These bands may also be compared with the model of Klick and Kabler by plotting the atomic energy levels of Li^0 against the difference in energy between the various L bands and the F band. Such a plot, shown in Fig. 3, gives a reasonable straight line. The curve indicates that on the basis of this model, the atomic levels of Li^0 are compressed by about 45% in LiCl. This compression is larger than has been found for the potassium and rudibidum salts. Since the compression is attributed to dielectric constant effects, a large value of compression would be expected for LiCl in view of its large dielectric constant.

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Temperature Dependence of the Ginzburg-Landau Coefficient in Type-I Superconductors*

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Making use of surface superconductivity measurements, it is possible to obtain relatively precise values for the Ginzburg-Landau parameter κ as a function of temperature in certain type-I materials. We have measured the ac susceptibility to obtain H_{c3}, and the dc magnetization to obtain the bulk critical field, for Ta and three dilute alloys of Bi in Pb. The data are sufficiently accurate to distinguish between the various existing theories for κ; the Ginzburg extension of the Ginzburg-Landau theory to low temperature predicts $\kappa(t)=\kappa(0)_{\mathrm{G-L}}(1+t^2)^{-1}$, while Gorkov predicts $\kappa(t)=\kappa(0)_{\mathrm{G}}(1-0.24t^2+0.04t^4)$, where t is the reduced temperature T/T_c. We find that the data fall on smooth curves which lie between the two theoretical predictions. Bardeen has used the two-fluid model to generate a temperature-dependent set of equations for the free energy, which yields the Ginzburg-Landau equations in the limit of $t\rightarrow 1$. Using the Bardeen two-fluid formulation, we find $\kappa(t)=\kappa(0)_{\mathrm{B}}(1+t^2)^{-1/2}$. We find that the data fit the two-fluid temperature dependence more closely than they fit either the Gorkov or the Ginzburg relationship.

I. INTRODUCTION

APPLICATION of the ac susceptibility technique[1] permits accurate experimental determination of thes urface critical field H_{c3} in certain type-I and type-II superconductors. The theory of the surface critical field of Saint-James and de Gennes[2] relates H_{c3} to the Ginzburg-Landau[3] (G-L) parameter κ and to the thermodynamic critical field H_c. In this paper, we present experimental measurements on the temperature dependence of H_{c3} and H_c from which precise values for the temperature dependence of κ are obtained. These values are then compared with several theories which predict somewhat different temperature dependencies of the magnetic properties. In order to make a useful comparison of theory and experiment, it is important to clarify the terminology used for the parameters which determine the ratios of the upper critical fields H_{c2} and H_{c3} to H_c. A brief historical summary of the G-L,[3] Gorkov,[4] and Bardeen[5] theories, and the pertinent parameters is presented followed by the experimental details, the results, and a comparison of the results with the theories.

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[1] M. Strongin, A. Paskin, D. G. Schweitzer, O. F. Kammerer, and P. P. Craig, Phys. Rev. Letters **10**, 442 (1964).

[2] D. Saint-James and P. G. de Gennes, Phys. Letters **7**, 306 (1963).

[3] V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

[4] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **37**, 833 (1959) [English transl.: Soviet Phys.—JETP **10**, 593 (1960)].

[5] J. Bardeen, Phys. Rev. **94**, 554 (1954); J. Bardeen, *Encyclopedia of Physics* (Springer-Verlag, Berlin, 1956), Vol. 15, p. 274.

II. THEORY

The phenomenological equations of Ginzburg and Landau have given good descriptions of the behavior of London-type superconductors in magnetic fields. In particular, experiments have confirmed the Abrikosov[6] relationship between the bulk upper critical field H_{c2}, and the thermodynamic critical field H_c in type-II superconductors. Recently, Saint-James and de Gennes[2] have obtained a solution to the G-L equations, which show that in certain classes of superconductors (notably type II but including some type I) a superconducting region can nucleate in a surface layer at values of the applied external field appreciably greater than those sufficient to quench the bulk superconductivity. Their theory predicts a relationship between the surface critical field H_{c3} and the thermodynamic critical field H_c. The Saint-James–de Gennes relationship between H_{c3} and H_c has been confirmed in appropriate type I and type II superconductors.

