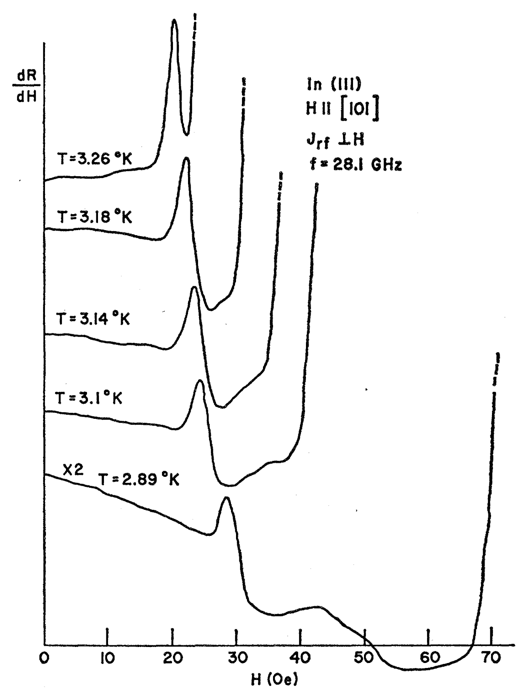

FIG. 4. Temperature variation of the dR/dH curves. Peaks decrease in amplitude and shift to higher fields.

The tin experiments[4] gave a qualitatively similar variation of the peak signals with temperature. The peak fields were plotted against an inverse penetration length derived from the approximate reltaion $\lambda(T) \approx \lambda_L^{2/3}\xi_0^{1/3}$, where $\lambda(T)$ is the London penetration length and ξ_0 the coherence length at zero temperature. This provided the motivation for plotting peak position versus $(1-t^4)^{1/3}$. Such plots, while providing a reasonably straight line, showed consistent small deviations.

Although our model of transitions from bound quasiparticle states correctly predicts the temperature variation, it does not provide an exclusive or critical test of Pincus's description of these states. The calculations based on Garfunkel's model give precisely the same result.

C. Dependence of Peak Signals on Field Orientation

We have illustrated the frequency and temperature dependence on hand of a judiciously chosen sample plane and field direction. The spectrum is dominated by a single, well-resolved peak (Fig. 2). Merged in the second dR/dH peak near 40 Oe are three additional peak signals, that become separated for other orientations of the field and have their own characteristic angular variations. We have mapped out the peak signals as a function of field direction in this and a number of other symmetry planes. The aim was to establish where on the Fermi surface of indium the peak signals originate. However, the bewildering variety of observed peaks and their many different angular variations have made an unambiguous identification of the signals impossible. Some of the peak signals have an angular variation that suggests that they are due to the ridges of the second zone hole surface, or possibly the third-zone electron-ring structure. Data on the angular variation of the most pronounced peaks in five distinct symmetry planes is included in Fig. 6, but without any attempt to systematically identify and assign these curves.

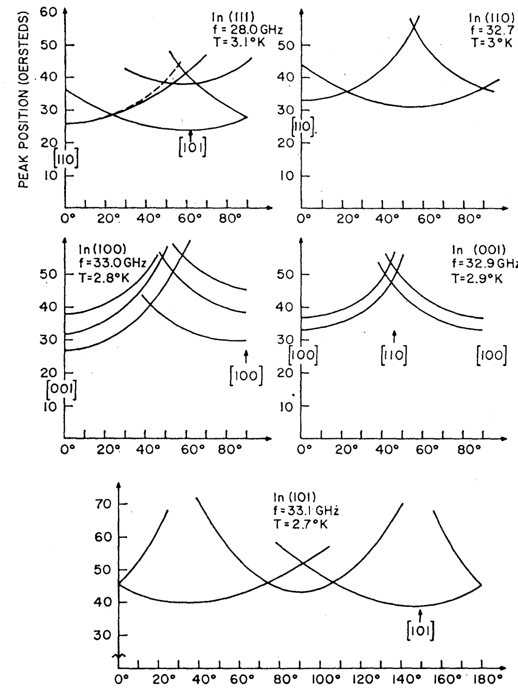

FIG. 6. Angular variation of the most prominent peak signals in the major symmetry planes of indium.

