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Fluctuation-Induced Diamagnetism above T_c in Superconductors*

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The results of an extensive investigation of the enhanced diamagnetism of superconductors above T_c due to thermal fluctuations are presented. Data are reported on a variety of superconductors, including In, Pb, Nb, and several In-Tl and Pb-Tl alloys. The versatile superconducting quantum magnetometer developed for these experiments, which is suitable for a variety of low-temperature magnetic measurements, is also described. The various theoretical treatments of the fluctuation-induced diamagnetism in superconductors are summarized and their predictions compared with experiment. It is found that at high fields $[H \gtrsim H_{c2}(0)]$ and high temperatures $(T \gtrsim 2T_c)$, the observed diamagnetism deviates markedly from that expected on the basis of the Ginzburg–Landau (GL) theory of superconductivity due to the important contribution of high-energy fluctuations in these regimes. These high-energy fluctuations are not properly described by the simple GL theory. Recent theoretical calculations based on the microscopic Gor'kov theory that attempt to treat these fluctuations properly are found to give a good account of our results for clean materials, once the effects of nonlocal electrodynamics are included, as in the work of Lee and Payne and of Kurkijärvi, Ambegaokar, and Eilenberger. For alloys, however, the theoretical picture is less satisfactory, and it appears possible that even Gor'kov theory may fail to provide an adequate description of high-energy fluctuations in dirty superconductors.

I. INTRODUCTION

There has been considerable interest recently in the effects of thermal fluctuations on the properties of superconductors as the transition temperature is approached from above. As originally predicted independently in several theoretical studies,[1–3] these fluctuations produce an enhancement of the diamagnetism above the superconducting transition that can be quite substantial—a precursor of the perfect diamagnetism of the superconducting state. In a recent series of papers[4,5] we have reported the preliminary results of an experimental study of this fluctuation-induced diamagnetism. In this paper we present a complete account of this earlier work and report the results of some additional measurements on alloys which considerably extend our earlier work.

The study of this fluctuation-induced diamagnetism has proved to be a novel and quite effective means of studying fluctuations in superconductors. Somewhat surprisingly, this effect is most readily observed in large bulk samples, whereas in almost all other studies of the effects of fluctuations in superconductors it has been necessary to use samples with restricted geometries (the so-called one- and two-dimensional superconductors such as whisker crystals and thin films) in order to enhance the fluctuations sufficiently to get an observable effect.[6] Moreover, the ability to use readily prepared bulk samples of high quality, along with the availability of extremely sensitive superconducting quantum-interference magnetometers, has made it possible to study this induced diamagnetism in a wide variety of superconductors and over a considerable range of magnetic fields and temperatures. Particularly important have been the high-field $[H \gtrsim H_{c2}(0)]$ and high-temperature $(T \gtrsim 2T_c)$ regions where, far from the transition, the elementary theories of fluctuations in superconductors fail and challenging theoretical difficulties arise.

Experimentally we find that in an applied field H the magnetization due to fluctuations M' increases roughly as $[T - T_{c2}(H)]^{-1/2}$ as the temperature is reduced toward the bulk superconducting nucleation temperature $T_{c2}(H)$. The nucleation temperature can be at or below the actual transition temperature, depending on whether the sample is a type-II or a type-I superconductor. This observed behavior is in general agreement with the prediction of the Ginzburg–Landau (GL) theory as originally worked out for bulk superconductors in the low-field limit by Schmidt[2] and Schmid,[3] and subsequently generalized to arbitrary fields by Prange.[7] However, as reported in Ref. 5 and intimated above, these elementary treatments of the fluctuations based on the GL theory appear to be quantitatively correct only in *very* weak fields $[H \ll H_{c2}(0)]$ and for temperatures very near T_{c2}. As either field or temperature is increased, the observed enhancement of the diamagnetism falls progressively below the predictions of the GL theory. Nevertheless, the observed behavior does remain remarkably simple, and we find that the data for all materials we have studied are well described by an apparently universal function of suitably scaled field and temperature variables.

Such deviations from the GL predictions were not unexpected, however. At high fields and temperatures, short-wavelength fluctuations [i.e., those fluctuations for which the order parameter varies significantly on the scale of the zero-temperature GL coherence length $\xi(0)$] make a significant contribution to the enhanced diamagnetism, and the GL theory, which is basically a long-wavelength theory, does not properly describe these fluctuations. These difficulties had been anticipated by Patton, Ambegaokar, and Wilkins[8] (PAW) who pointed out that the GL theory tends to overestimate the contribution of short-wavelength fluctuations. They attempted to deal with this problem by introducing an ad hoc cutoff energy into the fluctuation spectrum in a manner suggested from considerations of microscopic theory.

The results of their calculation were found to give a qualitative (but not quantitative) account of our data, including the observed universal behavior. However, their theory was unable to account for the particularly low scaling fields found experimentally for clean materials. As defined in Ref. 5 (and also in Sec. V of this paper), the scaling field H_s is a measure of the field at which deviations from the GL predictions become substantial. The magnitude of this field and its dependence on the material parameters of the samples (specifically the BCS coherence length ξ_0 and the electron mean free path l) have become an important focal point for comparing theory and experiment.

The apparent universality exhibited by our data in the high-field high-temperature regime where the GL theory has failed, and the partial success of the PAW theory in accounting for the observed behavior, have stimulated considerable additional theoretical work aimed at providing a satisfactory theory of fluctuations in superconductors at high fields and temperatures. This work has included systematic generalizations of the GL theory based on microscopic theory[9–12] as well as phenomenological extensions of the GL theory itself.[13] This recent theoretical work is summarized in Sec. II along with the earlier work based on the simpler GL theory.

The experimental results are presented in Sec. IV and compared with theory in Sec. V. The materials studied include In, Pb, Nb, and several In-Tl and Pb-Tl alloys. Both clean and dirty (ξ_0/l up to 16) superconductors were investigated. The superconducting quantum magnetometer used in these experiments, which was critical to their success, is described in Sec. III. This magnetometer can detect magnetization changes as small as 10^{-8} G (in a 0.1-cm^3 sample) and is suitable for a variety of magnetic measurements with the full quoted sensitivity in the temperature range 2–16 K and at fields as high as 300 Oe.

As discussed in detail in Sec. V, the agreement of theory and experiment in the clean limit now appears to be generally satisfactory. We find that our results on pure In and Pb, and to a somewhat lesser extent Nb, are in accord with the recent theoretical work of Lee and Payne[9,12] and Kurkijärvi, Ambegaokar, and Eilenberger,[11] who have calculated the fluctuation-induced diamagnetism in the clean limit using microscopic theory. These authors have, in effect, generalized the GL theory to include arbitrary wavelength fluctuations *and* the effects of nonlocal electrodynamics. The effects of nonlocal electrodynamics were not considered in the earlier work of PAW, and it is now evident that their inclusion is essential to account for the low scaling fields observed in clean materials. The experimentally determined scaling fields are in good agreement with those predicted theoretically for In and Pb, but the experimental value for Nb is anomalously low.[14]

For the dirty materials the situation is far less satisfactory. In this case the finite lifetimes of the high-energy fluctuations become important, necessitating the use of a full dynamical theory, even though a static property of the material is being calculated. Essentially identical calculations based on the Gor'kov theory including these dynamical effects have been undertaken by Kurkijärvi, Ambegaokar, and Eilenberger[11] and by Lee and Payne in their second paper.[12] However, Maki and Takayama,[10] also using the Gor'kov theory, are led to substantially different predictions. As shown in Sec. V, our results favor the predictions of Maki and Takayama, but their work has not been without criticism[15] and the issue remains far from settled. Indeed, if the Lee–Payne–Kurkijärvi–Ambegaokar–Eilenberger calculation is the correct one within the Gor'kov theory, our results would appear to signal the failure of even the Gor'kov theory for describing high-energy fluctuations in dirty superconductors.

II. THEORETICAL CONSIDERATIONS

The theoretical treatments of the fluctuation-induced diamagnetism in superconductors can be divided into two principal classes—those based on the ordinary GL theory[1–7] and those based on microscopic (i.e., Gor'kov) theory.[9–12] The former provide the simplest physical picture of the effect but have a limited range of validity. The latter are sometimes less physically transparent, but are essential in order to obtain a satisfactory theory of the fluctuations at high fields and temperature where the GL theory fails. However, no completely successful microscopic theory of the fluctuations, valid for arbitrary mean free path, exists at the present time. In between these two principal classes is an intermediate class of theories that attempt to approximately correct for the breakdown of the GL theory without undertaking a full microscopic treatment. The most important of these historically is the PAW theory,[8] and the most recent, that of Nam.[13] In our discussion of these theories emphasis is placed on the GL theory since, despite its limited range of validity, this simpler theory accounts for many of the observed features of the fluctuation-induced diamagnetism. Moreover, the GL theory, along with some conceptual input from microscopic theory, provides a simple yet satisfactory basis for discussing the more advanced theories and interpreting our experimental results.

A. Results of GL Theory

The calculation of the fluctuation-induced diamagnetism within the framework of the GL theory proceeds most straightforwardly using the formulation originally developed by Schmid.[3] Following Schmid we begin with the linearized GL free-energy functional

$$F_{\mathrm{GL}}(\psi)=\int d^3r\{\alpha|\psi|^2+(\hbar^2/2m^*)\times|[\vec{\nabla}/i+(2\pi/\Phi_0)\vec{A}]\psi|^2\}, \quad (1)$$

where ψ is the superconduction order parameter, $m^*=2m$ is the electron pair mass, $\vec{A}$ is the vector potential, and $\Phi_0=hc/2e$ is the flux quantum. The $|\psi|^4$ term in the GL free energy has been neglected since we are concerned with the behavior above the transition where (outside the exceedingly narrow critical region) the contribution of this quartic term is small. The parameter α is related to the GL coherence length $\xi(T)$ by $\alpha=\hbar^2/2m^*\xi^2(T)$. Near T_c, α is proportional to $(T-T_c)$, and we define $\xi(0)$ such that $\xi(T)=\xi(0)[T_c/(T-T_c)]^{1/2}$. The value of $\xi(0)$ can be related to the normal electronic properties of the material using the standard relations obtained from microscopic theory.[16]

Expanding the order parameter $\psi(r)$ in terms of the normalized eigenfunctions[17] $U_\nu(r)$ of the operator $[\vec{\nabla}/i+(2\pi/\Phi_0)\vec{A}]^2$, we have

$$\psi(r)=\sum_\nu C_\nu U_\nu(r), \quad (2a)$$

and the free-energy functional can be written

$$F_{\mathrm{GL}}=\sum_\nu|C_\nu|^2 f_\nu^{\mathrm{GL}}, \quad (2b)$$

where

$$f_\nu^{\mathrm{GL}}=\alpha+(n+\tfrac{1}{2})\,\frac{2\hbar e}{m^*c}H+\frac{\hbar^2}{2m^*}\,k_z^2 \quad (2c)$$

$$=\frac{\hbar^2}{2m^*}\,\xi^{-2}(0)\left(\frac{T-T_c}{T_c}+(2n+1)\times\frac{2\pi\xi^2(0)}{\Phi_0}\,H+\xi^2(0)k_z^2\right) \quad (2d)$$

is the free-energy density of the particular fluctuation mode labeled $\nu\equiv(n,\beta,k_z)$. The formal similarity between the energy spectrum given in Eq. (2c) and the Landau levels of a free particle (mass $2m$, charge $2e$) is evident. In fact, the fluctuation-induced diamagnetism can be thought of as qualitatively arising from the presence of evanescent Cooper pairs generated by the thermal fluctuations and moving in circular orbits at the cyclotron frequency.

The contribution to the total free energy resulting from fluctuations of ψ can be obtained from the partition function Z' generated by summing $e^{-F_{\mathrm{GL}}(\psi)/kT}$ over all possible $\psi(r)$ (or, equivalently, all C_ν). As shown by Schmid this procedure leads to the result

$$F'=-kT\ln Z'=-VkT\left(\frac{2eH}{2\pi\hbar c}\right)\times\int\frac{dk_z}{2\pi}\sum_{n=0}^{\infty}\ln\frac{\pi kT}{f^{\mathrm{GL}}_{n,k_z}}. \quad (3)$$

The factor $2eH/2\pi\hbar c$ accounts for the degeneracy of each mode (n,k_z) in the magnetic field H, and the primes are used to indicate that only the contribution due to the fluctuations has been calculated.

