OBSERVATION OF ENHANCED DIAMAGNETISM ABOVE T_c IN INDIUM DUE TO THERMODYNAMIC FLUCTUATIONS*

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(Received 12 May 1969)

We have observed a temperature-dependent enhanced diamagnetism above the critical temperature in pure bulk indium which we attribute to the effects of thermal fluctuations. The magnitude of the effect and the manner in which it scales with magnetic field are in agreement with a finite-field generalization of a zero-field result based on the Ginzburg-Landau theory.

Recently there has been considerable interest in the effects of evanescent Cooper pairs induced by thermodynamic fluctuations in superconductors just above the critical temperature T_c, especially the enhancement of the electrical conductivity of thin films having very short mean free paths.[1-3] It has also been suggested[3,4] that there should be an enhanced diamagnetism above T_c. Unlike the fluctuation-enhanced conductivity, the enhanced diamagnetism should be observable even in pure bulk samples. We have observed such an enhanced diamagnetism in pure bulk indium which we attribute to this mechanism.

The prediction of an enhanced diamagnetism above T_c is based on a model in which small superconducting regions spontaneously grow and decay as a result of thermodynamic fluctuations, leading to an average dc effect. Calculations[3,4] using the linearized Ginzburg-Landau theory yield a predicted susceptibility of about $-10^{-7} \times [T_c/(T-T_c)]^{1/2}$ for a pure bulk sample in the limit of zero magnetic field. More precisely, Schmid[4] finds[5]

$$\chi = -(\pi k T/6\Phi_0^2)\xi(T), \tag{1}$$

where $\Phi_0 = hc/2e$ is the fluxoid quantum and $\xi(T)$ is the usual Ginzburg-Landau coherence length. A typical bulk sample with such a susceptibility in a 1-Oe applied field will exclude an amount of flux equivalent to only a few flux quanta, even as close as a few millidegrees to T_c.

To observe such a small effect, we measured the magnetization with a point-contact superconducting quantum-interference device[6,7] which was coupled to the sample by a superconducting dc transformer wound with niobium wire. The indium sample for which results are reported here was an etched cylindrical single crystal, 4.4 mm diam and 23 mm long, zone refined from 99.9999% purity indium. Similar results were obtained from a polycrystalline sample of the same size prepared from 99.999% purity indium. We have measured the change in sample magnetization with decreasing temperature, from ~4 K to ~3.4 K (T_c), in constant applied fields of 0-2 Oe supplied by a niobium superconducting solenoid in the persistent-current mode. Typical results are presented in Fig. 1. For the higher fields shown, the magnetization is clearly temperature dependent for a few tenths of a degree above T_c. Each graph terminates on the left where the sample undergoes an abrupt transition to the superconducting state which we interpret as the first-order transition expected in the presence of a finite applied field. The first-order transition in the polycrystalline sample is somewhat less abrupt, indicating that this sample is less ideal. Whether or not the single crystal is exhibiting

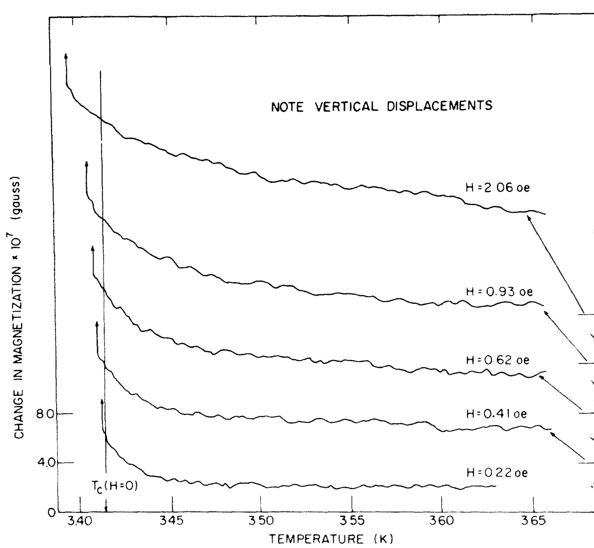

FIG. 1. Change in magnetization of a single crystal of indium versus temperature near the critical temperature, for various magnetic fields. The zero for each plot was adjusted to give the best agreement with (2). Each curve terminates on the left end at the field-dependent thermodynamic critical temperature, where there is a sharp first-order transition to the superconducting state.

any significant sample-dependent nonideal behavior is not definitely known.

