

Anomalous Behavior of H_{c3}/H_{c2} near T_c for Sn-In and In-Bi Alloy Systems*

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Previously reported measurements of the ratio H_{c3}/H_{c2} for tin-rich Sn-In alloys and indium-rich In-Bi alloys have been extended in further detail, and include variations in foil thickness (6 – 300 μ). The anomalous behavior in the ratio very near T_c is found to be dependent on foil thickness. Each alloy system is characterized by a certain thickness, above which H_{c3}/H_{c2} decreases markedly as T_c is approached, and below which the opposite behavior takes place. The results can be interpreted qualitatively in terms of a sandwich model in which the strength of the pairing interaction is depressed in a layer at the surface of the sample. For the thickest samples (most nearly “semi-infinite”), there is good quantitative agreement with the recent theory of this proximity effect given by Fink and Presson.

I. INTRODUCTION

There has recently been considerable interest in determining the temperature dependence of the ratio of the surface critical field H_{c3} to the bulk critical field H_{c2} in type-II superconductors. Theory¹⁻³ predicts an increase in this ratio as the temperature is decreased; the amount of the increase depends on the “mean free path” and the character of the scattering of the electrons by the surface. Experimental work⁴⁻⁶ seems to confirm these results. Also, an anomaly in the H_{c3}/H_{c2} ratio near T_c for pure and dirty type-II superconductors has been reported.⁷⁻¹⁰ Hu¹¹ has made a theoretical attempt to explain this anomalous behavior for Nb.⁸ In this paper we study the anomaly in the Sn-In and In-Bi alloy systems.⁹

We have measured the critical fields for tin-rich Sn-In and indium-rich In-Bi alloy plates of different concentrations and thicknesses. For the Sn-In system, the ratio H_{c3}/H_{c2} exhibits a marked decrease as T_c is approached for all concentrations, and a clear dependence of the critical temperature on the thickness of the sample is evident. For all samples it is possible to show that the linear extrapolation to $H = 0$ of the low-temperature data of H_{c3} and H_{c2} does not determine a unique critical temperature. Specifically, the critical temperature T_{c2} defined from the extrapolation to $H = 0$ of the low-temperature data of H_{c2} depends on the thickness of the sample, whereas the extrapolation of H_{c3} , T_{c3} , does not. For the In-Bi system, it has been reported⁹ that the ratio H_{c3}/H_{c2} increases as the critical temperature is approached. A detailed study of the behavior of H_{c3}/H_{c2} as a function of sample thickness has shown that as the thickness of the sample is increased the enhancement of the ratio diminishes. For the thickest sample, we have determined that the ratio decreases as T_c is approached, indicating a behavior similar to the Sn-In system.

Some of these results qualitatively support the

model proposed by Hu¹¹ to explain the results in Nb.⁸ He first considers the variation of the ratio H_{c3}/H_{c2} with temperature in a homogeneous semi-infinite superconductor to be given by the theory developed in Ref. 3. This theory predicts a smooth increase in the ratio as the temperature is lowered from T_c . This dependence can change if some perturbation in the free surface is allowed. In particular he assumes that the phonon-mediated interaction is depressed uniformly in a region of thickness D near the surface. We will refer to this weaker-interaction region as a surface “layer.” To obtain the value of H_{c3}/H_{c2} for this model he divides the whole temperature range into three regions: region A, in which the surface sheath lies entirely within the surface layer, i. e., $D > \xi_0(1-t)^{-1/2}$; region B, in which the surface sheath extends beyond the weak-interaction layer into the bulk, i. e., $D < \xi_0(1-t)^{-1/2}$; and region C, in which the layer may be treated as a perturbation, i. e., $D \ll \xi_0(1-t)^{-1/2}$. A different temperature dependence is found in each region, but resulting over all three in a continuous decrease of H_{c3}/H_{c2} below the value expected for a homogeneous system, and dropping to unity at $T = T_c$.

In principle the three different regions can be reached, for a given material, by changing the temperature. Region A corresponds to the lower temperatures. In this region the surface sheath sees a homogeneous system with a constant value for the pairing interaction, slightly depressed with respect to the value in the bulk. Consequently, the surface critical field for the weak-interaction layer is smaller than the surface critical field for the bulk. The bulk critical field H_{c2} of the sample should be relatively unaffected by the thin layer. If the value of H_{c3} of the surface layer and H_{c2} of the bulk are plotted with respect to temperature in region A, one obtains two straight lines with different extrapolations to $H = 0$. The surface critical field will extrapolate to a lower temperature than the bulk critical

field. Obviously the ratio H_{c3}/H_{c2} will decrease as T_c is approached.