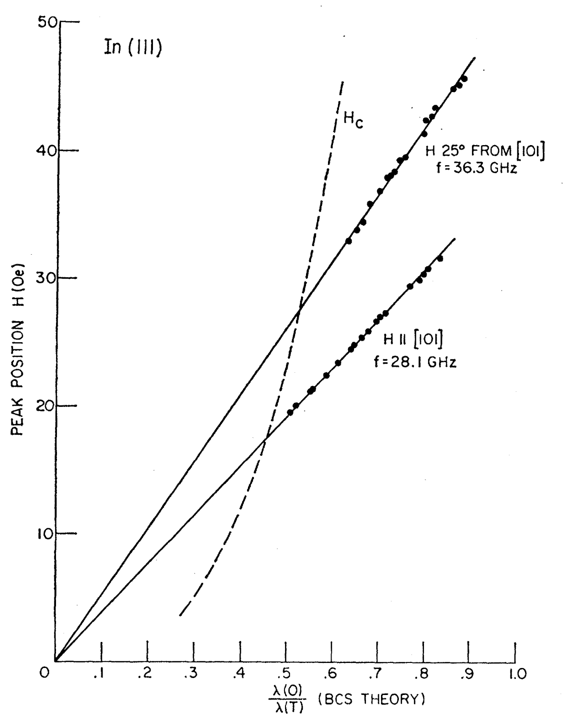

FIG. 5. Peak position versus $\lambda(0)/\lambda(T)$ for two peak signals. Peaks shift proportional to the inverse of the temperature-dependent penetration length.

There is, however, one feature of these curves that is central to our interpretation of the peaks and that forms the basis of our modification of the Garfunkel calculation. This feature is the characteristic upward shift of peak position with rotation of the field away from a major symmetry axis. Many of the curves are approximated well by a $1/\cos\theta$ function. The $1/\cos\theta$ dependence is expected for cylindrical Fermi-surface geometry. When the field is directed along the cylinder axis, the electron Fermi velocity and screening current flow are colinear. With rotation of the field the screening current flows at an angle θ to the Fermi velocity and binding energy according to Pincus is decreased as the cosine of the angle. At fixed microwave frequency this implies a proportionately higher field for the resonance peak. The deviations from true $1/\cos\theta$ variation, in this context, must be due to only approximately cylindrical geometry or a variation of the screening length $\lambda(T)$ with orientation of the field.

It should be apparent to the reader that, because only electrons moving parallel to the sample surface are involved in our considerations, one need not have a cylindrical geometry on a global scale. A cylindrical ridge suffices. It is equally apparent that an accurately spherical Fermi surface (as used in Garfunkel's calculation) would give rise to completely isotropic signals.

D. Surface Roughness Effects

The examination of the frequency, temperature, and orientation dependences of the peak signals in indium routinely reproduced results also obtained in the tin experiments. On the other hand, our efforts aimed at learning of the influence of surface roughness revealed a surprising new aspect. It was learned that peak position, amplitude, and linewidth all depended sensitively on the preparation of the sample surface.

The first indication of this dependence came when we tried to reproduce some of the Koch-Kuo data on a (101) tin crystal. Instead of the acetic anhydride-perchloric acid electropolish, routinely used in the earlier experiments, we repolished the specimen in a methyl alcohol-perchloric acid bath. We were able to achieve a shiny surface, but it appeared densely covered with small pits. Data on this sample gave peaks at different field values than had been obtained previously. Of the two peaks observed in the [101] direction, the low-field peak was shifted down by several Oe. The high-field peak was at nearly the same position but it was much weaker and broader. Reverting to the original polishing routine, we found curves that more nearly resembled the Koch-Kuo curves. Even then, variations in the current density, bath temperature, age, and condition of the polishing bath were found to influence the data. These observations prompted a more systematic effort to learn of the influence of surface preparation.