As is readily seen in Fig. 1, the magnetization is not divergent either at T_c or at the field-dependent thermodynamic critical temperature $T_c(H)$. Rather, it appears that it would diverge at a lower temperature $T_c^*(H)$ if the first-order transition did not intervene and preclude further observation. This can be understood with reference to the critical-field curves of Fig. 2. As the temperature is reduced in the presence of a finite field H, the sample state follows the dotted line. Although in practice a first-order transition usually occurs at (or slightly below) the intersection with the thermodynamic critical-field curve (point a), the normal state ideally remains metastable with respect to the superconducting state down to the intersection with the ideal supercooling field curve $H_{sc}(T)$ (point b). This defines a temperature $T_{sc}(H)$ down to which the sample can in principle be supercooled. One would expect the fluctuation-induced magnetization to diverge at $T_{sc}(H)$, where the energy cost of a small fluctuation toward the superconducting state vanishes. In other words, we would expect the temperature $T_c^*(H)$ at which the extrapolated experimental curve diverges to be the supercooling temperature $T_{sc}(H)$.

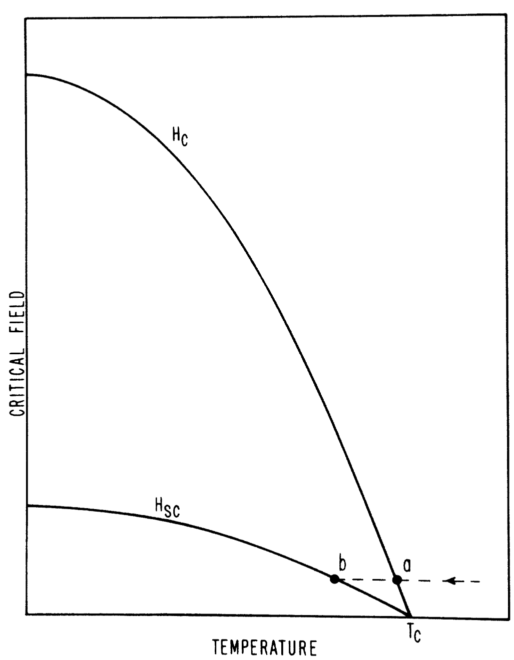

FIG. 2. Schematic diagram of the thermodynamic critical field H_c and the supercooling field H_{sc} versus temperature. The dotted line represents the sequence of sample states as temperature is reduced in the presence of a magnetic field H whose size is exaggerated for clarity. The sample becomes superconducting at a, but the fluctuation-enhanced diamagnetism would diverge at b, if the first-order transition did not intervene.

When these considerations are used to modify the zero-field expression (1), and if one identifies[8] H_{sc} with $H_{c2}=\Phi_0/2\pi\xi^2$, one obtains the prediction that the magnetization $M(H,T)$ should be given by

$$M(H,T)=-\frac{(\frac{1}{2}\pi)^{1/2}(\frac{1}{6}kT)\Phi_0^{-3/2}H^{1/2}}{[1+|dH_{c2}/dT|(T-T_c)/H]^{1/2}}. \qquad (2)$$

This expression equals χH with χ given by (1) and with T_c replaced by $T_{c2}(H)$. It reduces to (1) as H goes to zero, and moreover, this form of field dependence can be shown to follow from ordinary linearized Ginzburg-Landau theory.[9] The form of this result suggests that the data for all fields should lie on a universal curve if $M(H,T)/H^{1/2}$ is plotted versus $(T-T_c)/H$. However, to make such a plot it is necessary to determine a base line for the experimental data, since the level to which the temperature-dependent magnetization would extrapolate at high temperatures cannot be determined with any precision from our data. The criterion we used to adjust the baseline at each field for best agreement with the theoretical prediction (2) in the region of large $(T-T_c)/H$. Using this procedure, we found that the data for all fields fell on a universal curve when plotted as shown in Fig. 3. The solid line in this figure represents the behavior expected on the basis of (2), where $|dH_{c2}/dT|=\sqrt{2}\kappa|dH_c/dT|=13.4$ Oe/K was determined using accepted values[10,11] for $|dH_c/dT|$ and κ. The numerical value of the coefficent of $H^{1/2}$ in the numerator is 1.05×10^{-6} G/Oe$^{1/2}$ for $T=3.4$ K. At large $(T-T_c)/H$ the data follow the theoretical curve fairly well, but begin systematically to rise above it for $(T-T_c)/H \lesssim 0.05$ K/Oe. However, the significance of the results in this region is unclear for two reasons. First, the exact form of the theory for low $(T-T_c)/H$ is uncertain.[12] In addition, it is possible that some of the observed enhancement for low $(T-T_c)/H$ arises from broadening in the transition due to inhomogeneities, in spite of the fact that the first-order transition is almost complete within a few millidegrees. This possibility exists because the total observed effect is only about 10^{-5} of the perfect diamagnetism below T_c. Thus even parts per million of material with higher transition temperatures could give appreciable effects. The data from the polycrystalline sam-