In his original paper Schmid evaluated Eq. (3) only to second order in H and consequently his results are valid only in the low-field limit. The behavior expected in arbitrary fields was first obtained by Prange[7] who calculated the magnetization M' due to fluctuations from Eq. (3) with no approximations. Prange found that

$$M'=-2\pi^{1/2}kT\Phi_0^{-3/2}H^{1/2}g(x), \quad (4)$$

where $g(x)$ is a universal function of the variable

$$x=\frac{m^*\alpha/\hbar e}{H}=\left(\frac{dH_{c2}}{dT}\right)_{T_c}\frac{T-T_c}{H}.$$

Prange also showed that as $x\to-1$ [i.e., as the condition $H=H_{c2}(T)$ is approached], $g(x)$ diverges as $(x+1)^{1/2}$. For fixed field this implies that M' diverges as $[T-T_{c2}(H)]^{-1/2}$ as the temperature is reduced. Here $T_{c2}(H)$ is defined as the temperature at which $H_{c2}(T)$ becomes equal to the applied field H as temperature is varied. Since the energy cost of the lowest fluctuation mode $f_{k_z=0,n=0}$ vanishes at this temperature, T_{c2} represents the bulk superconducting nucleation temperature. As illustrated in Fig. 1, $T_{c2}(H)$ is also the actual transition temperature for a type-II superconductor where the transition is second order. However, for a type-I superconductor, the transition is first order and occurs at a temperature $T_c(H)>T_{c2}(H)$. In this case the divergence of the fluctuations at T_{c2} will be inaccessible in the absence of supercooling.

The divergence of M' at T_{c2} reflects the large fluctuations of the order parameter expected in the region where the energy cost of the fluctuations is going to zero. This divergence would be limited by the nonlinear $|\psi|^4$ term in the GL free energy that was neglected in obtaining Eq. (3), but only so near to T_{c2} as to be lost in the finite breadth of the transition in any real sample. Hence we do not consider any such effects.

At $T=T_c$ (the *zero-field* transition temperature), the Prange result is particularly simple and predicts that

$$M'(T_c)/H^{1/2}T_c = -0.323k\Phi_0^{-3/2}, \qquad (5)$$

a constant independent of any material parameters. At sufficiently high temperatures or low fields where $H/[\Phi_0/2\pi\xi^2(T)] \ll 1$, Prange's result reduces to the expression

$$\chi' = M'/H = -\tfrac{1}{6}\pi kT\Phi_0^{-2}\xi(0)[T_c/(T-T_c)]^{1/2}, \qquad (6)$$

which is the expression found earlier by Schmid and also by Schmidt, who derived Eq. (6) from the GL theory using linear response theory.

This last result can be understood on very simple physical grounds using a droplet model of the fluctuations. Assuming that each droplet acts like a small superconducting particle, we can estimate the diamagnetism produced by the droplets using London's expression $\chi = -(1/40\pi)(r/\lambda)^2$ for the susceptibility of a small superconducting sphere with radius r much smaller than the London penetration depth $\lambda = [m^*c^2/4\pi|\psi|^2(2e)^2]^{1/2}$.[18] For weak magnetic fields ($A \approx 0$), Eq. (1) indicates that the energy required to produce a droplet of radius r is approximately $\alpha|\psi|^2r^3$. Equating this energy cost to the available thermal energy ($\sim kT$), we find that in the droplet $|\psi|^2 \approx kT/\alpha r^3$ and, consequently, $\chi \approx -\frac{1}{10}\pi^2 kT\Phi_0^{-2}\xi^2(T)/r$. Clearly, the smaller droplets make the largest contribution to the enhanced diamagnetism. But since droplets with radii much smaller than $\xi(T)$ are inhibited due to the large kinetic energy associated with sharp gradients in ψ, we expect the resultant diamagnetism to be due primarily to droplets with $r \approx \xi(T)$. Making this substitution in the expression for χ above and assuming that, on the average, the sample is filled with such spheres, we are led to the Schmid-Schmidt result within a factor of nearly unity.

The predictions of the GL theory outlined above are in qualitative agreement with the behavior observed experimentally. In fact, at low fields and for temperatures sufficiently near T_{c2}, the GL predictions appear to be *quantitatively* correct (see Sec. IV). Evidently the GL theory contains the essentials of the correct physical description of the fluctuation-induced diamagnetism in superconductors. However, it is clear that the GL theory must break down at high fields and temperatures. At $T=T_c$, it predicts that $M' \sim H^{1/2}$ for all H no matter how large, and it predicts that M' *increases* at $T^{1/2}$ for large temperatures. Such behavior is physically unreasonable and indicates that far from the critical point ($T=T_c$; $H=0$) the GL theory overestimates the effects of the fluctuations.

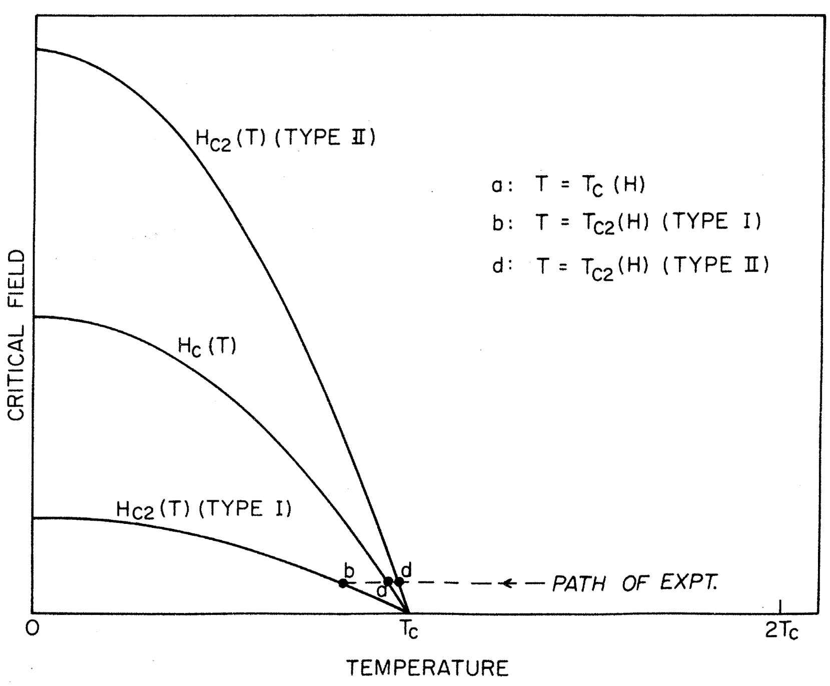

FIG. 1. Schematic diagram of the critical-field curves for type-I and type-II superconductors. The field $H_{c2}(T)$ is the bulk nucleation field and $H_c(T)$ is the thermodynamic critical field. As indicated in the text, in a field H the fluctuation-induced diamagnetism diverges at the temperature $T_{c2}(H)$ defined by the condition $H=H_{c2}$ (e.g., points b and d in the figure) where the energy cost of a fluctuation vanishes For a type-II superconductor $H_{c2}(T) > H_c(T)$ and a second-order transition occurs at $T_{c2}(H)$. Consequently, the divergence temperature of the fluctuations coincides with the actual transition temperature (point d). For a type-I superconductor $H_c(T) > H_{c2}(T)$ and a first-order transition occurs at $T_c(H)$. In this case the divergence temperature (point b) is lower than the actual transition temperature (point a), and in the absence of supercooling the region between $T_c(H)$ and $T_{c2}(H)$ is inaccessible.

B. Breakdown of GL Theory

As indicated above it is evident that the GL theory breaks down at high fields and temperatures. A more specific picture of this breakdown can be obtained from elementary considerations. As is well known,[19] the GL free-energy functional, Eq. (1), contains only the leading terms of an expansion of the free energy in powers of $|\psi|$ and derivatives of ψ, and thus it is valid only when $|\psi|$ is small and when ψ varies slowly in space—the so-called slow-variations approximation. Outside the exceedingly narrow critical region $[(T-T_c)/T_c \lesssim 10^{-8}$ for a bulk superconductor], $|\psi|^2$ is certainly small above T_c and the higher powers of $|\psi|$ can be safely neglected. The same is *not* true for higher derivatives, however. The slow-variations approximation requires that ψ vary slowly on the scale of $\xi(0)$, the zero-temperature GL coherence length. As a result, the GL theory is valid only for long-wavelength fluctuations and fails in those regimes where short-wavelength fluctuations make a significant contribution to the total effect of the fluctuations. This occurs at high temperatures as can be seen qualitatively from the fact that above T_c, ψ is correlated[20] only over a range $\sim \xi(T)$ and consequently, as T increases and $\xi(T)$ decreases, short-wavelength fluctuations play an increasingly important role. When T exceeds twice T_c and $\xi(T)$ becomes less than $\xi(0)$, the slow-variations approximation has certainly failed. Moreover, when the effects of a magnetic field are included, the gradient term in the GL free energy becomes $|\nabla/i + (2\pi/\Phi_0)\vec{A})\psi|^2$, and the application of a field alone can introduce rapid spatial variations into ψ. This behavior is also reflected in the correlations of ψ. In strong fields the correlation function $\langle\psi(r)\psi(0)\rangle$ falls off as $e^{-\pi H r^2/2\Phi_0}$ for displacements perpendicular to the field direction.[21] For $H \gtrsim 2\Phi_0/\pi\xi^2(0) \approx H_{c2}(0)$, the range of this function becomes less than $\xi(0)$ and the slow-variations approximation again fails. Finally, in accounting for the effects of a magnetic field, it is not sufficient to simply generalize each gradient operator ∇/i in the zero-field expansion of the free energy to $\nabla/i + (2\pi/\Phi_0)\vec{A}$ as required by gauge invariance. In general, additional field-dependent terms must be included. These latter terms are the so-called nonlocal electrodynamic corrections to the GL theory and become important in strong fields, particularly in clean materials.

The corrections to the GL theory when $|\psi|$ is small have been discussed by Werthamer[19] in a review article. Using his results we find that the leading correction to the free-energy density [Eq. (2d)] for nonlocality is of the form $(2\pi\xi'^2/\Phi_0)^2 H^2$, where $\xi' \approx \xi_0/(1+\xi_0/l)^{3/4}$, while the leading correction for the breakdown of the slow-variation approximation is

$$\xi^4(0)\,|\,[(\vec{\nabla}/i) + (2\pi/\Phi_0)\vec{A}]^2\psi\,|^2 \approx [2\pi\xi^2(0)/\Phi_0]^2 H^2 .$$

Although highly schematic and based only on the leading corrections to the GL theory, this result suggests that the breakdown of the GL theory as the field is increased should be governed by two characteristic fields, $\Phi_0/2\pi\xi^2(0)$ and $\Phi_0/2\pi\xi'^2$, associated with the failure of the slow-variation and local approximations of the GL theory, respectively. In the clean limit both of these effects may play an important role, but since $\xi'/\xi(0) \rightarrow 0$ as $l \rightarrow 0$, in the dirty limit the nonlocal effects should be unimportant. The necessity of these corrections to the GL theory can be appreciated by recalling that the order parameter ψ physically represents the wave function of the paired electrons (Cooper pairs) which produce superconductivity. Thus when ψ varies rapidly on the scale of the size of a Cooper pair, the theoretical description of ψ necessarily becomes more complicated, reflecting the need to include a more complete description of the detailed microscopic interactions leading to the electron pairing.

Another basic approximation underlying the GL theory, one which is not usually emphasized in elementary discussions of the GL theory, is the so-called static approximation.[22] Above the superconducting transition in the fluctuation regime, the physical consequence of this approximation is to restrict the validity of the GL theory to those fluctuation modes which are long lived. When short-lifetime fluctuations make a significant contribution to the free energy, the GL theory fails, and it is necessary to include additional dynamical corrections to the theory. In effect, it becomes necessary to use a full time-dependent theory even to calculate the static susceptibility. Recent theoretical work described below has shown that these dynamical corrections become very important for dirty materials.

Since it is the high-energy fluctuations (large k_z and n) that have rapid spatial variations, any improvement over the GL theory must provide a more accurate description of these high-energy fluctuations. In addition, it is just these high-energy fluctuations which have short lifetimes. (In the time-dependent GL theory we have $\tau_\nu^{GL} \propto 1/f_\nu^{GL}$; see Ref. 23.) Of course when a magnetic field is present the nonlocal corrections become important as well. Only at low fields and near T_{c2} where low-energy long-wavelength long-lifetime fluctuations dominate and the electrodynamics is local should the GL theory be adequate.