Of central importance in both the G-L theory and in the Saint-James–de Gennes solutions is the linearized form of the equations and the fundamental parameter

[6] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **32**, 1442 (1957) [English transl.: Soviet Phys.—JETP **5**, 1174 (1957)].

κ. The G-L equations and the parameter κ were originally justified only in the temperature region near the critical temperature T_c. The apparent agreement between experiment and theory over a range of temperatures, suggests that the G-L equations may be approximately valid over a wider range than was originally expected. Ginzburg,[7] following an approach of Bardeen,[5] arbitrarily introduced explicit temperature relationships into various coefficients appearing in the G-L equations, and arrived at an explicit form for the temperature dependence of κ. This temperature dependence is found to agree exactly with that which is obtained, by introducing into the original G-L definition of κ, the experimentally observed temperature variations of H_c and the weak field-penetration depth δ, namely,

$$\kappa_{\text{G-L}}(t)=(2e^*/\hbar c)H_c\delta^2=2(1+t^2)^{-1}\kappa_{\text{G-L}}(1). \quad (1)$$

Here $\kappa_{\text{G-L}}(1)$ is the value of $\kappa_{\text{G-L}}(t)$ at the reduced temperature $t=1$, where $t=T/T_c$. Thus, we may use the Ginzburg modified form of the G-L equations or (equivalently) the original form of the G-L equations with the implicit temperature dependence of κ to arrive at temperature dependent relationships involving the critical fields. For example, the Abrikosov relationship is then

$$H_{c2}/H_c=\sqrt{2}\kappa_{\text{G-L}}(t). \quad (2)$$

and the Saint-James–de Gennes relationship is

$$H_{c3}/H_c=2.39\kappa_{\text{G-L}}(t). \quad (3)$$

Gorkov has used the microscopic theory of superconductivity, and has justified the G-L equations in the vicinity of $t=1$. He further derived a relationship between H_{c2} and H_c in the vicinity of $t=0$. By interpolating the results over a range of temperatures, Gorkov[4] finds

$$\begin{aligned} H_{c2}/H_c&=\sqrt{2}[(1.25-0.3t^2+0.05t^4)\kappa_{\text{G-L}}(1)].\\ &=\sqrt{2}\kappa_{\text{G}}(t). \end{aligned} \quad (4)$$

We have introduced $\kappa_{\text{G}}(t)$ to denote the term in the brackets. If we were only interested in comparing H_{c2}/H_c in type-II superconductors, the identification of the term in the brackets in Eq. (4) with $\kappa_{\text{G}}(t)$ would be a matter of semantics. However, we shall be interested also in type-I superconductors and in comparing measurements of H_{c3}/H_c with theory. As the Saint-James–de Gennes relationship is based on the linearized G-L equations we cannot rigorously compare the Gorkov temperature-dependent relationship of Eq. (4) with experiments at temperatures other than at $t\approx 1$ where the Gorkov and G-L formulations yield identical equations. We can only assume that the same coefficient κ_{G} that appears in the microscopic relationship for H_{c3}/H_c will likewise appear in a microscopic treatment of the surface at all temperatures. Therefore, we will assume that κ_{G} can simply replace $\kappa_{\text{G-L}}$ in Eq. (3). In the light of the rather weak justification of the G-L equations at all temperatures, and hence of the validity near $t=0$ of Eq. (3) based on the form of the G-L equations, we have re-examined the Bardeen two-fluid formulation. This alternative phenomenological formulation generates a set of differential equations equally valid at all temperatures. At $t\approx 1$, the Bardeen equations reduce to the G-L equations. By assuming that the superconducting order parameter is small at fields approaching the upper critical fields, the Bardeen two-fluid formulation is found to yield high field equations which at all temperatures have the form of the linearized G-L equations. A relationship is derived for $\kappa_{\text{B}}(t)$, the coefficient which would appear in all critical field relationships such as that of Eq. (3). The Bardeen formulation and Eq. (1) must of course be modified by introducing $2e$ in place of e^*, to take into account Cooper pairing of the superconducting electrons.