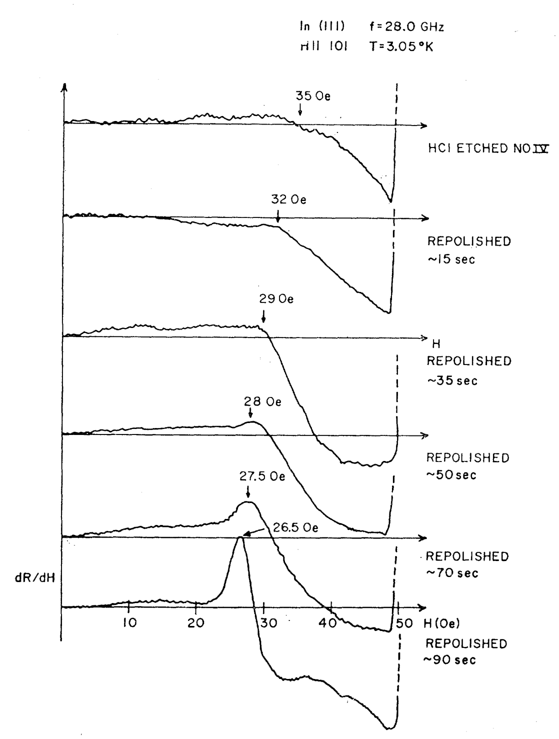

FIG. 7. Dependence of dR/dH curves on surface roughness. For the best electropolish of this same specimen the peak appears at 24.5 Oe (compare Fig. 2).

We found that the most satisfactory technique for achieving a controlled degree of uniform surface roughness was the etch-and-repolish procedure. We start with a heavily etched crystal, which is subsequently repolished for controlled lengths of time until the initial polish is reproduced. Figure 7 gives the dR/dH curves for the same (111) sample, considered earlier (see Fig. 2). The top tracing shows the result of a light and uniform vapor etch, which produced micron-sized random pits on the surface. No peak can be identified in the tracing, but a negative dR/dH signal comes in at 35 Oe. With successive repolish treatments a distinct peak emerges and is observed to shift to successively lower fields, until in the last trace it is at 26.5 Oe. Additional polishing allowed us to reproduce the trace of Fig. 2. A more severe etching gives zero dR/dH right up to the critical field.

It would seem that the trace in Fig. 2 represents the ultimate in polishing and possibly a limiting-field position for the peak. This is not the case. The same crystal was subsequently immersed in a few cm^3 of distilled water with several drops of concentrated NHO_3. No noticeable etching occurred, but with a repetition of the run we found the peak appeared more narrow and shifted down to 23 Oe. The high-field peaks instead were shifted to increased field. On the basis of these observations in tin and indium, we have become convinced that surface preparation plays a significant role in determining the dR/dH peak spectrum. Reproducibility of the data curves can only be expected with identical surface preparation and treatment.

To convince ourselves that the observed effects were not due to chemical contamination incurred in the etching or polishing, we used the technique of very lightly brushing the surface. The stroke direction determines the orientation of resultant scratch marks. This suggested an interesting variation of the experiments. There are two equivalent [101] axes separated about 120° in the (111) plane. With scratch marks directed perpendicular to one of these [101] axes, we compare data curves for each of the two directions. For the case where the field is normal to the scratches (and along a [101] axis) we find practically no change in the data. For the other [101] the peak is broad and shifted to higher field in a manner suggestive of a light etch. With a random crisscross pattern of scratches both signals eventually disappeared.

The differential effect with unidirectional roughness has a very natural explanation in terms of electron motion. With the field normal to the scratches, and supposing the cylindrical geometry suggestive of the angular dependence in the previous section, electrons move along the scratch directions practically unimpeded. Motion at 60° to the scratches (as for the case of the other [101]) will be hindered by frequent scattering. We suspect that the scattering of electrons near a rough surface is responsible for our observation of upward field shifts and broadening of the peaks. In conversations with Pincus, we have come to conclude that scattering from a rough surface will decrease the lifetime and on the average enhance the α value of a surface state. For nonspecular scattering an electron with small initial kinetic energy of motion normal to the surface ($\alpha \approx 0$), can acquire an increased value of this energy after reflection. As we see from Fig. 1, increased α means a lowering of the binding energy, and hence at fixed frequency a larger magnetic field for the resonance. The increase in linewidth we associate with a decreased lifetime of the surface electron.

If such an explanation could be substantiated by a calculation, it seems that the roughness effect would confirm Pincus's description of the bound states. From Garfunkel's point of view such a shifting of the peaks is not immediately apparent. One would have to require that increased scattering reduce the velocity of screening current flow in the penetration depth.

It is of interest to compare the effect of surface roughness on the bound-electron states known to exist in the normal state of a metal.[10] It has been shown[11] that roughness causes a field dependent decrease of surface-state lifetime, but definitely no shifting of the energy levels and resonance peaks.