Before comparing our measurements to this theory, we direct our attention to an effect that should be present within the same model, but was not considered in Ref. 11. We can look at the same system as a sandwich made out of a semi-infinite superconductor S with a critical temperature T_{cs} , and another superconductor of thickness D with a lower critical temperature T_{cn} in contact with the free surface of S . That is, we are considering a proximity effect between a superconductor and a normal material of critical temperature T_{cn} . The proximity effect in the critical temperature and in the critical magnetic field has been extensively studied.¹² In general, the boundary condition at the junction is¹²

$$(\vec{\nabla} - 2ie\vec{A}/\hbar c)_n \Delta = \Delta/b, \quad (1)$$

where Δ is the pair potential, b has the dimensions of a length and, at zero field, is a measure of the slope of the pair potential at the boundary. The "extrapolation length" b is fixed by the properties of the normal metal and is a function of temperature and field (b goes to infinity at $T = T_{cn}$). If $T_{cn} \ll T_{cs}$, and if the electrical conductivity of the normal material σ_n is much smaller than the conductivity of the superconductor σ_s , then b can be taken as independent of field and temperature.^{12,13} Under these circumstances, and for finite thickness in the superconductor S , the measurement of the variation of the critical temperature of the sandwich and/or the change in the critical magnetic field, as a function of the thickness of S , allows the determination of b .¹² In the case in which we are interested, T_{cn} should be very close to T_{cs} , and b would be a function of temperature. It is also quite possible that the electrical conductivities of both regions of the sample are the same, in which case b is also a function of field. Until very recently¹⁴ there was no theoretical treatment of the case $T_{cn} \approx T_{cs}$ and $\sigma_n \approx \sigma_s$. Fink and Presson¹⁴ have solved the proximity effect between two semi-infinite normal and superconductor metals in a general way. The results of their calculations are shown in Fig. 1. H_{c3}/H_{c2} is expressed as a function of a temperature parameter α , defined by

$$\alpha(T) = \gamma_p \frac{n_n}{n_s} \frac{T_{cs}}{T_{cn}} \frac{T_{cn} - T}{T_{cs} - T}, \quad (2)$$

where n_n and n_s refer to the number of electrons per unit volume in the normal and superconductor metals, respectively, and $\gamma_p = \sigma_s/\sigma_n$ in the dirty limit. The value of α can be positive or negative depending on the temperature as compared to T_{cn} . It is interesting to point out that if the temperature is low enough ($\alpha > 0$), there is a surface sheath, even

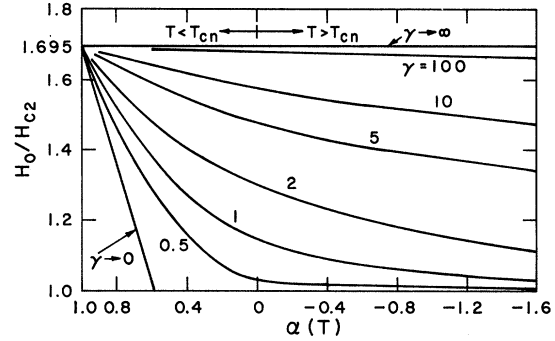


FIG. 1. Theoretical results obtained by Fink and Presson (Ref. 14) showing the nucleation field ratio as a function of $\alpha(T)$ for various γ values.

as $\gamma \rightarrow 0$, in disagreement with previous calculations.¹³ We see from Fig. 1 that we can expect a decrease in H_{c3}/H_{c2} if a proximity effect is present. The difference between the results found by Hu and those obtained using the same sandwich model, but taking into account the proximity effect, is the interpretation of the H_{c3} determined experimentally. We believe we measure not the surface critical field of the weak-interaction layer, but the surface critical field of the bulk S , as modified by the proximity of the layer (see Sec. IV).