[7] V. L. Ginzburg, Zh. Eksperim. i Teor. Fiz. **30**, 593 (1956) [English transl.: Soviet Phys.—JETP **3**, 621 (1956)]; and Dokl. Akad. Nauk SSSR **110**, 368 (1956) [English transl.: Soviet Phys.—Doklady **1**, 541 (1956)].

III. BARDEEN TWO-FLUID FORMULATION

Bardeen has used the Gorter-Casimir two-fluid model to obtain an expression for f, the difference in free energy between the superconducting and normal phases. The Bardeen expression is equally valid at all temperatures, whereas the form of the G-L equations can only be justified in the region $t\sim 1$. The ensuing discussion of the Bardeen two-fluid equations uses results which are derived in detail in Bardeen's review article.[5] The notation as well as many of the equations are taken directly from this article.

We restrict ourselves to the one-dimensional case where the applied field is taken along the z direction. Bardeen's equation describing the variation in concentration of the superconducting electrons along the x direction is

$$d^2U/d\xi^2=(\kappa_{\text{G-L}}(t)^2 4\pi)(2H_c^2)^{-1}df/dU+V^2U. \quad (5)$$

Here

$$U=\psi/\psi_e,\quad \xi=x/\delta,\quad \delta=m_sc^2(4\pi e^{*2}n_0\psi_e^2)^{-1},$$
$$V=e^*A\delta/\hbar \quad\text{and}\quad e^*=2e,$$

where $n_0|\psi|^2$, and $n_0|\psi_e|^2$ are the concentration of superconducting electrons with and without a field, respectively, n_0 is the concentration of superconducting electrons at $t=0$, δ is the London penetration depth, A is the vector potential, and the effective electronic charge $e^*=2e$. With $\psi_e^2=1-t^4$ and $H_c=H_0(1-t^2)$, Bardeen obtains the following relationships for the

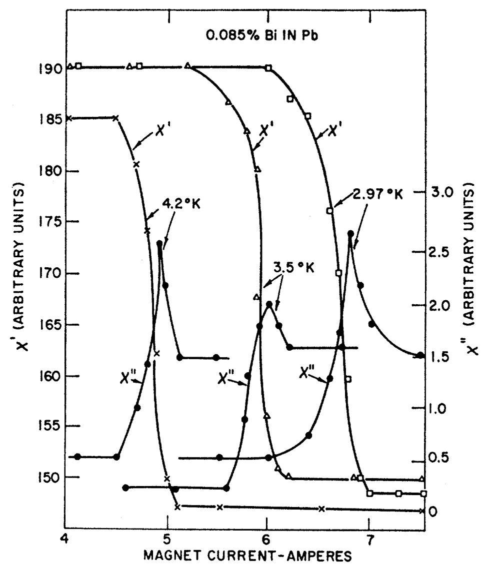

FIG. 1. Typical curves illustrating the precision with which the upper critical field H_{c3} may be determined using the ac technique. The real part (χ') and the imaginary part (χ'') of the ac susceptibility are shown for 0.085% Bi in Pb. The peaks in χ'' are used to determine H_{c3}.

free energy and its derivative:

$$(4\pi/H_c^2)f(U) = (1-t^2)^{-2}\{t^2[1-(1-U^2\psi_e^2)^{1/2}]-0.5U^2\psi_e^2\}, \quad (6)$$

and

$$-(4\pi/H_c^2)(df/dU) = (1+t^2)(1-t^2)^{-1}[1-t^2(1-U^2\psi_e^2)^{-1/2}]U. \quad (7)$$