The first attempt to provide an improved treatment of these high-energy fluctuations was undertaken by Patton, Ambegaokar, and Wilkins[8] who attempted qualitatively to predict the effects of the breakdown of the GL theory on the fluctuation-induced diamagnetism. They compared the microscopic and GL theory expressions for the free-energy functional and concluded that the GL theory overestimates the contribution of the short-wavelength fluctuations. In order to correct qualitatively for this deficiency, they introduced a cutoff energy into the energy spectrum of the fluctuations in a manner suggested by microscopic theory. The resulting expression for the free energy F' reduced to the GL form [Eq. (3)] for the low-energy modes but was less for the high-energy modes. In effect, they replaced f_ν^{GL} with $f_\nu^{\mathrm{PAW}} = E(1 - e^{f_\nu^{\mathrm{GL}}/E})$ in Eq. (3), where E is the cutoff energy, which they estimated would lie in the range $\hbar^2/2m^*\xi^2(0) \lesssim E < kT_c$. Using this modified form of the free energy they found that M' should be strongly suppressed below the GL prediction if $H > H^* \equiv m^*cE/\hbar e$ or $T > T^* \equiv 2m^*\xi^2(0)T_c\,E/\hbar^2$. [For $E \approx \hbar^2/2m^*\xi^2(0)$, as they thought more likely, $H^* \approx \Phi_0/2\pi\xi^2(0)$ and $T^* \approx 2T_c$.] In addition, they found that $M'/H^{1/2}\,T$ is a universal function, but only if the field H is scaled by H^* in addition to using the scaled temperature introduced by Prange. The PAW theory successfully eliminates the unreasonable nature of the GL predictions at large T and H, and qualitatively accounts for the observed behavior, most importantly anticipating the scaled variables necessary to describe the data in universal form. But the PAW theory is quantitatively inadequate, especially (but not solely) for the clean materials, where the best fit to the data requires values of E considerably smaller than their lower limit. This deficiency has been rectified by the microscopic calculations discussed below.

In a more straightforward calculation, Mikeska and Schmidt[23] have extended the earlier low-field results of Schmidt[2] to strong fields using a generalized form of the GL theory. However, their calculations were restricted to the region near T_{c2}, and therefore their results do not apply to most of our data. More recently, Nam[13] has discussed a phenomenological extension of the GL theory based on a "boson model" of the fluctuations which he finds gives a good account of our published data.[5] However, as discussed later by Lee and Payne,[12] this theory is mathematically similar to the PAW theory and gives a good agreement with experiment only when an adjustable parameter is introduced.

C. Results from Microscopic Theory

Full microscopic calculations of the fluctuation-induced diamagnetism based on the Gor'kov theory have been undertaken by several groups. In effect, these calculations systematically generalize the GL theory to include arbitrary spatial variations of the order parameter, the effects of nonlocal electrodynamics, and, in some cases, the dynamical corrections to the GL free energy. The results for the clean limit were first reported by Lee and Payne[9] (LP) and subsequently confirmed by Kurkijärvi, Ambegaokar, and Eilenberger[11] (KAE) who had independently carried out essentially the same calculation. These authors find that in this limit $M'/H^{1/2}T$ is a universal function of the scaled field variable (we use the notation of Lee and Payne) $b_c = (hv_F/4\pi T_c)^2(eH/hc) = 0.097\,H/(\Phi_0/2\pi\xi_0^2)$ and the reduced temperature $\mathcal{E} = (T - T_c)/T_c$, or, equivalently, b_c and the scaled temperature variable $(dH_{c2}/dT)_{T_c}(T - T_c)/H$ introduced by Prange. This equivalence follows from the fact that $(dH_{c2}/dT)_{T_c}(T - T_c)/H = 0.177\mathcal{E}/b_c$. The temperature scaling given by $\mathcal{E} = (T - T_c)/T_c$ is much simpler than the temperature scaling used by Prange and PAW, and since both lead to universal behavior in the clean limit, it would appear preferable to use $\mathcal{E}$. However, the experimental evidence suggests that alloys and clean materials exhibit the same universal temperature dependence only if the Prange temperature scaling is used. This point will be discussed further in Sec. V.

The field dependence of $M'/H^{1/2}\,T$ found by LP–KAE in the clean limit for $T = T_c$ is shown in Fig. 2. The behavior expected for $T = T_c$ is particularly convenient for comparing various theories and also theory and experiment since it avoids the more complicated question of the detailed temperature dependence of M'. Also shown in the figure are the predictions of the GL theory, the PAW theory [assuming only that $E = \hbar^2/2m^*\xi^2(0)$], and the predictions of microscopic Gor'kov theory neglecting nonlocal electrodynamics (local approx.). As we shall show in Sec. V, the LP-KAE result is in good agreement with our data, and it is now evident that the principal shortcoming of the PAW theory in the clean limit was a failure to include nonlocal electrodynamics. (For a more detailed discussion of this point see the paper by KAE, Ref. 11.)

The appropriate generalization of these microscopic calculations to finite ξ_0/l has been discussed by KAE and also by LP in their second paper.[12] Maki and Takayama[10] have also discussed this regime, although their calculations are restricted to the very dirty limit ($\xi_0/l \gg 1$). All of these calculations use the Gor'kov theory as their basic starting point. They differ in their detailed predictions, however, due to differences in the particular manner in which the dynamical corrections are taken into account. These dynamical corrections are small in the clean limit but become increasingly more important as ξ_0/l increases. LP and KAE treat these corrections similarly and find that they *increase* M' above that obtained using the static

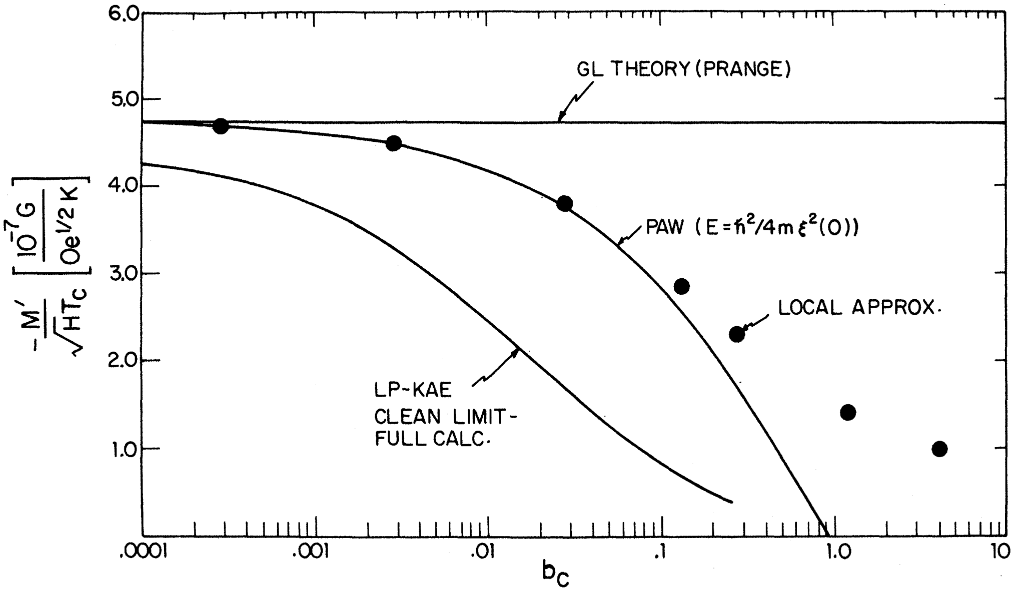

FIG. 2. Theoretical predictions—clean limit. The predicted field dependence of M' at $T=T_c$ is shown for various theories. The full microscopic calculation including nonlocal electrodynamics is seen to predict a falloff from the GL result at much lower fields than found using a local approximation. The dramatic effect of nonlocal electrodynamics on the suppression of the fluctuations by a magnetic field in clean materials is clearly seen. The approximate PAW theory [with $E=\hbar^2/2m^*\xi^2$ (0)] is seen to correspond most clearly to local microscopic theory.

approximation (no dynamical corrections). Maki and Takayama (MT) find that M' is strongly *decreased*. The differences between these two treatments have been discussed by LP in Ref. 12. Also, to facilitate comparison between the various theories and theory and experiment, LP have carried out numerical calculations in the small ξ_0/l regime using the MT treatment of the dynamical corrections.[24]

A comparison of the predictions obtained from these competing calculations is shown in Fig. 3. The solid lines show the LP-KAE results and the dashed lines (labeled MT) those obtained by LP using the MT treatment of the dynamical corrections. As is evident from the figure, for a given ξ_0/l the MT result falls off from the GL value sub-

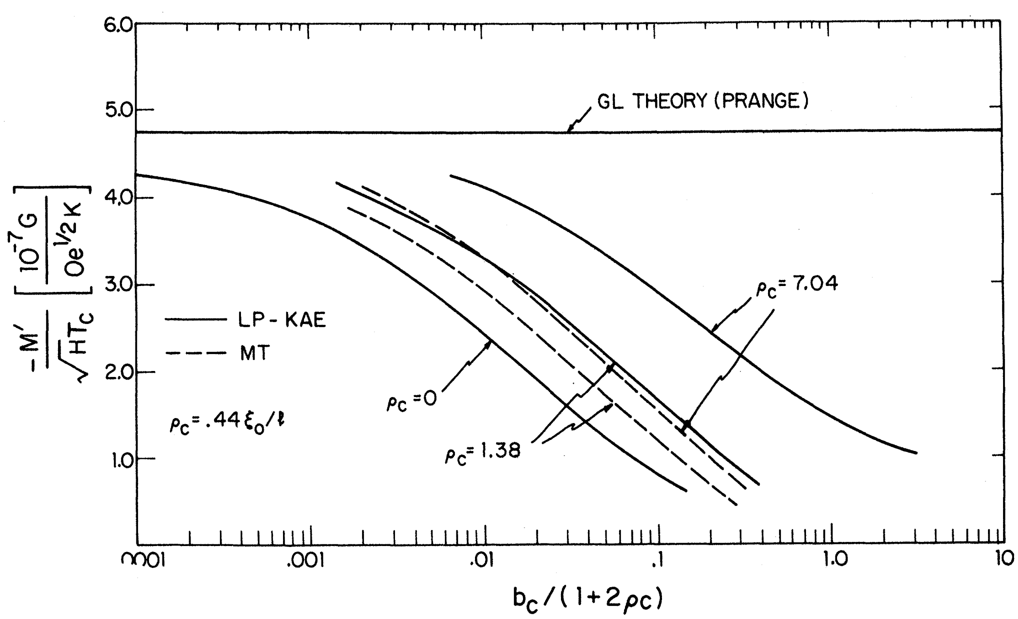

FIG. 3. Theoretical predictions—dirty limit. The theoretical predictions of LP-KAE and MT for the field dependence of M' at $T=T_c$ are illustrated. It is seen that for a given $\rho_c=0.44\xi_0/l$, the MT calculation predicts a suppression of the fluctuation at a lower field than the LP-KAE calculation.

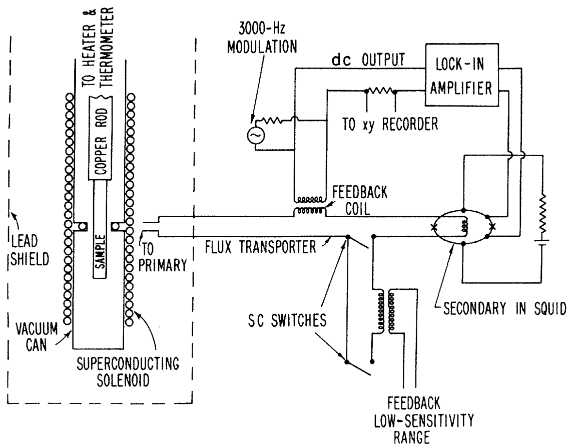

FIG. 4. Schematic diagram of the apparatus. A superconducting dc flux transporter is used to couple the sample and SQUID detector. The feedback circuit nulls the current in the flux transporter and provides an output voltage which is proportional to the magnetization change of the sample. Mechanical superconducting switches are used to change from high to low sensitivity mode of operation.

stantially sooner than that of LP–KAE. In this figure the scaled field variable used is $b_c/(1+2\rho_c) = 0.097H/[(\Phi_0/2\pi\xi_0^2)(1+0.88\xi_0/l)]$. This particular scaling arises naturally in the calculations using the Gor'kov theory but does not contain the complete mean-free-path dependence of the theory and therefore does not lead to universal behavior. Since $\xi(0)=0.74\xi_0/(1+0.88\xi_0/l)^{1/2}$ except for small corrections at large ξ_0/l, $b_c/(1+2\rho_c)$ is the field scaling associated with the zero-temperature GL coherence length. Based on our discussion of the leading corrections to the GL theory presented in Sec. II B, we would not expect this field scaling to lead to universal behavior in the low ξ_0/l limit where the effects of nonlocal electrodynamics are important. However, over the range of ξ_0/l shown in Fig. 3, the shape of the falloff from the GL value for both the LP–KAE and MT predictions is very similar to that found in the clean limit, and universal behavior can be obtained, at least approximately, using either prediction by an appropriate empirical rescaling of the field variable. Thus both calculations yield universal behavior for small ξ_0/l,[25] although the scaling fields obtained in the two cases are quite different. We shall return to this point and the physical significance of this universal behavior in Sec. V after we have discussed the experimental data.