II. EXPERIMENTAL PROCEDURE

We have measured four Sn-In alloy samples of approximately 100 μ thickness with concentrations of 6-, 5.5-, and 4.7- at.% in (see Table I), six samples of 5.5- at.% In with thicknesses between 6 and 240 μ (see Table II), and five samples of In-Bi (2.9-at. % Bi) with thicknesses between 40 and 300 μ (see Table III). The samples, plates of 4 mm width and 10 mm length, were prepared by rolling the alloy between Mylar sheets to avoid contamination from the stainless-steel rollers. The samples were maintained under a helium gas atmosphere to avoid surface oxidation, and all were annealed for 24 h.

The samples were placed inside a pair of coils; the transition fields were determined by measuring the variation of the mutual inductance with field. The shape of the transition was as in Ref. 9, and the points B of that reference were chosen as the critical fields.¹⁵ The surface critical field H_{c3} was determined with the external dc magnetic field parallel to the large surface of the sample, while H_{c2} was the transition field for H perpendicular to that surface. Using a pressure regulator¹⁶ the temperature could be stabilized within 0.5 m°K. Further details on the experimental technique have been reported elsewhere.⁹

TABLE I. Experimental data for the Sn-In alloy samples of different concentrations. Also indicated is the critical temperature T_{cn} of the surface layer, as determined by the best theoretical fit (Ref. 14) of the data.

| Concentration | (at. % In) | 6 | 5.5 | 5 | 4.7 |
|---------------------------------|-----------------------|-------------------|-------------------|-------------------|-------------------|
| T_{c2} | (°K) | 3.620 | 3.635 | 3.625 | 3.620 |
| T_{c3} | (°K) | 3.615 | 3.614 | 3.615 | 3.607 |
| "Low-temperature" region begins | (reduced temperature) | 0.98 | 0.98 | 0.98 | 0.97 |
| $T_{c2} - T_{c3}$ | (°K) | 0.005 ± 0.002 | 0.021 ± 0.002 | 0.010 ± 0.003 | 0.013 ± 0.003 |
| T_{cn} | (°K) | 3.609 ± 0.001 | 3.580 ± 0.005 | 3.600 ± 0.002 | 3.594 ± 0.001 |

To determine if the relative orientation⁹ of the primary pick-up field of the mutual inductance with respect to the surface of the sample had any influence on the results, most of the samples were measured with the primary ac field parallel to the large surface of the sample, and again with the ac field perpendicular.

III. RESULTS

A. Sn-In

Four samples of 6-, 5.5-, 5-, and 4.7-at.% In concentration were measured. The thicknesses of these samples were not determined precisely, ranging between 80 and 110 μ . The relevant experimental parameters for these samples are shown in Table I.

No systematic dependence of the critical temperature on concentration was found in the range of concentrations investigated. All samples showed an anomalous behavior in H_{c3}/H_{c2} similar to the one reported in Ref. 9.

A study of H_{c3} and H_{c2} as a function of thickness, for samples of the same concentration (5.5-at.% In) revealed a systematic variation of T_{c2} with thickness. Figures 2 and 3 show H_{c3} and H_{c2} as a function of temperature for the thinnest and thickest samples investigated. The relevant experimental

parameters for these and other samples are shown in Table II. It can be seen that T_{c3} remains constant but T_{c2} is shifted towards T_{c3} as thickness is decreased. For the "thin" samples of 24, 14, and 6 μ , T_{c2} is lower than T_{c3} . The shift in T_{c2} is seen to have a strong influence in the ratio H_{c3}/H_{c2} , plotted as a function of reduced temperature¹⁷ in Fig. 4. For the "thick" samples of 56, 100, and 240 μ , T_{c3} is lower than T_{c2} . For these samples, H_{c3} and H_{c2} can be easily fitted by straight lines for temperatures lower than $t = 0.975$. At higher temperatures H_{c3} leaves the straight lines, and in a less noticeable way, so does H_{c2} . We specify these as "tails" off the straight lines near T_c , and we will denote as the "low-temperature region" the one in which H_{c3} and H_{c2} are described by straight lines. In this region ($t \lesssim 0.975$) the variation of the ratio H_{c3}/H_{c2} with temperature corresponds, inside the experimental error, to the variation of the ratio of two straight lines having different intercepts with the horizontal ($H = 0$) axis. For the thinner samples, the low-temperature region is larger. The tails, present in H_{c3} and H_{c2} for the thick samples, tend to disappear and H_{c3} and H_{c2} are well described by straight lines over temperatures closer to T_c than $t = 0.99$. As a consequence of the shift in T_{c2} , the ratio remains constant over a wider range of temperature. In the three thinnest samples the ratio