We are interested in the form of the differential equations as the fields approach the upper critical fields H_{c2} or H_{c3}, and hence, as the order parameter approaches zero. Substituting Eq. (7) in Eq. (5) and taking the limit $U^2 \ll 1$, we find

$$d^2U/d\xi^2=[V^2-(1+t^2)\kappa_{\text{G-L}}(t)^2/2]U, \quad (8)$$

as the linearized two-fluid form of differential equation. In the limit $t \rightarrow 1$, Eq. (8) is identical to the one-dimensional linearized G-L equation. Examining the form of Eq. (8), it is apparent that we may make use of all the relationships derived using the linearized G-L equation, if we replace κ^2 by $(1+t^2)\kappa_{\text{G-L}}(t)^2/2$ for the two-fluid formulation. Therefore, we define

$$\kappa_{\text{B}}(t)=[(1+t^2)/2]^{1/2}\kappa_{\text{G-L}}(t)=\sqrt{2}(1+t^2)^{-1/2}\kappa_{\text{G-L}}(1), \quad (9)$$

and subsequently make use of the Saint-James–de Gennes relationship with κ_{B} replacing $\kappa_{\text{G-L}}$ in Eq. (3). It might be noted that the form of the linearized differential equations on the two-fluid model at all temperatures is the same as the G-L equations at $t \cong 1$. The two-fluid formulation thus justifies the extension of the G-L equations to all temperatures in the high field limit.

In the above derivation, the definition of κ at temperatures $t \neq 1$ follows in a natural way from the G-L definition at $t=1$, and κ is seen to be the coefficient of a term in a linear set of differential equations. With this definition, the temperature dependence of the coefficient κ in each theory becomes apparent, and ambiguities as to which parts of certain temperature-dependent terms are to be ascribed to κ are eliminated.

The question has recently been raised as to whether the temperature dependence of κ in turn depends on the mean free path. In the two-fluid formulation, the mean free path only enters in a phenomenological manner in its effect on the bulk critical field and the penetration depth. Although a mean-free-path dependence could be introduced into such a phenomenological treatment if the mean-free-path dependence of the free energy were known, no attempt was made to do so in the light of the conflicting results that have been observed experimentally.[8,9]

IV. EXPERIMENTAL

Because the determination of H_c in type-II superconductors is subject to considerable experimental error we have concentrated upon those type-I superconductors exhibiting surface superconductivity. We have determined H_c from bulk magnetization measurements and H_{c3} from ac susceptibility measurements. We discuss first the determination of H_{c3}.

The surface layer predicted by the Saint-James–de Gennes solutions to the G-L equations nucleates at the surface of a superconductor in decreasing magnetic fields. In increasing magnetic fields, a superconducting surface layer remains until the field reaches the value H_{c3} at which point all superconductivity disappears. In our measurement technique, we are able to obtain values for both the real component χ' and the imaginary component χ'' of the ac susceptibility. In the superconducting state, the sample is diamagnetic, and no power absorption exists. Hence $\chi'=-1/4\pi$ and $\chi''=0$. In the normal state and at the low frequencies used in these experiments negligible power absorption takes place in the sample, and both χ' and χ'' are approximately zero. In the superconducting-normal transition region, χ' changes smoothly from $-1/4\pi$ to zero, and simultaneously χ'' goes through a maximum. The relationship between χ' and χ'' can in principle yield information about the details of the transition region. In the case of the Saint-James–de Gennes surface layer, we may consider our samples (long cylinders) to be insulators surrounded by a superconducting sheath. The relationship between χ' and χ'' is derived in the Appendix, where it is found that $\chi''^2=(-\chi'/4\pi-\chi'^2)$, so that the maximum in χ'' is expected to occur when $\chi'=-(1/2)(4\pi)^{-1}$. This result

[8] S. Gygax and R. H. Kropshot, Phys. Letters **12**, 7 (1964).
[9] C. K. Jones, J. K. Hulm, and B. S. Chandrasekhar, Rev. Mod. Phys. **36**, 74 (1964).

is in contrast to that found in bulk materials,[10] where the maximum in χ'' occurs when $\chi' = -0.39(4\pi)^{-1}$. Although this difference permits one in principle to distinguish between the surface and bulk effects, in practice small phase shifts resulting from coupling of the measuring coils into external apparatus, such as the dc magnet (see below) preclude any conclusions on this point.