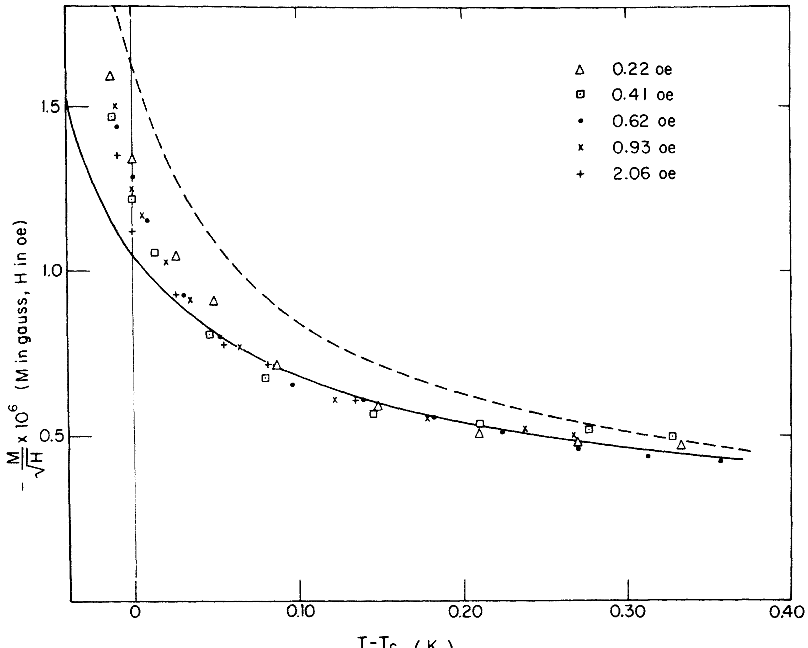

FIG. 3. The data of Fig. 1 replotted to exhibit the scaling with magnetic field predicted by (2). The baselines for the experimental curves have been adjusted to give the best agreement with (2) (solid curve) in the region of large $(T-T_c)/H$. The dashed curve represents the result of a recent calculation of Prange (see Note added in proof).

ple also fall on a universal curve of the same qualitative shape and magnitude, but, over much of the temperature range of observation, the magnetization rises somewhat more rapidly with decreasing temperature than is predicted.

We also find that all of our data can be described extremely well over the entire temperature range, even at low $(T-T_c)/H$, by introducing two adjustable parameters into (2), to obtain

$$M(H,T) = -AH^{1/2}[1+B(T-T_c)/H]^{-1/2}. \qquad (3)$$

The baselines which are used for this fit differ from those in Fig. 1. For the indium single crystal, we find $A = 1.10 \times 10^{-6}$ G/Oe$^{1/2}$, which is only 5% larger than expected from (2). However, the best value of B is 37 Oe/K, which is nearly three times the theoretical value of 13.4 Oe/K. Equivalently, the magnetization would diverge at a temperature $T_c^* = T_c - H/B$ which is higher than our earlier remarks on supercooling lead us to expect. The polycrystalline sample gives results which are also well described by (3) with the same value of B, but with a value of A higher by a factor of 1.7. Although this suggests a trend toward better agreement with theory as sample quality improves, such agreement may be fortuitous, since the exact magnitude expected theoretically is uncertain[5] at this time.

Finally, one consequence of the baseline uncertainty is that our data do not enable us to prove that the temperature dependence actually follows the analytical form of (3). For example, the data can be fitted almost as well by an expression of the form

$$M(H,T) = -A'H^{1/2}[1+B'(T-T_c)/H]^{-1} \qquad (4)$$

with $B' = 22$ Oe/K corresponding to a $T_c^*(H)$ considerably closer to that expected if $H_{sc} = H_{c2}$ and $\kappa = 0.062$. However, there is at present no theory which would suggest that this form is plausible.

In conclusion we feel that, despite the ambiguity which arises from the baseline uncertainty and the lack of a sufficiently complete theory, the existence in these very clean samples of an enhanced diamagnetism which is of the expected magnitude and which exhibits the expected scaling over a wide range of fields provides sufficient basis for the assertion that the observed enhancement is due to thermal fluctuations. A definitive test will require both a theory which rigorously takes the finite applied field into account and more extensive experimental work. We are continuing to investigate other materials as well as samples prepared in different ways, and we hope to extend the measurements to higher temperatures.