III. INSTRUMENTATION

An extremely sensitive superconducting quantum magnetometer was used to detect the small diamagnetism above T_c. A schematic diagram of the apparatus is shown in Fig. 4. The magnetic flux detector is a double-point-contact superconducting quantum-interference device (SQUID) made of Nb foils, but any of the currently popular types of SQUID's would be satisfactory.[26] More importantly, the SQUID is magnetically coupled to the sample by a superconducting dc flux transporter (or transformer) made of Nb wire. This arrangement permits the thermal and magnetic environment of the SQUID and sample to be controlled and optimized independently. The transporter circuit consists of a primary coil L_1 around the sample, a secondary coil L_2 in the SQUID, and a small feedback coil L_f into which an external current can be inductively coupled to keep the current in the transporter nulled. Mechanical superconducting switches controlled from outside the cryostat permit a large dropping inductor L_d to be switched into the circuit in order to reduce the amount of flux sensed by the SQUID. This low-sensitivity mode is particularly useful for measuring the large flux change at the superconducting transition. Similar switches are used to open the transporter circuit when large changes of the applied field are made.

Signal detection is accomplished by current-biasing the interferometer near its critical current, coupling a very small (10^{-6}-Oe) 300-Hz modulating field to the SQUID via the flux transporter, and detecting the resulting flux-dependent ac signal with a lock-in amplifier preceded by a transformer (not shown) having a voltage gain of 100. The dc output of the lock-in amplifier provides a feedback current that keeps the transporter current nulled. For sufficiently high loop gain, this feedback current is proportional to the magnetization change of the sample independent of the specific SQUID characteristics.

The SQUID, transporter circuit, and sample chamber are enclosed in a superconducting lead can to shield them against spurious flux changes. The ambient magnetic field is reduced to less than 1 mOe by two concentric Moly Permalloy shields from Allegheny Ludlum Steel Corp. The entire apparatus and electronics are located inside an rf shielded enclosure manufactured by the Ray Proof Corp., and rf filters are used on the feedback and current-bias leads. These precautions are necessary to prevent rf signals from degrading the performance of the magnetometer by inducing spurious currents in the SQUID and transporter circuit.

The samples are thermally bonded to a copper rod and suspended inside a vacuum can having a narrow constriction around which the transporter primary is wound. The constriction is necessary in order to obtain good coupling to the sample. The sample can be withdrawn from the primary in order to measure its total magnetization. The temperature of the sample can be varied continuously between 2 and at least 16 K by means of a heating resistor and thermal link attached to the copper rod, while the SQUID and transporter circuit are maintained at the constant liquid-helium–bath temperature. The sample temperature is determined from the resistance of a Solitron germanium cryogenic sensor, type SP2301, which was calibrated below 4.2 K against the helium vapor pressure, and above 4.2 K by comparison with a similar sensor whose calibration, performed by the manufacturer, is claimed to be accurate to at least 0.1 K. Additional checks were obtained from the transition temperatures of indium and lead, which were correct to 0.003 and 0.06 K, respectively. Temperature resolution is about 10^{-4} K.

The applied magnetic field is produced by an end-corrected Nb solenoid operated in persistent-current mode. The magnetic detection system was calibrated by simulating the uniformly magnetized sample with an equivalent closely wound solenoid of nearly identical dimensions. This procedure automatically corrects for the shielding effects of the persistent-current magnet and the imperfect coupling to the transporter primary. A consistency check on the combined calibrations of the SQUID and solenoid was obtained by measuring the total exclusion of flux from a sample at the superconducting transition in a 1-Oe applied field. Actual measurements are made by sweeping temperature and recording the flux changes $\Delta\Phi$ with the magnetometer. Magnetization changes $\Delta M = \Delta\Phi/4\pi A$ are then computed using the measured area of the sample. Magnetization changes measured with this system are estimated to be accurate to within 3%.

The major limitation in the performance of this magnetometer is a small field-independent-background flux change that occurs when the sample temperature is changed. Its origin is not known with certainty, but the available evidence suggests that it is due to thermoelectric currents associated with thermal gradients near the heater in the copper rod. (Such currents could be eliminated by using a high-thermal conductivity dielectric rod to replace the copper one.) This small background must be subtracted from the observed magnetization changes in order to obtain accurate measurements. This effect limits the minimum detectable magnetization change to about 1×10^{-8} G, which is adequate for the present experiments. The sensitivity at constant temperature is about a factor of 10 better than this and is limited by Johnson-noise currents in the sample. At "high" fields ($H > 10$ Oe) the performance is further degraded by long-term drifts due to flux creep in some part of the magnetometer. This effect can be circumvented to a large degree by repetitive measurements.

IV. EXPERIMENTAL RESULTS

Measurements have been carried out on the pure superconductors In, Pb, and Nb, and on several Pb-Tl and In-Tl alloys. These materials include both type-I and type-II superconductors. Measurements on type-I materials were restricted to temperatures above $T_c(H)$, where the first-order transition occurs. For the type-II materials where $T_{c2} > T_c$ and the transition is second order, it was possible to make measurements through the entire transition into the mixed state and to investigate the effects of surface superconductivity. The most complete results were obtained on In and Pb, because high-quality samples of these materials could be prepared whose transitions had very little extrinsic broadening and because measurements over the entire range of relevant fields could be made. For the alloys and Nb, considerably greater broadening was present. Also, due to the deteriorating performance of the superconducting magnetometer for fields above ~ 300 Oe, it was not possible to make measurements on the alloys and Nb at fields sufficiently high to completely suppress the fluctuations.

Except for niobium, the samples used in these experiments were cylindrical single crystals 39 mm long and 5 mm in diameter prepared from 99.9999%-pure components. They were cast in Pyrex tubes lightly lubricated with Dow Corning No. 710 fluid, slowly drawn through a vertical zone melter for recrystallization, and then spark cut to the desired length. The samples were etched and examined for crystal perfection (dislocations and grain boundaries). The indium samples, which were quite soft, showed a few small dislocations near the ends from the cutting process. Otherwise no grain boundaries were seen on the ends of the samples and only some very faint longitudinal striations were seen on the cylindrical surfaces. These are believed to be due to small-angle misalignments at the surface. The other samples were of similar quality, although the In-Tl samples showed somewhat more pronounced striations. X-ray diffraction studies of the lead sample indicated that its longitudinal axis was 7° from a [110] direction. However, the sample orientation is not believed to play an important role in the interpretation of these experiments. Single crystals were used mainly to obtain nearly ideal samples with minimal extrinsic broadening of the transition. The alloy samples had ξ_0/l ratios ranging from 5 to 16. The Nb sample was a single crystal 28 mm long by 2.9 mm in diameter and had a residual resistivity ratio $\rho_{300\,K}/\rho_{4.2\,K} = 350$.

A. Type-I Superconductors: In and Pb

Figure 5 shows the complete diamagnetic transition for indium in a 0.109-Oe applied field. For

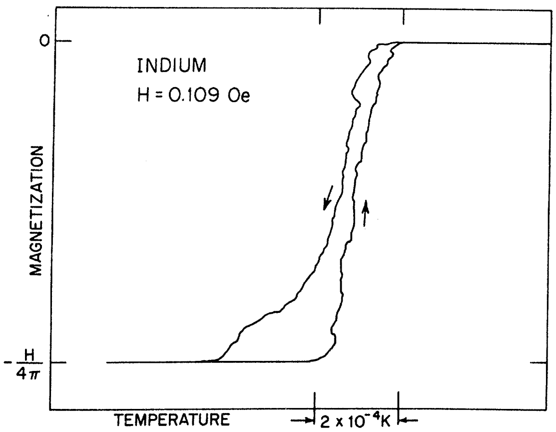

FIG. 5. Complete superconducting transition of a single-crystal indium sample. This measurement was made using the low sensitivity mode of the magnetometer. The extrinsic broadening of the transition is seen to be approximately 2×10^{-4} K.

this measurement the magnetometer was operated in its low-sensitivity mode in order to follow the large flux change due to the Meissner effect. Viewed with this "conventional" sensitivity, the width of the transition for increasing temperatures is only 2×10^{-4} K. At higher fields it was slightly broader and somewhat rate dependent, presumably indicative of some slight flux pinning. By conventional standards this is quite a sharp transition. In fact, the upward sweep shows a magnetization which is decreasing faster than exponentially with temperature. The total width due to extrinsic broadening is apparently less than 1 mK, thus enabling us to confidently exclude gross broadening as an explanation of the temperature-dependent diamagnetism above T_c. The diamagnetic transition of our second indium sample was similar to that shown and the lead sample was about twice as broad.

The temperature dependence of the magnetization of indium above $T_c(H)$ measured with high sensitivity is shown in Fig. 6, where the enhanced diamagnetism due to fluctuations is seen. In obtaining these data, changes in magnetization with temperature were measured up to about 11.5 K or roughly $3T_c$. Only part of this region is shown in the figure. The zero of magnetization was determined as follows. For each curve there was a temperature region at least 4 K wide in which no magnetization change was observed ($\Delta M < 0.15\times10^{-7}$ G). Since the normal susceptibility is not expected to have any strong temperature dependence, it seems reasonable to assume that the fluctuation-induced magnetization is essentially zero in this region, and it is with respect to this choice of zero that the data in this paper are presented. That is,

$$M'_{\text{expt}}(H,T) \equiv M(H,T) - M(H, T \gg T_c) .$$

The subscript will normally be omitted. This procedure eliminates the baseline uncertainty present in our earliest results.[4]

The results for In are typical of those observed in type-I superconductors. As temperature is reduced, $|M'|$ increases smoothly until $T = T_c(H)$, where a sharp first-order transition into the Meissner state occurs. This behavior is best seen in the curve for 34.9 Oe in Fig. 6(b) where the data clearly exhibit a finite slope as T approaches $T_c(H)$. As the field is increased, $|M'|$ initially *increases*, and the region over which it is temperature dependent appears to become wider. However, the magnetization eventually begins to *decrease* with increasing field. For sufficiently high fields, the fluctuations are completely suppressed, and M' is not measurably temperature dependent at all. In the case of In, a 70-Oe applied field was sufficient to completely suppress the fluctuations.

The data are reproducible and are sample independent, except for the region below T_c in high fields, where the curvature appears to reverse for the sample of Fig. 4(b), but not for other samples. In general, the magnetization measurements are estimated to be accurate to about 0.3×10^{-7} G or 3%, which ever is greater. The accuracy at low levels is limited mainly by the necessity of correcting for the instrumental temperature-dependent background, and by the long-term drifts discussed in Sec. III.

In addition to measurements of the magnetization change with temperature, the total magnetization $M = M' + M_n$, including the normal magnetization M_n, was measured by withdrawing the sample from the flux transporter at 4.6 K. At this temperature, M' is less than 0.5% of M at any field, so that $M = M_n$ to within the accuracy of the measurement ($\approx 3\%$). This measurement gave a normal-state susceptibility $\chi_n = M_n/H = -2.00 \pm 0.06\times10^{-6}$ emu/cm^3 for In, which was field independent for fields between 0.6 and 70 Oe.

Representative data for In are plotted in Fig. 7 using the scaled variables suggested by theory. The prediction of the GL theory is also shown for reference. The quantitative failure of the GL theory over the range of fields and temperature shown is evident.

The results on our Pb sample were qualitatively similar to that described for In. The data are shown in Fig. 8 plotted using scaled variables. Note that at the highest fields ($H > 50$ Oe), the data are still temperature dependent at 16 K (our highest conveniently attainable temperature), indicating that for $H = 218$ Oe there is some baseline uncertainty.