The observation of a peak in χ'' provides a precise method for identifying the external magnetic field corresponding to H_{c3}. Typical curves illustrating the precision of the determination are presented in Fig. 1. This type of determination may be compared to that obtained from resistivity measurements in which extrapolations are always required from finite measuring currents to zero measuring current. Microwave surface-impedance measurements also show broad transitions.[11]

The complex ac susceptibility of the samples was measured by placing the samples in a coil system which formed one arm of a mutual inductance bridge. The primary coil of the cryostat mutual inductance applied a sensing field of about 0.03 Oe (peak-to-peak) at the sample. The basic featuıes of the bridge are similar to the instrument described by Pillinger, Jastram, and Daunt.[12] The output of the bridge secondary circuit was fed into a low-level amplifier which could be tuned to discrete frequencies of 1.5, 5, 18, 35, 100, and 250 cps. The output from the low-level amplifier was then fed into a Princeton Applied Research lock-in amplifier, which could be tuned to either the in-phase or out-of-phase component of the bridge imbalance voltage.

The cryostat mutual inductance also was composed of two bucking secondary coils, one of which contained the sample. A change in the real part of the sample susceptibility caused a change in the real part of the mutual inductance containing the sample, which then appeared as an in-phase bridge imbalance voltage. A similar explanation applies for the imaginary part of the sample susceptibility.

Magnetization curves of the samples were obtained by connecting the mutual inductance bridge secondary circuit to a sensitive fluxmeter galvanometer, and then moving the sample from coil to coil. The electric charge, and therefore the galvanometer deflection are proportional to the sample magnetization.

The dc magnetic fields used in these experiments were obtained by using a copper solenoid immersed in liquid nitrogen. It is worth pointing out that the magnet couples into the ac bridge circuit owing to currents induced in the magnet from the bridge primary. These currents in the magnet circuit produce alternating fields at the bridge frequency, which cause induced voltages sensed by the amplifiers. This effect was reduced to a negligible value by inserting a large impedance in the magnet circuit, which lowered the induced ac currents.

[10] E. Maxwell and M. Strongin, Phys. Rev. Letters **10**, 212 (1963).
[11] B. Rosenblum and M. Cardona, Phys. Letters **9**, 220 (1964).
[12] W. L. Pillinger, P. S. Jastram, and J. G. Daunt, Rev. Sci. Instr. **29**, 159 (1958).