Note added in proof. — Subsequent to the submission of this Letter for publication, the theoretical situation has evolved somewhat. H. Schmidt (private communication) has corrected his result to agree with (1), thereby apparently eliminating most of the uncertainty in the overall magnitude of the predicted effect. More importantly, R. Prange (to be published) has made a calculation, based on Schmid's formulation, which properly incorporates the finite applied field. His result confirms our expectation of a divergence at $T_{c2}(H)$ of the form $[T-T_{c2}(H)]^{-1/2}$ and it exhibits the same field-scaling properties as (2). Moreover, it reduces to (1) in the limit of large $(T-T_c)/H$. In fact, it can be expressed as multiplying (2) by a function $F(x)$, where $x=|dH_{c2}/dT|\times(T-T_c)/H$, which varies from $F(\infty)=1$ to $F(-1)=6$; in the range where data are available, $1.1\lesssim F(x)\lesssim 1.6$. Prange's prediction has been added to Fig. 3 (dashed curve), where it can be seen that, over most of the region of observation, the new theory varies more rapidly with temperature than the observed results. (Note that in comparing the data with the theoretical curves in Fig. 3, it is permissible to shift the experimental results vertically for best agreement. As discussed in the text, such a shift simply corresponds to selecting a new set of baselines for the original data.) More satisfactory agreement would be obtained if either Prange's prediction were smaller or the experimental results larger by roughly a factor of 2. We have recalibrated our magnetometer using an independent procedure and have found no systematic error which would account for such a discrepancy.

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*Work supported in part by the National Science Foundation, the Office of Naval Research, and the Advanced Research Projects Agency.

†Danforth Foundation Graduate Fellow.

‡National Science Foundation Graduate Fellow.

[1]R. E. Glover, Phys. Letters 25A, 542 (1967); R. A. Ferrell and H. Schmidt, Phys. Letters 25A, 544 (1967).

[2]L. G. Aslamazov and A. I. Larkin, Phys. Letters 26A, 238 (1968).

[3]H. Schmidt, Z. Physik 216, 336 (1968).

[4]A. Schmid, Phys. Rev. (to be published). We thank Dr. Schmid for kindly providing us with a copy of his paper prior to publication.

[5]The result of Ref. 3 for the diamagnetic susceptibility appears to be smaller than (1) by a factor of 4, for reasons that we do not understand. J. Tucker (private communication) in an independent calculation using microscopic theory has obtained a result larger than (1) by a factor of $\frac{3}{2}$. Pending resolution of these differences, we have chosen to use the result of Ref. 4, since it appears to be in the best agreement with our results.

[6]A. H. Silver and J. E. Zimmerman, Phys. Rev. 141, 367 (1966).

[7]M. R. Beasley and W. W. Webb, in Proceedings of the Conference on the Physics of Superconducting Devices, University of Virginia, Charlottesville, 1967 (Office of Naval Research, Washington, D.C., 1967), p. V-1; M. R. Beasley, R. Labusch, and W. W. Webb, Phys. Rev. (to be published).

[8]The supercooling field $H_{sc}(T)$ is normally taken to be $H_{c3}(T)=1.7\sqrt{2}\kappa H_c(T)$, the field at which nucleation of superconductivity can occur at the sample surface. On the other hand, nucleation in the interior of the sample cannot occur with zero energy barrier until a field $H_{c2}=\sqrt{2}\kappa H_c(T)=\Phi_0/2\pi\xi^2(T)$ is reached. It seems plausible that for temperatures at which the normal state is still absolutely stable, fluctuations throughout the volume should dominate, and we identify $H_{sc}(T)$ with $H_{c2}(T)$ for the interpretation of our results. To eliminate the possibility of surface superconductivity playing a significant role in the enhanced diamagnetism, we gold plated one of our samples. No change was observed in the effect.

[9]M. Tinkham, unpublished.

[10]J. Feder and D. S. McLachlan [Phys. Rev. 177, 763 (1969)] find $\kappa(T_c)=0.062$ for indium from supercooling experiments.

[11]A. M. Toxen, M. J. Burns, and D. J. Quinn [Phys. Rev. 138, A1145 (1965)] find $|dH_c/dT|=153$ Oe/K near T_c for indium.

[12]Our method of adapting (1) to the case of finite fields does not preclude the possibility of additional terms in the susceptibility which vary more quickly with temperature than (2) and are large only near T_c*.