B. Type-II Superconductors: Pb-Tl Alloys

In order to study the fluctuations near the divergence at T_{c2} and to investigate the effects of finite mean free path, experiments were carried out on several type-II superconducting alloys. In addition, since $H_{c3} > H_{c2} > H_c$ in such materials, surface superconductivity is present and can also be studied. Of course it must be suppressed in order to study the fluctuation-induced diamagnetism of the bulk for temperatures near T_{c2}.

Figure 9 shows the temperature dependence of the magnetization in the region of surface superconductivity for a Pb–4-at.%-Tl sample. Also illustrated is the successive reduction of surface effects as the surface is gold plated. For curve (a)

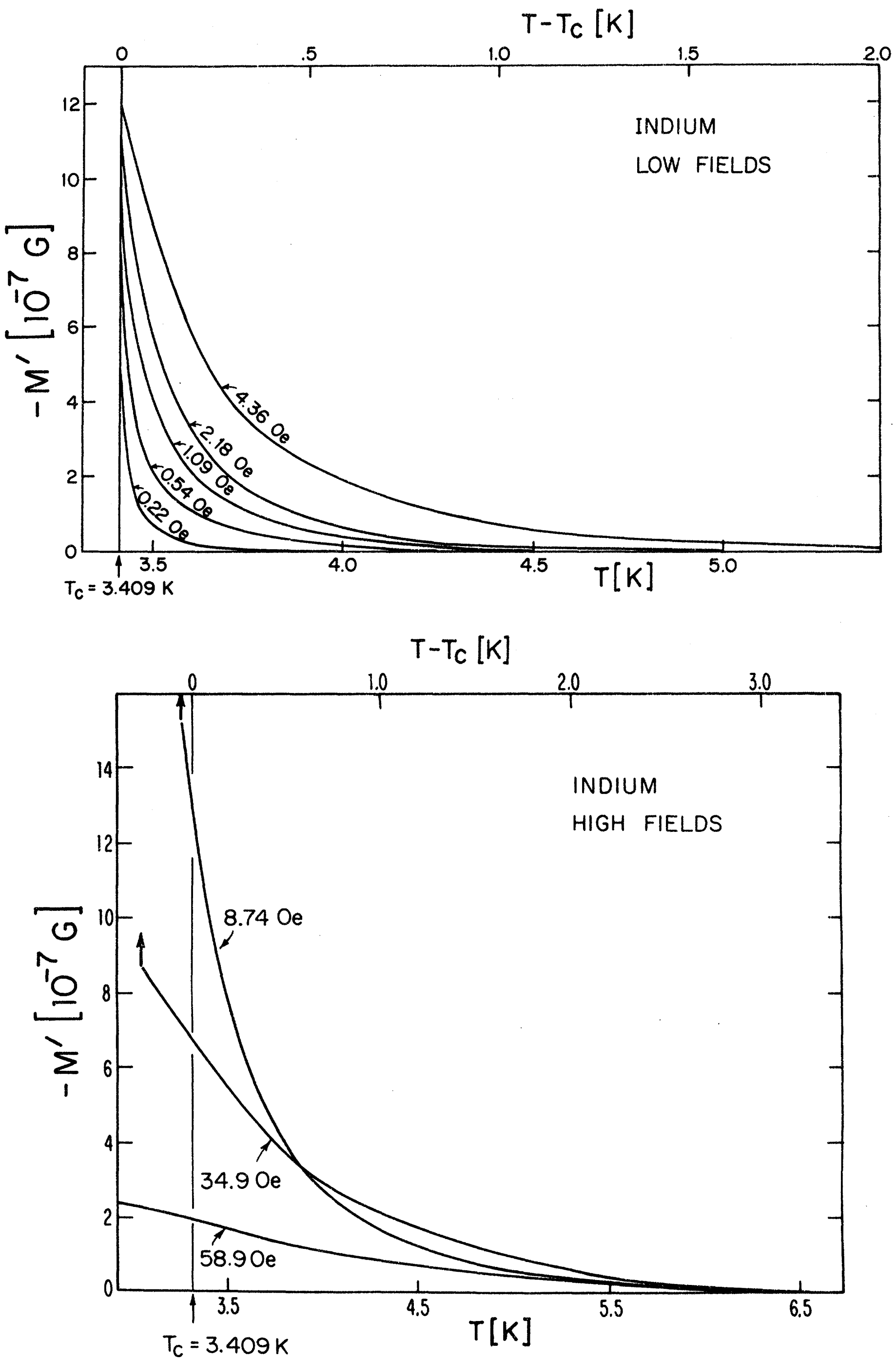

FIG. 6. Fluctuation-induced diamagnetism of indium above the superconducting transtion. The baseline for these curves has been taken as the high-temperature limit of the measured magnetization changes. (a) For $H < 6$ Oe, $-M'(T_c)$ is an increasing function of H. The data below T_c are not shown for clarity. (b) For larger applied fields, $-M(T_c)$ is a decreasing function of H. The vertical arrows indicate the first-order transitions at $T_c(H)$.

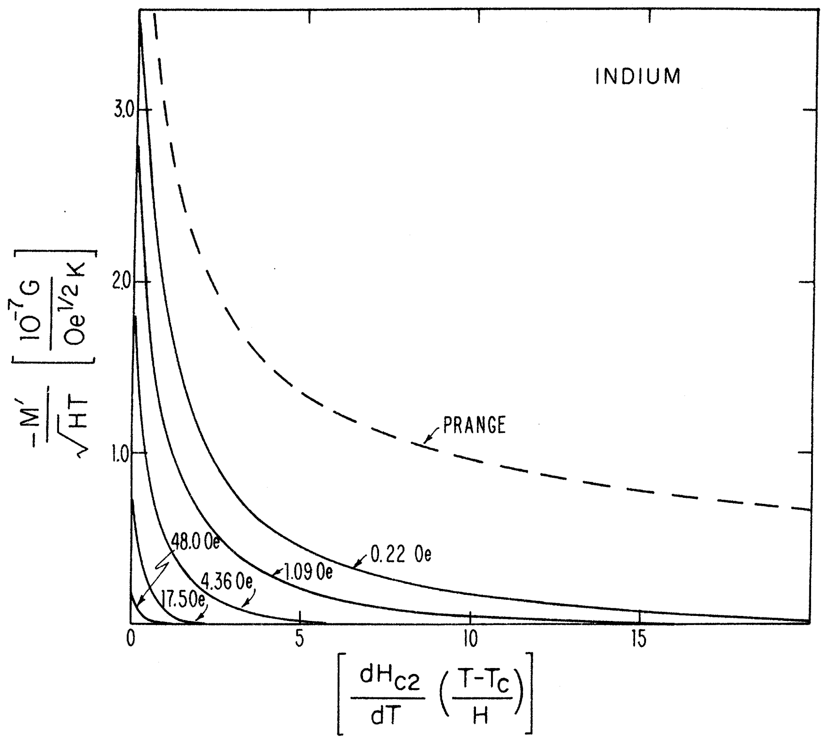

FIG. 7. Fluctuation-induced diamagnetism of indium above T_c plotted using scaled variables and compared with the predictions of the GL theory as worked out by Prange. The progressive breakdown of the GL theory as field increases is evident.

the surface has been chemically polished but is otherwise untreated. As the temperature is reduced, the sample gradually becomes diamagnetic due to the fluctuations. However, at the temperature T_{c3}, the temperature dependence reverses sign until a lower temperature T_{c2} is reached. Between T_{c2} and T_{c3} the magnetization exhibits hysteresis as shown. Measurements at reduced sensitivity show the magnetization to be proportional to $(T_{c2}-T)$ below T_{c2}, thus confirming the identification of the temperature labeled T_{c2} with the onset of the mixed state.

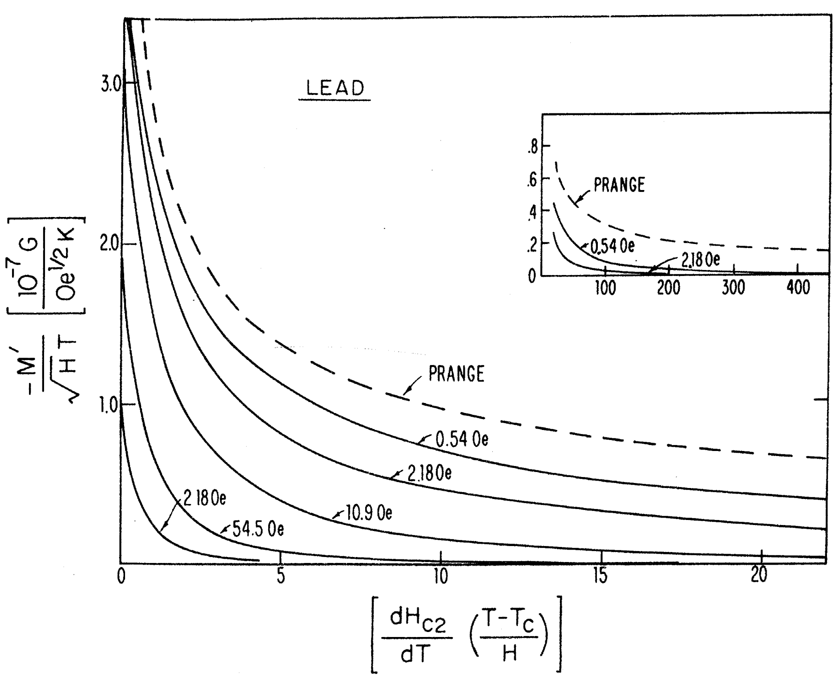

FIG. 8. Fluctuation-induced diamagnetism of lead above T_c plotted using scaled variables.

In order to support the identification of the temperature labeled T_{c3} with the onset of surface superconductivity, temperature sweeps were made at various fields, and the temperatures $T_{c2}(H)$ and $T_{c3}(H)$ were used to construct critical-field curves. Examination of the critical-field curves showed that $H_{c2}(T)$ was linear in temperature up to nearly 200 Oe and extrapolated to zero at T_c. $H_{c3}(T)$ was also linear in temperature with a slope larger by a factor of 1.60, only slightly less than the expected value of 1.69.[27]

The sign reversal of dM'/dT at T_{c3} is not understood. The equilibrium diamagnetism of the surface sheath should cause the sample to be *more* diamagnetic below T_{c3} than would be the case for the fluctuation-induced diamagnetism alone. It seemed possible to us that the slope reversal and the accompanying hysteresis were related to the multiply connected character of the surface sheath. To test this hypothesis, a strip of gold approximately 2 mm wide and 3500 Å thick was evaporated along the length of the sample in order to suppress the surface superconductivity in this region and thus prevent surface currents from going all the way around the sample. The magnetization then became steeper at T_{c3} [Fig. 9(b)] and exhibited less hysteresis there, in better agreement with our original expectations.

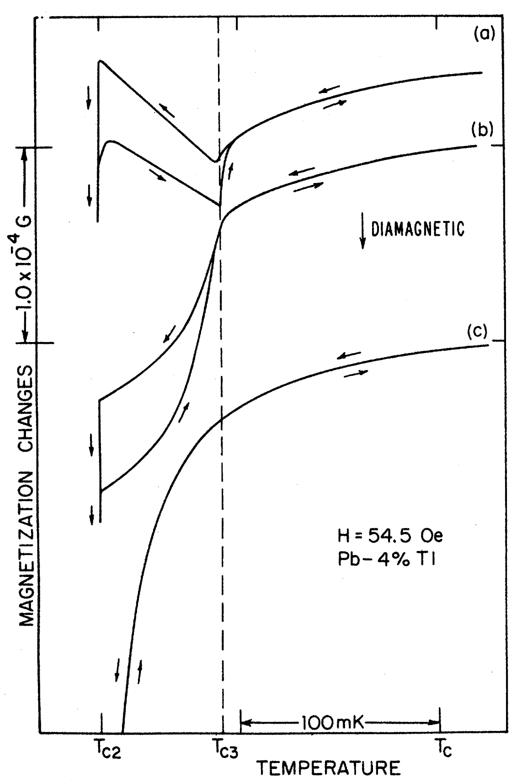

FIG. 9. Effects of surface superconductivity on the magnetization above T_{c2} in a type-II superconductor: (a) with a chemically polished surface; (b) with a gold strip plated along the axis in order to make the superconducting surface sheath singly connected; (c) with surface superconductivity completely suppressed, revealing the unperturbed fluctuation-induced diamagnetism. Note that the curves are separated vertically for clarity.