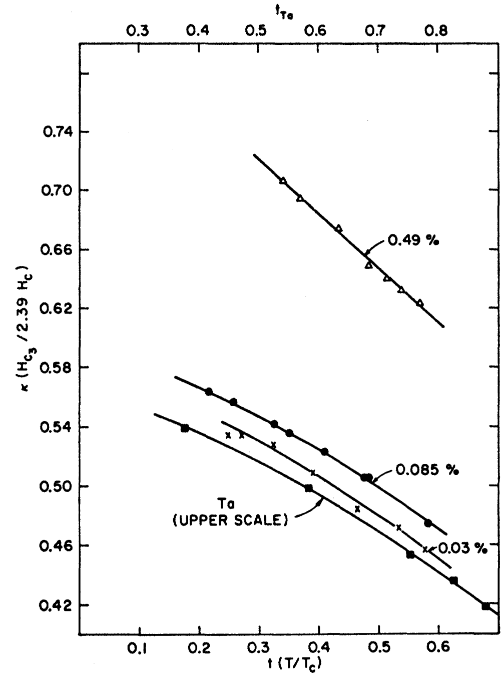

FIG. 2. Temperature dependence of the Ginzburg–Landau coefficient (defined as $H_{c3}/2.39\ H_c$) in type-I superconductors, Ta, and three percentages of Bi in Pb (0.03% Bi, 0.085 % Bi and 0.49% Bi). The upper critical field H_{c3} is obtained from ac susceptibility measurements while the bulk critical field H_c is determined by bulk magnetization measurements. The reduced temperature t is T/T_c.

V. RESULTS

We wish to compare measurements of κ (as defined by the relation $\kappa = (1/2.39)\ H_{c3}/H_c$, where H_{c3} and H_c are determined from ac susceptibility and magnetization measurements made on the same sample) with the theoretical calculations discussed in part II. The usual technique for such comparisons involves plots of experimental values of κ versus T and theoretical plots of the same quantities. Such plots are always normalized to agree at a reduced temperature $t = T/T_c = 1$ where all theories are in agreement. In Fig. 2, plots of the Ginzburg-Landau parameter κ obtained as described above are presented for four type-I superconductors exhibiting surface superconductivity: Ta and the percentages 0.03%, 0.085%, and 0.49% Bi in Pb.

The procedure discussed above suffers certain drawbacks when experimental data are considered, for in practice it is difficult to extend the experiments sufficiently close to $t = 1$. We have therefore chosen an additional, somewhat different, method of displaying our results which is not open to this objection, and

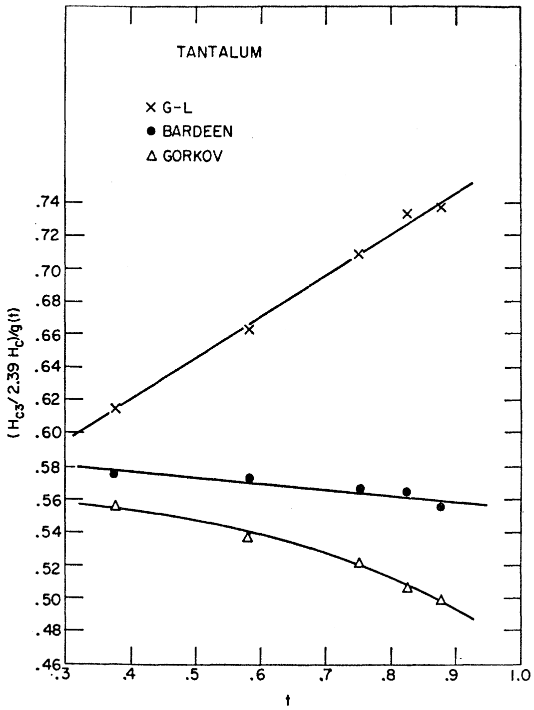

FIG. 3. Temperature dependence of the reduced Ginzburg–Landau coefficient $H_{c3}/(2.39H_c g(t))$ for Ta. A normalized form is used in which the same data is plotted for three different theories. Agreement with a particular theory is signified by the data falling on a horizontal line. $H_{c3}/2.39H_c$ is taken from the data for Fig. 2 and the forms of $g(t)$ relevant to the Ginzburg–Landau, Bardeen, and Gorkov theories are given in the text.

hence provides a more sensitive and critical technique for testing theoretical models.

In our method, we use a normalized plotting system in order to compare our experimental results with the theories given [e.g., Eq. (3)]. At each reduced temperature t we have divided our experimental values of κ by the κ values predicted by the various theories. That is, we plot $(H_{c3}/2.39g(t)H_c)$, where $g(t)$ takes on the forms $(1+t^2)^{-1}$, $(1-0.24t^2+0.04t^4)$, and $(1+t^2)^{-1/2}$ for the Ginzburg model, for the Gorkov model and for the Bardeen models, respectively. With this method of plotting, agreement with a particular theory is signified by the reduced data lying on a horizontal line. Deviations between experiment and a particular theory are signified by failure of the data to lie on a horizontal line.