V. SURFACE-IMPEDANCE CALCULATION

Mattis and Bardeen[12] have calculated the surface impedance of a type-I superconductor in the limit of small λ/ξ and zero magnetic field. With the application of a magnetic field, as we have seen in the foregoing discussions, we expect a marked modification of the energy spectrum of quasiparticle states that includes states with energies in the gap of the BCS spectrum. Garfunkel's description of this modified energy spectrum, involves a shift of energy by $\mathbf{P}_F \cdot \mathbf{v}_s$ for the group of electrons participating effectively in the surface screening currents. All of the electrons are assigned the same $\mathbf{v}_s$.

Using a model where the electromagnetic absorption involves transitions from among this special group of surface electrons to states unaffected by magnetic field and described by the BCS spectrum, Garfunkel[7] has carried out calculations of the surface impedance in the presence of applied field and for a wide range of experimental frequencies and temperatures. His calculation involves only the modification of the density of states and statistical occupation factors in the Mattis and Bardeen approach. While this may be a satisfactory first-order approximation, it ignores some obvious complications. Probably most significant is the fact, that the wave functions of electrons bound in the surface region in quantum-mechanical states are quite different from those on which the Mattis-Bardeen calculation of matrix elements is based.

An examination of Garfunkel's calculated curves for the regime of frequencies and temperature of interest to our experiments, i.e., $\hbar\omega/\Delta$ between 0.05 and 0.3, and t from 0.6 to 0.95 (Fig. 6 in Ref. 7), raised some tantalising questions. For one, there is no evidence for the sharp dR/dH resonance peaks so prominent in our data. We have generated derivative curves from Garfunkel's $R(H)$ curves to find very broad derivative peaks at values of magnetic field that closely corresponded to the observed field values. Scaling such derivative maxima between different frequencies, we discovered an approximately linear variation reminiscent of our data.

When we examined the temperature variation of the curves we discovered that it differed substantially from the observations. We have since uncovered the source of this discrepancy. The calculation involves $\lambda(t)$ as an independent parameter and not the temperature directly. Garfunkel in his numerical work uses the London penetration length $\lambda_L(t)$ obtained from Mühlschlegel's tables.[12] For a type-I superconductor in the limit of long mean free path, the penetration length instead should be taken as $\lambda(t) \approx \lambda_L^{2/3}\xi^{1/3}$, or better yet from Eq. (4) as in this paper. Reinterpreting Garfunkel's t values resolved the discrepancy and gave a temperature dependence more nearly in line with that observed.

Coming back to the question of the very narrow observed dR/dH peaks, we take our clues from the angular variation of the signal. This had led us to conclude that cylindrical sections of the Fermi surface were responsible sharp peak signals. The Garfunkel calculations are based on spherical Fermi-surface geometry, which is expected to mask sharply varying features in the impedance curve. Our calculations of the surface impedance are based on the case of a cylindrical sheet of the Fermi surface. We follow the calculational procedure described in detail by Garfunkel[7] and refer the interested reader to this reference. An example of our results is contained in the curves of Fig. 8. These curves are intended to reproduce the peak feature observed in the (111) plane data as in Fig. 2. We choose a value of $\hbar\omega/\Delta = 0.228$, appropriate for the case of indium at 28.0 GHz. The energy shift incurred by the surface electrons we choose such that at 24.5 Oe (the field at which the dR/dH peak occurs) it exactly equals $\hbar\omega$. In terms of more fundamental parameters, and referring back to Eq. (1), this is equivalent to choosing the product $v_F\lambda$ at a temperature $T = 3.05°$ ($t = 0.84$) as

[11] J. F. Koch and T. E. Murray, Phys. Rev. (to be published).
[12] B. Mühlschlegel, Z. Physik **155**, 313 (1959).