Finally, the evaporated strip was removed and the entire sample was electroplated with gold. (Electroplating was used rather than evaporation because it was found to be more adherent and therefore presumably more effective in suppressing the surface sheath.) The magnetization [Fig. 9(c)] then showed no obvious evidence of surface superconductivity at any temperature above T_{c2}. However, at high fields $H > 150$ Oe, the surface effect reappeared and showed hysteresis similar to Fig. 9(a). In general, hysteresis in $M'(T)$ usually seems to accompany the appearance of surface superconductivity. The absence of hysteresis, while not foolproof, appears to be a good indication that surface effects are not contributing to the magnetization.

After eliminating the surface effects, the extrinsic transition broadening of the transition was measured in a field of 0.1 Oe, where the expected temperature width of the ideal mixed-state regime is estimated to be only 0.5 mK. The sample was cooled below T_c in zero applied field to eliminate any flux trapping. The field was then turned on, and the magnetization measured as the temperature was increased through the transition. The resulting transition width (to completion) was about 10 mK. When the temperature was subsequently reduced again, there was considerable flux trapping in the sample, leading to a Meissner effect that was only 10% complete. (This figure is larger at higher fields.) This irreversibility and the 10-mK transition width indicate that the sample is not as homogeneous as might be desired. This behavior is typical of all the alloys studied and of the pure niobium sample as well.

In a type-II superconductor where the transition is continuous the observed magnetization changes smoothly over a huge range from the minimum detectable 10^{-8} G to nearly the full diamagnetic value $-H/4\pi$ as the temperature is reduced from well above T_{c2}. A panoramic view of this behavior for the Pb-5-at.%-Tl sample is shown in Figs. 10 and 11, which are composite logarithmic graphs obtained by joining together data taken from a number of separate temperature sweeps using different magnetometer sensitivities. Figure 10 shows the behavior in the neighborhood of T_{c2}; this region is of particular interest since it was inaccessible in our type-I samples. In this graph, M' (16 K) has been taken to be zero, since the magnetization is changing only very gradually there. This does not introduce any significant uncertainty in M' near T_{c2} where M' is becoming orders of magnitude larger.

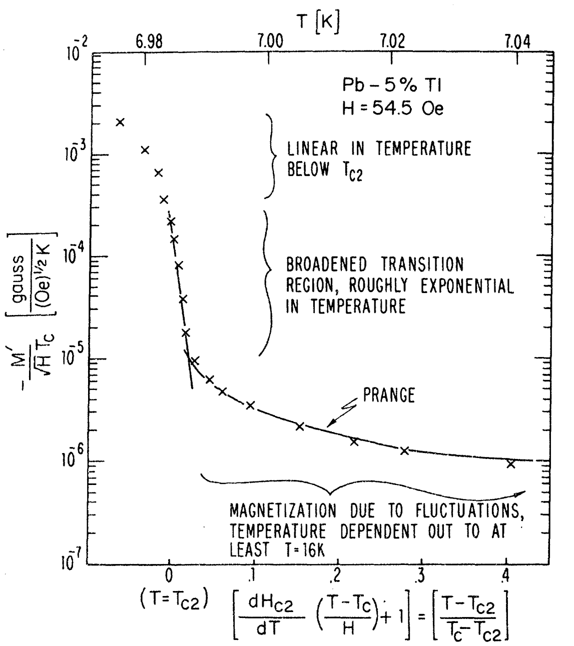

FIG. 10. Temperature dependence of the magnetization near T_{c2}. The data show that in weak fields and for temperatures just above T_{c2}, the GL theory correctly predicts the observed fluctuation-induced diamagnetism. For the data shown $H/H_{c2}(0) \approx 0.03 \ll 1$.

Three different regions can be distinguished. Below T_{c2}, the magnetization is, as expected, linear in temperature, although it appears curved on this semilogarithmic plot. In the immediate vicinity of T_{c2}, the broadened transition, combined with the fluctuations, gives rise to a temperature dependence which is roughly exponential (a straight line on this plot). The effect of the broadening appears to be negligible above $(dH_{c2}/dT)(T - T_c)/H = -0.95$. Finally, above (but very near) T_{c2}, the data are in good agreement with Prange's result, represented by the curved solid line. Thus, in weak fields and sufficiently close to T_{c2}, it *does* appear that the simple GL theory is valid. The agreement with Prange's result gradually worsens as T is increased above T_{c2}. This is illustrated in Fig. 11 where the high-temperature behavior is shown.

A complete presentation of the data above T_c for this Pb-5-at.%-Tl sample is shown in Fig. 12 using the usual scaled variables. As is the case for Pb, the observed magnetization is still slightly temperature-dependent at $T = 16$ K for $H > 10$ Oe. Therefore, for the higher fields some baseline uncertainty remains, but this has little effect on the data near T_c. For $H \lesssim 5$ Oe some effects of the broadened transition are evident above T_c, but fortunately they are readily recognized. The horizontal error bar on the low-temperature data is a measure of the uncertainty in the definition of the mean T_c (due to the finite transition width). The vertical uncertainties are of the order of the width of the line, except for baseline questions.

C. Some Additional Results

In addition to the results described above, some measurements were also carried out on Nb and two In-Tl alloys in order to obtain data on a wider variety of materials, particularly alloys. For these samples attention was focused mainly on the field dependence of M' at $T = T_c$, and detailed measurements of the temperature dependence of the magnetization were not made. These results are presented in Sec. V.

V. DISCUSSION

From the experimental results presented in Sec. IV it is evident that, on the whole, the GL theory gives only a qualitative account of the observed fluctuation-induced diamagnetism. While in very weak fields and at temperatures just above T_{c2} the GL theory is found to be quantitatively correct (see Figs. 10 and 11), at high fields and temperatures the observed behavior falls markedly below the GL predictions. In fact, at very high fields and temperatures the predictions of the GL theory become physically unreasonable (see Sec. II A).

The origins of this breakdown of the GL theory have been discussed in Sec. II B. Basically, the GL theory breaks down at high fields and temperatures because it fails to properly describe the high-energy (short-wavelength) fluctuations which

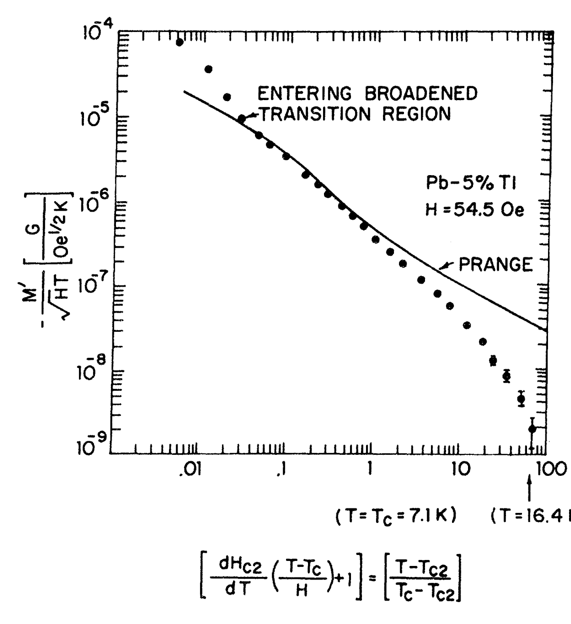

FIG. 11. The breakdown of the GL theory as $(T - T_{c2})$ increases is illustrated using the same sample as shown in Fig. 10.

become important in those regimes, and also, in the clean materials, because of the extremely important effects of nonlocal electrodynamics. Moreover, for alloys, the so-called dynamical corrections to the GL theory, made necessary by the short lifetimes of the high-energy fluctuations, create additional theoretical difficulties. Only for $H \ll \Phi_0/2\pi\xi^2(0) \approx H_{c2}(0)$ and $(T - T_{c2}) \ll T_{c2}$, where long-wavelength long-lifetime fluctuations dominate and the electrodynamics are local, is the GL theory expected to be valid, in agreement with our experimental observations.

In the clean limit these deficiencies of the GL theory appear to have been rectified by the recent work of Lee and Payne[9,12] and Kurkijärvi, Ambegaokar, and Eilenberger[11] who, building on the earlier approximate work of Patton, Ambegaokar, and Wilkins,[8] have calculated the fluctuation-induced diamagnetism directly from microscopic (Gor'kov) theory. As discussed in Sec. II C, their calculations, in effect, generalize the GL theory to include arbitrary spatial variations of the superconducting order parameter and a complete description of the nonlocal effects. The results of these calculations were shown in Fig. 2. For the alloys the predictions of the microscopic theory are still uncertain due to the additional complications introduced in this case by the dynamical corrections. (These corrections are small in the clean limit.) At the present time two distinct treatments of these dynamical effects have been presented: one by Maki and Takayama,[10] and a second worked out independently by LP[12] and KAE.[11] These calculations were discussed in Sec. II C and their predictions compared in Fig. 3.

A considerable impetus to this recent theoretical work has been the universal behavior exhibited by our experimental results in the regimes where the GL theory has broken down. As we reported in Ref. 5, for a wide variety of superconductors, including clean materials and alloys, the observed fluctuation-induced diamagnetism is described remarkably well by a universal function of the temperature variable $(dH_{c2}/dT)_{T_c}(T - T_c)/H$ and a scaled field variable H/H_s, where H_s is an empirically determined scaling field. The possibility of universal behavior of this general form was first suggested in the early theoretical work of PAW. As shown below, our more recent data provide further support for such universal behavior, particularly for alloys, although unfortunately the data on the temperature dependence of M' for alloys is still limited. On the theoretical side the recent calculations of LP and KAE show that universal behavior in the clean limit follows naturally from the microscopic theory with the characteristic field $\Phi_0/2\pi\xi_0^2$ determining the field scaling required. For alloys the theoretical picture is less certain. The available calculations based on the differing treatments of the dynamical effects both provide

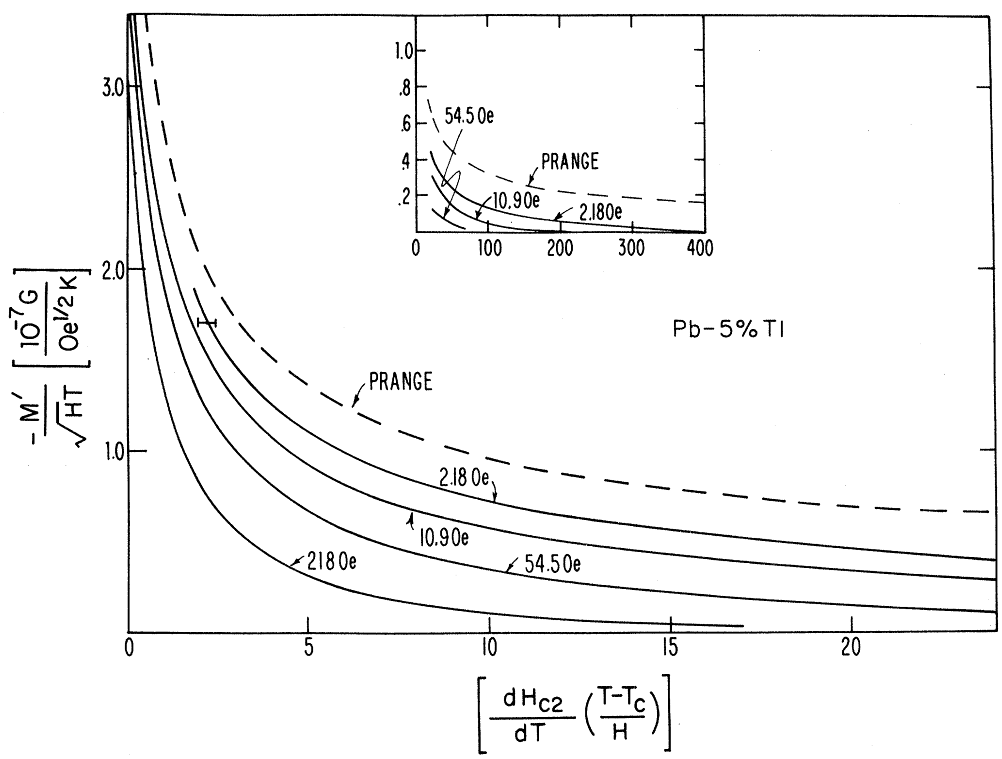

FIG. 12. Fluctuation-induced diamagnetism of Pb–5-at.% Tl above T_c plotted using scaled variables.