In our measurements the accuracy of the temperature determinations is about 2% and the relative values of H_{c3}/H_c are accurate to about 1%.

Figure 3 presents such plots for Ta for the above mentioned three theories. The temperature dependence derived from the Bardeen theory is seen to offer a significantly better fit to the data than either of the other two theories. Figure 4 shows typical data for 0.085% Bi in Pb. While none of the theories are entirely satisfactory for the Bi-Pb system, the Bardeen theory is the best of the three.

Rosenblum and Cardona[11] have determined the ratio of H_{c3} to H_c for 1% Tl in Pb for $0.2<t<1$. Their data has been similarly treated to check which theory best accounts for the temperature dependence of this alloy. The ratio H_{c3}/H_c to the three theoretical predictions is plotted against t in Fig. 5. Here too, the data fit the two-fluid temperature dependence more closely than either the Gorkov or Ginzburg relationships.

Rosenblum and Cardona[13] recently have observed that the temperature dependence differs in superconductors with weak and strong coupling, with Hg and Pb being the examples of strongly coupled superconductors. It is interesting to note that both Hg and Pb deviate from the Tuyn relationship[14] $H_c=H_0(1-t^2)$ in an opposite manner from Sn, In, V and Ta. Deviations from Tuyn's relationship basic to the two-fluid calculation would affect the temperature dependence of κ. The advantage of the two-fluid model is its simplicity, and we have not attempted to refine the two-fluid model to include such small effects.

VI. CONCLUSIONS

The prediction of surface superconductivity by Saint-James and de Gennes and its subsequent verification have lead to a new and precise technique for determining the temperature dependence of the coefficient $\kappa(t)$. A

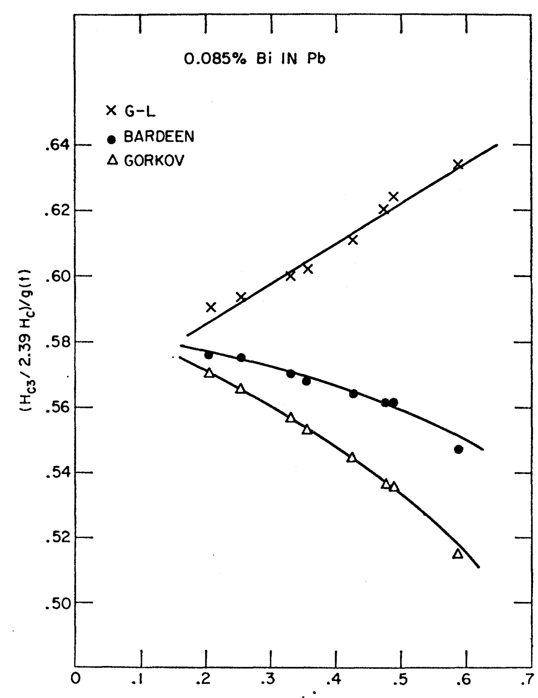

FIG. 4. A plot similar to that of Fig. 3 for 0.085% Bi in Pb.

[13] B. Rosenblum and M. Cardona (to be published).

[14] J. Bardeen and J. R. Schrieffer, *Progress in Low Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1961), Vol. III, p. 170.