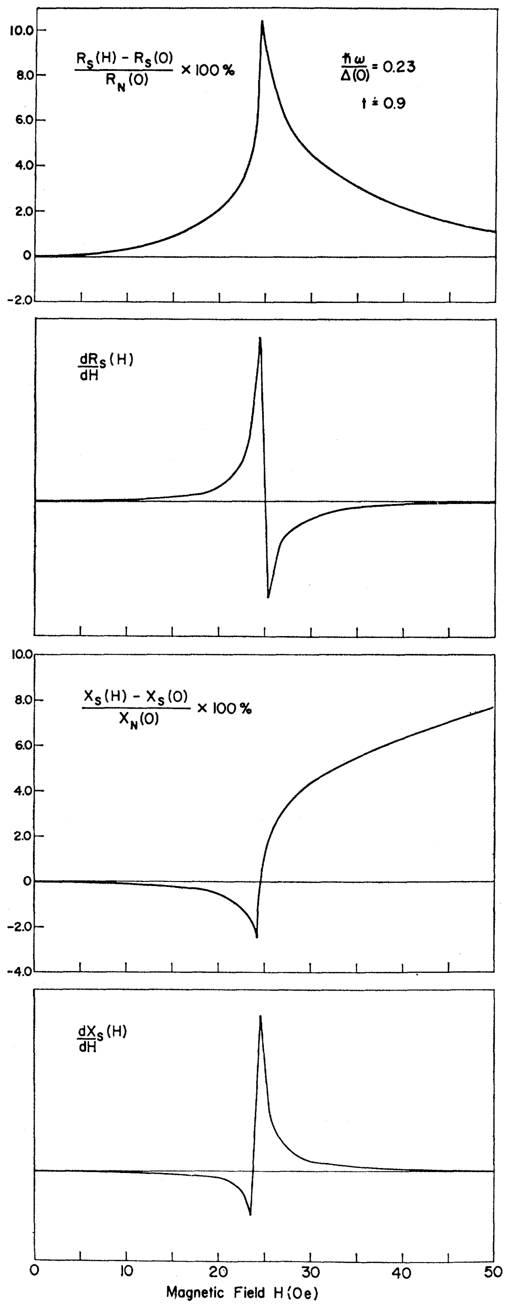

FIG. 8. Surface impedance ($R, dR/dH, X, dX/dH$) versus magnetic field as calculated for the case of a cylindrical section of Fermi surface. Parameters are chosen to fit the case of the (111) plane specimen at 28.0 GHz (compare the calculated dR/dH curve with the data of Fig. 2).

equal to 4.7×10^2. This implies $v_F\sim10^8$ cm/sec and $\lambda\approx500$ Å, if you like. Curves of R, X and the corresponding derivatives, calculated on the basis of a limited grid of field values, are given in the figure. The infinities expected in the derivative curves at 24.5 Oe are smoothed out by the numerical differentiation.

Comparing the calculated dR/dH curve with the data in Fig. 2, it is evident that the Garfunkel calculation reproduces the sharp peaks of the experimental curve when we choose cylindrical Fermi surface geometry. Moreover the dR/dH peak occurs when $\hbar\omega$ equals the bound state energy. This fact makes the predicted frequency and temperature scaling of the calculated peak a foregone conclusion. When frequency is changed in the calculation the peak moves linearly with the frequency change. Variation of the temperature implies changes in $\lambda(t)$ and the peak is found to shift as $1/\lambda(t)$. The calculation therefore reproduces the essential experimental dependences.

A more thorough comparison of the calculated and experimental curves, especially with regard to impedance variation away from the dR/dH peak, reveals that the calculation does not give a completely satisfactory account of the experimental curve. The region of negative dR/dH values above the peak field, is quite different. The experimental curve has several other peaks due to other sections of the Fermi surface in that region. Since the calculation involved only a single cylindrical sheet of Fermi surface, no such peaks are expected in the calculation. One might think of improving the calculation by working with a more realistic Fermi-surface model, but in view of the remaining discrepancies this effort is not warranted at present.

VI. CONCLUDING REMARKS

The central feature of our data are the sharp dR/dH peaks that can be accounted for in terms of a model of transitions from a type of bound-surface-electron state. The notion of such a state has been made plausible by the Pincus calculation, but there remain fundamental questions that have not been answered satisfactorily. The Pincus calculation is based on a square-well potential (equivalent to a step function for the magnetic field), and is suspected when it comes to the evaluation of how the bound-state energy varies with field. It would be desirable to work with a more realistic potential, possibly even a selfconsistent one, i.e., the surface screening currents due to bound-electron states are themselves responsible for the space dependence of the vector potential. The Pincus calculation allows a nonlinear dependence of binding energy on field for $\alpha\neq0$ and higher-lying bound states. In the experiments we have only observed states whose energy varies linearly with applied field. Our explanation of both the sharp peaks and the linearity of frequency scaling requires that the microwave absorption is preferentially due to $\alpha=0$ electrons. It remains to show that this assumption is justified. Also, there is as yet no definite evidence for the multiple bound states and transitions between such states. It also remains to translate the qualitative discussion of the surface roughness effects into a sound theoretical explanation. Most importantly it remains to carry out a detailed calculation of surface impedance based on the wave functions and density of states of the Pincus surface states.