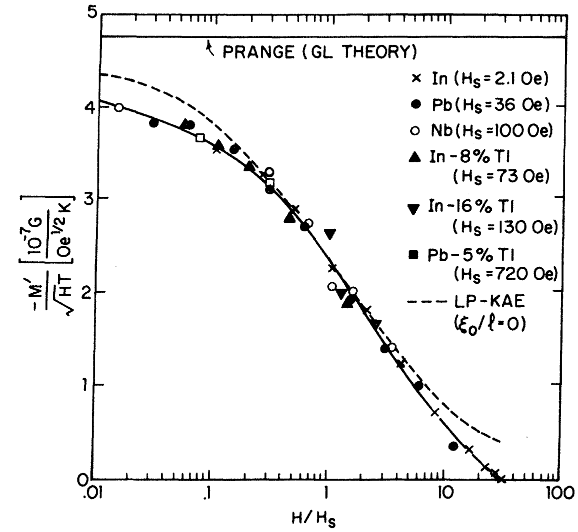

FIG. 13. Observed universal field dependence of the scaled magnetization $M'/H^{1/2}T$ at $T=T_c$ compared with the LP–KAE prediction. The empirically determined scaling fields for each material are shown in the figure. The predictions of the GL theory are also shown for reference.

circumstantial evidence for universal behavior in the field dependence of M' at $T=T_c$ approximately like that found in the clean limit (see Fig. 3 and the discussion in Sec. II C), but they predict *dramatically* different scaling fields. Also, detailed calculations of temperature dependence of M' for alloys have not been carried out.

The universal behavior observed experimentally is illustrated in Figs. 13–15, along with the theoretical predictions of LP–KAE in the clean limit (dashed lines). Figure 13 shows the universal field dependence of $M'/H^{1/2}T$ at $T=T_c$ exhibited by our samples, including those for which the data were not explicitly presented in Sec. IV. In plotting this figure the applied field H has been scaled arbitrarily by a different scaling field H_s for each material such that the data for all materials coincide as closely as possible and fall below the GL prediction in a similar fashion. This defines relative values of H_s for all the samples; the absolute values are then fixed by arbitrarily defining H_s as the field at which the experimental curve has dropped to half the GL value. The values of H_s obtained in this manner have the convenient property that their magnitude closely reflects the field at which the deviations from the GL theory become substantial. The observed scaling fields range from 2.1 Oe for In to 720 Oe for Pb–5-at.% Tl. These scaling fields are shown in the figure and tabulated in Table I along with the predicted values of H_s obtained for the clean materials using the theoretical results of LP–KAE.[28] Also shown in

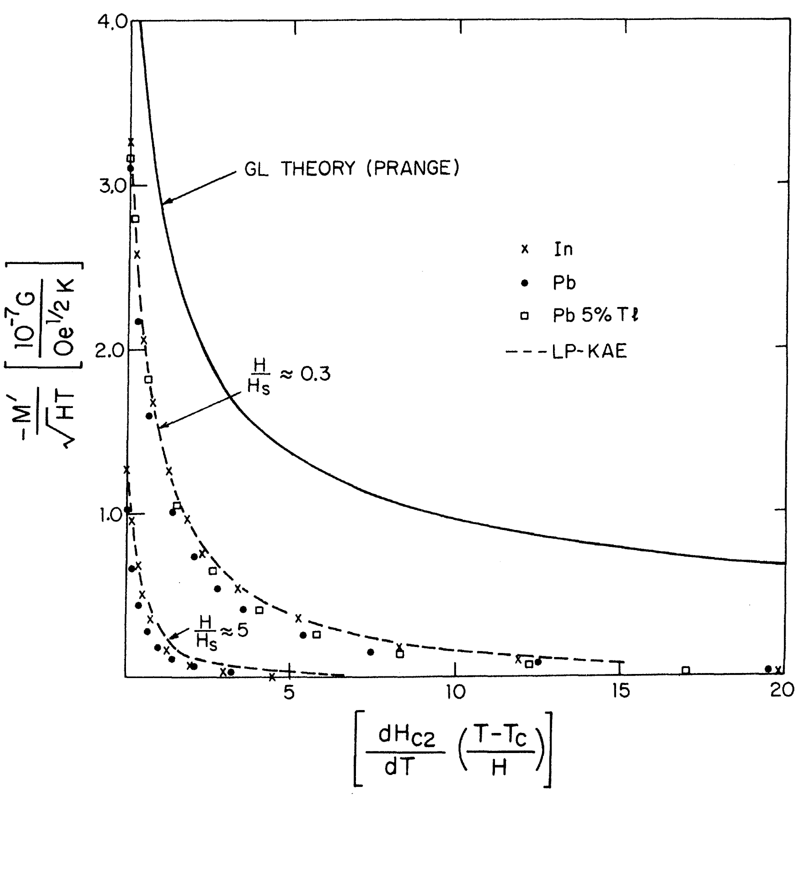

FIG. 14. Observed universal temperature dependence of $M'/H^{1/2}T$ compared with the LP–KAE prediction. Universal behavior which includes the data on alloys is obtained only if the Prange temperature scaling, $(dH_{c2}/dT)(T-T_c)/H$, is used. The predictions of the GL theory are also shown for reference.

TABLE I. Superconducting material parameters for our samples.

Material	T_c[a] (K)	$\left.\frac{dH_{c2}}{dT}\right\vert_{T_c}$ (Oe/K)	ξ_0[b] (μm)	ξ_0/l[c]	H_s(expt.) (Oe)	H_s (theory)[d] (Oe)
In	3.41	13.4[e]	0.364	0	2.1(±.2)	2.8
Pb	7.2	81[e]	0.102	0	36(±4)	35
Nb	9.2	432[a]	0.039	0	100(±10)	240
Pb–5-at.% Tl	7.1	402[a]		4.8	720(±150)	
In–8-at.% Tl	3.26	100[e]		7.2	73(±8)	
In–15-at.% Tl	3.23	182[a]		16	130[f]	

[a]From this work.

[b]Determined from the standard relation $T_c\, dH_{c2}/dT\vert_{T_c} = \Phi_0/2\pi(0.74\xi_0)^2$.

[c]Determined from the relation $(T_c\, dH_{c2}/dT)_{\text{pure}}/(T_c\, dH_{c2}/dT)_{\text{alloy}} = \chi(\xi_0/l)$, where χ, the Gor'kov function, is a known function of ξ_0/l (see Ref. 19, p. 338).

[d]Calculated using the expression $H_s = 0.11\Phi_0/2\pi\xi_0^2$ obtained from the LP–KAE calculation (see Ref. 28).

[e]Calculated from $dH_{c2}/dT\vert_{T_c} = \sqrt{2}\,\kappa dH_c/dT\vert_{T_c}$ using $\kappa_{\text{In}} = 0.062$ [J. S. Feder and D. S. McLachlan, Phys. Rev. 177, 763 (1966)], $\kappa_{\text{Pb}} = 0.240$ [F. W. Smith and M. Cardona, Solid State Commun. 6, 37 (1968)], and $\kappa_{\text{In-8-at.\% Tl}} \approx 0.45$ [P. C. Wraight, Phys. Letters 26A, 140 (1968)].

[f]The scaling field for this alloy is probably an upper limit (see Ref. 29).

Table I are some relevant material parameters of our samples.

The data in Fig. 13, which include a wide variety of superconductors, both clean and dirty, conform remarkably well to a single universal curve. For the clean type-I materials, In and Pb, the data span almost the entire curve, whereas for the alloys (also Nb), in each case the data unfortunately cover only a limited range of H/H_s along the curve.[29] Collectively, however, the alloy data span the curve from $H/H_s \approx 0.06$ up to 2.5 and provide substantial evidence for universal behavior. The theoretical prediction (dashed curve) of LP–KAE for $\xi_0/l = 0$ (i.e., the clean limit) is seen to account fairly well for the over-all shape of the observed universal behavior, although the fit is not perfect at low and high H/H_s. Also, as seen in Table I, with the exception of Nb, the observed scaling fields for the clean materials are found to be in quite good agreement with those expected theoretically. The common universal behavior exhibited by the clean materials and alloys (ξ_0/l in the range $4.8 \lesssim \xi_0/l \lesssim 16$) is consistent with both of the available theoretical calculations for $\xi_0/l > 0$, although as we shall see below, the observed scaling fields are in much better agreement with the predictions based on the work of Maki and Takayama.

The observed universal temperature dependence of $M'/H^{1/2}T$ at fixed H/H_s is illustrated in Fig. 14. The experimental data shown in this figure are for In, Pb, and Pb-Tl only since, as mentioned in Sec. IV, detailed measurements of the temperature dependence of M' for the other samples are not available at the present time. The observed universal behavior is illustrated further in Fig. 15, which shows the field dependence of $M'/H^{1/2}T$ for two nonzero values of $(dH_{c2}/dT)_{T_c}(T-T_c)/H$. In these figures, as in Fig. 13, the LP–KAE clean-limit calculation is seen to account quite well for the observed universal behavior, although the the-

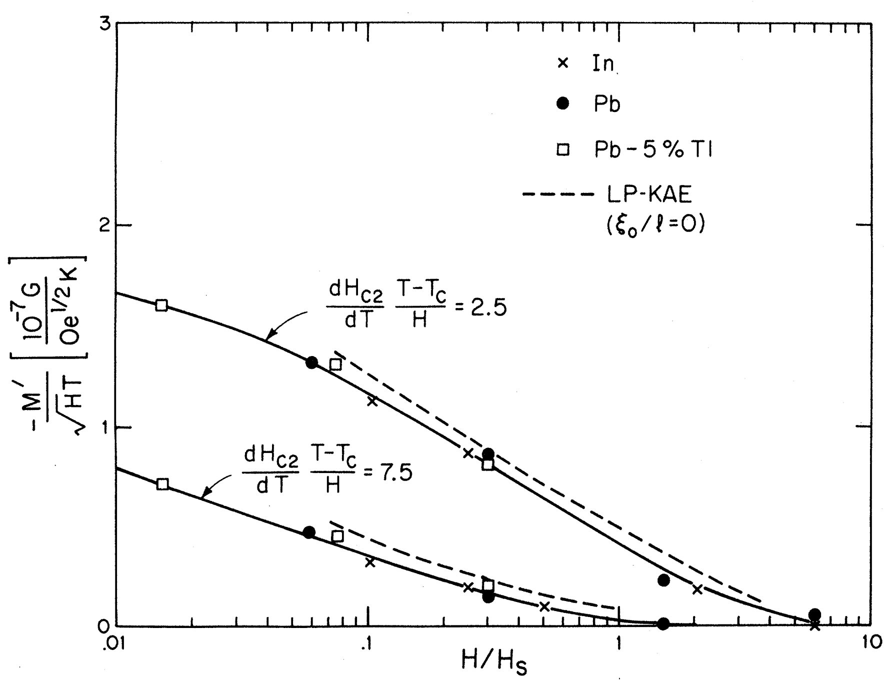

FIG. 15. Observed universal field dependence of $M'/H^{1/2}T$ for temperatures above T_c compared with the LP–KAE predictions.

oretical prediction appears to be falling off a little too slowly at high temperatures. It should be noted, however, that in Figs. 14 and 15 the alloy data would not show the same universal behavior as the clean materials if the simpler temperature scaling $(T-T_c)/T_c$ were used rather than the more complicated Prange scaling $(dH_{c2}/dT)_{T_c}(T-T_c)/H$. As discussed in Sec. II C, in the clean limit LP and KAE have shown that universal behavior is obtained theoretically using either of these temperature scalings, the two being equivalent in this case. However, our results suggest that when alloys are included the latter scaling may be more general, although admittedly this conclusion is based on data from a single alloy. Unfortunately, as mentioned above, detailed calculations of the temperature dependence of M' for alloys based on microscopic theory are not available, and so it is not possible to test this conclusion theoretically.