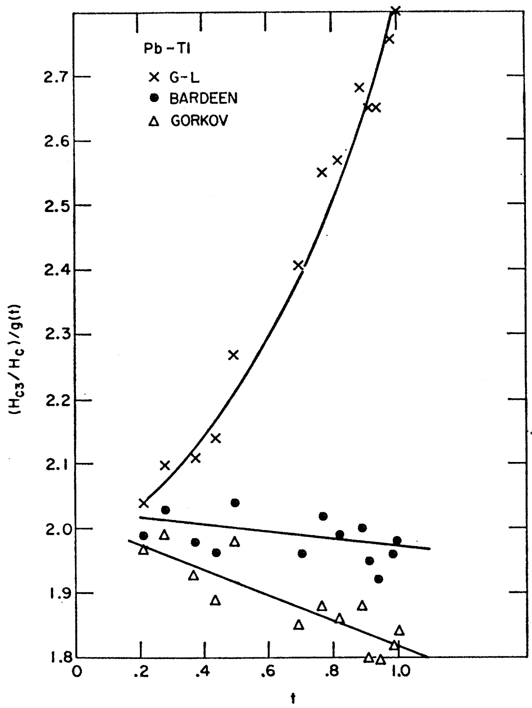

FIG. 5. A plot similar to that of Fig. 3 for 1% Pb in Tl. The experimental data are taken from Rosenblum and Cardona (Ref. 11). Note that the ordinate differs by a numerical factor from that of Figs. 3 and 4.

number of measurements utilizing this technique are presented and compared to theoretical temperature dependence of κ based on the formulations of G-L, Gorkov, and Bardeen. A derivation of the temperature dependence of κ based on the Bardeen two-fluid formulation is outlined in order to indicate precisely the relationship between κ and the experimentally measured parameters, and to demonstrate the origin of the temperature-dependent terms in this theory. It is found, in all cases, that the temperature dependence derived from the Bardeen two-fluid formulation offers the best agreement with experiment of the three theories. However, in alloy systems deviations exist even from the Bardeen theory, and it appears that no entirely satisfactory theory of the temperature dependence of the coefficient $\kappa(t)$ has been given.

APPENDIX

We consider here the relationship between the real part χ' and the imaginary part χ'' of the ac susceptibility $\chi=\chi'+j\chi''$ for an annular superconducting film of thickness d and radius a. The interior of the annulus is assumed to have negligible conductivity. When an external field H_e is applied along the cylinder axis, shielding currents are set up within the annular ring. For complete shielding, the susceptibility is real and equals $-1/4\pi$. As the penetration depth increases, or as the ring develops resistance, this susceptibility rises to zero. Accompanying the resistive transition is a peak in the loss component χ''. In an external field ac H_e we have for the field inside the sample

$$B_{ac}=H_{ac}+4\pi M_{ac}=H_{ac}+\alpha i_{ac},$$

where the ac magnetization M_{ac} results from shielding currents i and $\alpha=4\pi/l$ for currents flowing in a thin surface layer on a long cylinder of length l. If the resistance around the surface layer is R, then V, the induced ac voltage, is $V=iR=\pi a^2 dB_{ac}/dt$. In the ac measurements, $H_{ac}=H_0\exp(j\omega t)$, and $B_{ac}=B_0\exp(j\omega t)$, and we find

$$M_{ac}/H_{ac}=\chi=(j/4\pi/[(R/\omega\alpha\pi a^2)+j].$$

Separating real and imaginary components, we find

$$\chi'=\frac{1}{4\pi}\frac{1}{(R/\pi\alpha\omega a^2)^2+1},$$

$$\chi''=\frac{1}{4\pi}\frac{(R/4\pi\alpha\omega a^2)}{(R/4\pi\alpha\omega a^2)^2+1},$$

and finally

$$\chi''^2=-\chi'/4\pi-\chi'^2.$$

As χ' varies from $-1/4\pi$ to zero, χ'' shows a loss peak of magnitude $(1/2)(1/4\pi)$ with the peak occuring where χ' has experienced 1/2 of its total change, at $\chi'=-(1/2)\times(1/4\pi)$. A bulk transition on the other hand shows a χ'' peak at $\chi'=-0.39(1/4\pi)$, which has been discussed by Maxwell and Strongin.[10] Thus, in principle the resistive transition of a surface layer can be distinguished from that of a bulk superconductor by the observed relationship of χ' and χ''.