Garfunkel's simple model of a $\hbar\mathbf{k}_F\cdot\mathbf{v}_s$ energy shift, as we have shown can account equally well for the important frequency-temperature scaling of the data. But it is most certainly a much oversimplified description, especially in view of what is known about electron surface states in normal metals. The calculation based on cylindrical Fermi surface geometry and the $\hbar\mathbf{k}_F\cdot\mathbf{v}_s$ shift reproduces the derivative peak features, but falls short of detailed agreement with the experiments.

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Bardeen-Kümmel-Jacobs-Tewordt Theory of a Vortex near T_c†

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An expression for the free energy of a superconductor containing magnetic flux is derived for temperatures near T_c. To order T_c-T, the result is identical to that of Ginzburg-Landau as derived by Gor'kov. A term proportional to $(T_c-T)^{1/2}$ is shown to vanish in perturbation theory. The validity of the variational functions of Bardeen *et al.* is verified near T_c where the critical value of κ is almost identical to $1/\sqrt{2}$.

I. INTRODUCTION

It has been shown by Bardeen, Kümmel, Jacobs, and Tewordt how a variational calculation for the free energy of a superconductor containing magnetic flux may be performed.[1] They begin with a variational principle of Eilenberger.[2] Two trial functions for the order parameter and magnetic flux are taken for a superconductor containing a vortex and the result is minimized with respect to a parameter d for the order parameter and s for the magnetic flux. The variational functions of Ref. 1 are $\Delta(r)=\Delta_\infty\tanh(dr/\xi)$ and $(e/c)A(r)=\cosh(sr/\xi)/(2r)$, where $\xi=p_F/m\pi\Delta_\infty$ is the temperature-dependent coherence length, and Δ_∞ is the order parameter far from the vortex core in a gauge where $\Delta(r)$ is real. This calculation provides the variational values of s and d for a given κ, the Ginzburg-Landau (GL) parameter, and also the lower critical field H_{c1} may be derived as a function of κ by equating the vortex-state free energy to that of a superconductor in the Meissner state.[3] These calculations have been performed at 0 deg and can be extended to finite temperatures. Here we examine the free energy of a superconductor containing a vortex at temperatures near T_c. We assume that the free energy per unit length of vortex vanishes as $1-T/T_c$ as Gor'kov and Eilenberger have shown.[2,4]

The coefficient of $1-T/T_c$ is exactly proportional to the GL free energy. There is also a term of order $(1-T/T_c)^{1/2}$ which should vanish identically for any given smooth variational functions. We are only able to show that it vanishes in lowest-order perturbation theory at this time. Numerical calculations indicate that this term does indeed vanish.[5]

In Sec. II we summarize some of the basic equations of Bardeen *et al.* and proceed to isolate the free-energy terms to order $(1-T/T_c)^{1/2}$ and $1-T/T_c$. The coefficient of the linear term is calculated explicitly and is shown to be proportional to the GL free energy.

In Sec. III it is shown that the leading term in the temperature expansion will vanish identically in lowest-order perturbation theory for arbitrary, analytic, variational functions. This is unsatisfactory and it should be shown that the term vanishes for large variational functions. In Sec. IV the variational functions of Bardeen *et al.* are employed to calculate $H_{c1}(\kappa)$ using the GL free energy. The value of κ_c, the critical GL parameter separating type-I from type-II behavior is close to $1/\sqrt{2}$.

II. FREE ENERGY

The free energy of a superconductor may be derived from the expression[1]

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[1] J. Bardeen, R. Kümmel, A. Jacobs, and L. Tewordt, Phys. Rev. (to be published).
[2] G. Eilenberger, Z. Physik **182**, 427 (1965).
[3] V. L. Ginzburg and L. D. Landau, Zh. Eskperim i Teor. Fiz. **20**, 1064 (1950) [English transl: L. D. Landau, in *Men of Physics*, edited by D. ter Haar (Pergamon Press, Ltd., Oxford, 1965), Part 2, p. 138].
[4] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **35**, 1918 (1959) [English transl: Soviet Phys.—JETP **6**, 1364 (1959)].
[5] A. Jacobs (private communication); and (to be published).