Despite the fact that to a remarkable degree the fluctuation-induced diamagnetism in clean materials and alloys alike can be described quite well by the same universal function, the principal mechanism suppressing the fluctuations (or at least the diamagnetism they produce) at high fields appears to be quite different in the two cases. In the clean materials the effects of nonlocal electrodynamics are almost certainly dominant. The first evidence for this conclusion was presented in Ref. 5 where on the basis of our preliminary results we observed that the scaling fields for In, Pb, and Pb-5-at.% Tl ($\xi_0/l\approx 4.8$) were approximately described by the formula $H_s=C(\Phi_0/2\pi\xi_0^2)(1+\xi_0/l)^2$, suggesting that the Pippard electrodynamic coherence length $\xi_p^{-1}=\xi_0^{-1}+l^{-1}$, and not the GL coherence length $\xi(0)$, is the important characteristic length in accounting for the effects of magnetic fields on the fluctuations in materials with small ξ_0/l. (Note also that ξ_p is close to the length ξ' found in Sec. II to roughly characterize the leading nonlocal corrections to the GL theory.) The importance of the nonlocal effects has been most clearly demonstrated by the theoretical results of LP-KAE, which show that the nonlocal corrections reduce H_s from the value $2.26(\Phi_0/2\pi\xi_0^2)$ (roughly the PAW result) obtained using a local approximation to the much lower value $0.11(\Phi_0/2\pi\xi_0^2)$ which is in very good agreement with the experimental data.

However, our more recent data on alloys suggest that at sufficiently large ξ_0/l, the nonlocal effects cease to dominate, and the GL coherence length $\xi(0)$ finally determines the scaling field. This is shown in Fig. 16 where the dependence of H_s on ξ_0/l is shown. Also shown are the various theoretical predictions obtained from microscopic theory. In this figure H_s has been normalized by $(\Phi_0/2\pi\xi_0^2)\times(1+0.88\,\xi_0/l)$, the characteristic field associated with the GL coherence length. The experimental data show that for $\xi_0/l\gtrsim 5$, $H_s\approx 0.4(\Phi_0/2\pi\xi_0^2)\times(1+0.88\,\xi_0/l)$ to a very good approximation. Recent work on Al alloys also confirms this result and further demonstrates its generality.[30] As seen in Fig. 16 the observed behavior is in good qualitative agreement with the predictions obtained from the MT treatment of the dynamical effects but provides little support for the LP-KAE result except perhaps for the Pb-5-at.%-Tl data point. However, in view of the criticisms of the MT paper,[14] the possibility remains that the LP-KAE calculation is the correct one within the framework of the Gor'kov theory and that the disagreement between their predictions and the observed behavior is indicative of a failure of the microscopic theory, as presently constituted, to provide a complete physical description of the high-energy fluctuations. This point of view has been set forth recently by Patton and Wilkins.[31] In any event, the behavior of H_s shown

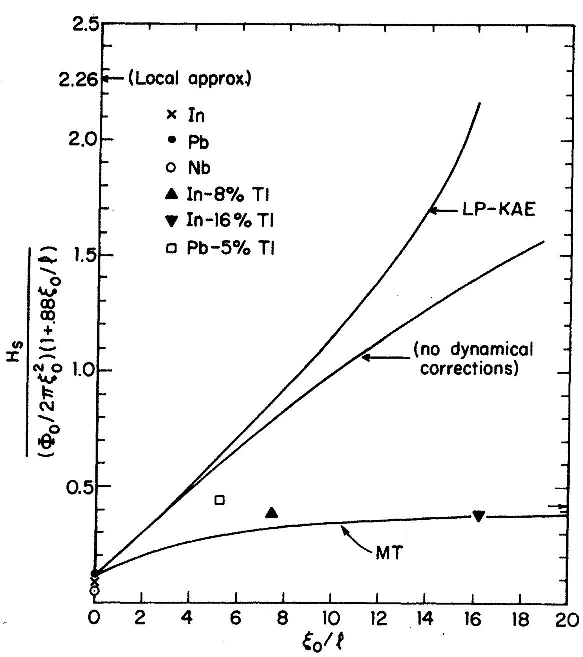

FIG. 16. Mean-free-path dependence of the observed scaling fields compared with various theories. The observed scaling fields are seen to be in qualitative agreement with the MT calculations but not that of LP-KAE except in the clean limit. For comparison the result obtained from microscopic theory using the static approximation (no dynamical corrections) is also shown. The importance of these dynamical corrections in the dirty limit is evident. The arrow on the left-hand side indicate the scaling field predicted by microscopic theory in the clean limit neglecting nonlocal electrodynamics, and the arrow on the right-hand side indicates the MT prediction in the very dirty limit ($\xi_0/l\rightarrow\infty$). For $\xi_0/l>5$ the observed scaling fields are seen to be proportional to $(\Phi_0/2\pi\xi_0^2)$ $(1+0.88\xi_0/l)$, the characteristic field associated with the GL zero-temperature coherence length ξ (0).

in Fig. 16 clearly indicates that for large ξ_0/l, the relatively straightforward extension of the GL theory based on the static form of the Gor'kov theory which is adequate in the clean limit must be replaced by a more complete theory. Moreover, it suggests that for large ξ_0/l the important characteristic length entering this more complete theory should be the GL coherence length.

In view of the rather different situations prevailing in the clean and dirty limits, the significance of the common universal behavior exhibited by the clean materials and alloys is not entirely clear. It may be that the origins of the universal behavior are not closely tied to the specific mechanism suppressing the fluctuations (as, say, in the PAW model). In any case, the observed universal behavior is a tantalizing feature of the experimental results which seems to suggest that some basic simplification of the theoretical picture may be possible.

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[15]Criticism of the calculation carried out by Maki and Takayama have been set forth by Lee and Payne in Ref. 12. Also, B. R. Patton and J. W. Wilkins [Phys. Rev. B 6, 4349 (1972)] have presented arguments indicating that for alloys the existing microscopic theory does not contain the correct physical description of the high-energy-fluctuation modes, and therefore all existing calculations based on the Gor'kov theory are incomplete.

[16]A. L. Fetter and P. C. Hohenberg, in *Superconductivity*, edited by R. D. Parks (Marcel Decker, New York, 1969), p. 822.

[17]The functional form of the eigenfunctions $U_\nu(r)$ depends on the specific gauge used. For the gauge $\vec{A}=\vec{H}\times\vec{X}$ these functions are of the form $U_{n,\beta,k_z}=u_{n,\beta}(x)\, e^{i\beta y}e^{ik_z}$, where $u_{n,\beta}(x)$ are the eigenfunctions of the harmonic-ocisllator problem in quantum mechanics. [For example, see J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U.P., Cambridge, England, 1964), p. 269.] For the gauge $\vec{A}=\frac{1}{2}(\vec{H}\times\vec{r})$, they are of the form $U_{n,m\,k_z} = e^{-\zeta/2}\zeta^{|m|/2}\omega_{n,m}(\zeta)e^{im\phi}e^{ik_z z}$, where $\omega_{n,m}(\zeta)$ are the confluent hypergeometric functions, $\zeta=\pi H\rho^2/\Phi_0$, and ρ is the radial displacement. [For example, see R. Cohen, J. Lodenquai, and M. Ruderman, Phys. Rev. Letters 25, 467 (1970).]

[18]F. London, *Superfluids* (Dover, New York, 1961), Vol. 1, p. 37.

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[20]For $H=0$, $<\psi(r)\psi(0)>\propto(1/r)e^{-r/\xi(T)}$. A derivation of this standard result can be found in L. P. Kadanoff *et al.*, Rev. Mod. Phys. 39, 395 (1967).

[21]As shown by one of the authors (M. T.), in finite magnetic fields the correlation function $\langle\psi(r)\psi(0)\rangle$ behaves asymptotically as $e^{-k_0|z|}e^{-\pi H(x^2+y^2)/2\Phi_0}$, where $k_0^{-2} = \xi^2(T)+\Phi_0/2\pi H$. Since $k_0\to 0$ as $T\to T_{c2}$, the correlations grow along the field direction but not laterally as the transition is approached.

[22]For a discussion of the static approximation of the GL theory and its consequences for fluctuation effects see Refs. 10–12.

[23]H. J. Mikeska and H. Schmidt, Z. Physik 230, 239 (1970).

[24]P. A. Lee and M. G. Payne (private communication). These calculations are also mentioned in Ref. 12.

[25]The LP–KAE calculations do not continue to show universal behavior at large ξ_0/l. In fact for sufficiently large ξ_0/l, their results have the property that $M'/H^{1/2}T$

rises *above* the GL prediction before ultimately going to zero at large fields and temperatures. As can be seen in Fig. 3, even at $\rho_c = 7.04$, $M'/H^{1/2}T$ falls off somewhat more slowly at large H/H_s than for the other curves. In the MT-type calculations, universal behavior appears to persist even into the very dirty limit.

[26]For a recent review of superconducting quantum devices see, J. E. Zimmerman, J. Appl. Phys. 42, 30 (1971).

[27]D. Saint-James and P. G. DeGennes, Phys. Letters 7, 306 (1963).

[28]From Fig. 2 we see that $M'/H^{1/2}T$ falls to half the GL value at $b_c = 0.011$, which leads to the prediction $H_s = 0.11\ \Phi/2\pi\xi_0^2$.

[29]The range of fields over which data are shown for niobium and the alloys is determined at high fields by the high-field limit of reliable magnetometer operation (~ 300 Oe) and at low fields by broadening of the transition. Data judged to be affected by broadening are not shown in the figure. Inclusion of such data would have the effect of making the curve for each material rise rapidly above the indicated universal curve with a distinct change in slope at a point just below the lowest field data point shown for that material. The one exception is for In–16-at.% Tl where an unambiguous change in slope was not apparent and only a gradual departure from the universal curve was observed. The beginning of this departure can be seen in the point for this sample at $H/H_s \approx 1$. Since broadening may still be affecting the data in this one case, the indicated value of H_s for In–16-at.% Tl probably should be considered as an upper limit. (Suppose the observed magnetization were due solely to broadening. Then the fluctuations would have to have been suppressed at a lower field.)

[30]J. H. Claassen and W. W. Webb; H. Kaufman, F. de la Cruz, and G. Seidel, Proceedings of the Thirteenth International Conference on Low Temperature Physics, Boulder, Colorado, 1972 (unpublished).

[31]See Ref. 15.

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Temperature and Thickness Dependence of Critical Magnetic Fields in Lead Superconducting Films

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The parallel-field magnetic transitions of the pure Pb films have been determined from microwave absorption measurements as a function of the specimen thickness (700 to 15 000 Å) and of the temperature (3.2 °K to T_c). The parallel critical magnetic field H_{cF} values are in good agreement with the Ginzburg–Landau theory for $d < \sqrt{5}\lambda(t,d)$ and in the limit $d \gg \xi$; a general semiempirical expression for H_{cF} for all the values of the ratio $d/\lambda(t,d)$ has been determined. The order of the magnetic transition as a function of the specimen thickness and of the temperature has been studied. The surface-superconductivity properties as a function of the thickness have also been investigated and our results are in fairly good agreement with the Saint-James and de Gennes theory. From the data concerning the surface critical magnetic field H_{c3}, it was possible to compute the values of the penetration depth $\lambda(0,d)$ for any specimen thickness.

I. INTRODUCTION

The aim of this work is to make detailed studies on the magnetic behavior of pure lead films in a magnetic field parallel to the sample surface. The parallel magnetic critical field H_{cF} was measured as a function of temperature and specimen thickness. Lead, chosen for the present investigation, is an attractive material since it is a nearly local superconductor. Several measurements of the critical fields of lead films have been reported by a number of investigators,[1–5] whereas in these reports each of such measurements covers only a limited thickness or temperature range. Our measurements cover a range of specimen thickness varying from 700 to 15 000 Å and a temperature range between 3.2 °K and the critical temperature of the specimen T_c. This wide range enables us to study the phase-transition order by varying either the thickness or the temperature.

It is well known[6–9] that for thicknesses d, when $d < d_c = \sqrt{5}\,\lambda(t, d)$, a second-order transition is expected at H_{cF}, while for $d > d_c$, a first-order transition should occur at the critical field H_{cF}. Studies were also made to ascertain how thin-film behavior is replaced by the characteristic behavior of bulk specimen. For each sample thickness $d > \sqrt{5}\,\lambda(0, d)$ we determined a reduced critical temperature t_{d_c} so that for $t < t_{d_c}$ a first-order transition could be expected, while for $t > t_{d_c}$ a second-order transition should be observed.

In general, it was found that the temperature dependence of H_{cF} for thin films and for thicknesses $d \gg \xi(t)$, is in good agreement with the Ginzburg–Landau (GL) theory.[6,10] For films of intermediate thicknesses, no expression for H_{cF} yet exists; we found, however, a semiempirical functional expression to fit all the experimental data concern-