TABLE II. Experimental data for the Sn-In (5.5-at.% In) samples of different thicknesses. T_{cn} for the thick samples was determined from best theoretical fit (Ref. 14).

| Thickness | (μ) | 240 | 100 | 56 | 24 | 14 | 6 |
|---------------------------------|-----------------------|-------------------|-------------------|-------------------|--------------------|--------------------|--------------------|
| Transition width | (m °K) | 20-25 | | 10-20 | 10-15 | 10-20 | 15-20 |
| T_{c2} | (°K) | 3.633 | 3.635 | 3.619 | 3.612 | 3.608 | 3.609 |
| T_{c3} | (°K) | 3.616 | 3.614 | 3.614 | 3.615 | 3.613 | 3.616 |
| "Low-temperature" region begins | (reduced temperature) | 0.977 | 0.978 | 0.984 | 0.993 | 0.992 | 0.99 |
| $T_{c2} - T_{c3}$ | (°K) | 0.017 ± 0.002 | 0.021 ± 0.002 | 0.005 ± 0.002 | -0.003 ± 0.001 | -0.005 ± 0.002 | -0.007 ± 0.002 |
| T_{cn} | (°K) | 3.600 ± 0.003 | 3.580 ± 0.005 | | | | |

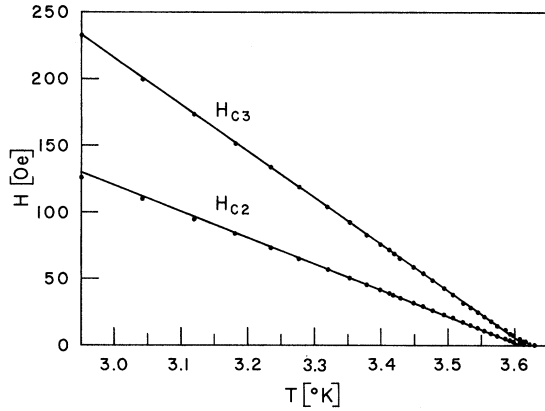


FIG. 2. H_{c3} and H_{c2} for a Sn-In (5.5-at. % In) sample 6 μ thick as a function of temperature.

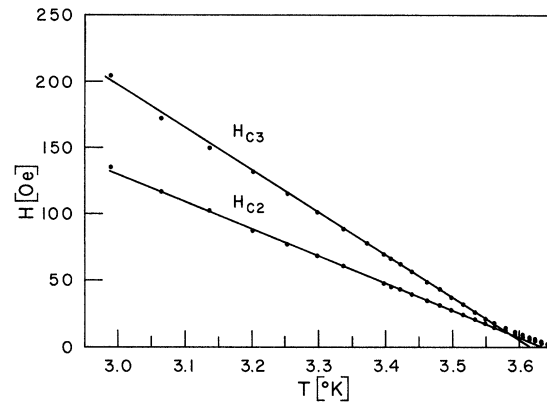


FIG. 3. H_{c3} and H_{c2} for a Sn-In (5.5-at. % In) sample 240 μ thick as a function of temperature.

increases as T approaches T_c , a consequence of the fact that T_{c2} is lower than T_{c3} . Over the range of concentrations in which the measurements were done the critical temperatures and the main superconducting characteristics of the alloy were independent of concentration. Further, the decrease in T_{c2} and the disappearance of the tail were also observed for 4.7% samples with smaller thickness.

The transition width at zero field was measured for five of the 5.5% In samples. The results are shown in Table II and Fig. 5; in the same figure is indicated the value of T_{c3} and T_{c2} obtained for each sample. It can be seen in Fig. 5 that T_{c2} coincides, in all cases, with the temperature at which the mutual inductance begins to change as the temperature is increased. It is possible, then, to associate T_{c2} with the transition temperature of the bulk of the sample. The transition width at zero field is in general associated with the presence of inhomogeneities in the sample. For all our samples the zero-field transitions are narrower than those reported by Wipf.¹⁸ In order that the superconducting characteristics of the alloy be reproducible, it was

necessary to anneal the samples at 120 °C for at least 24 h. Otherwise the magnetic transition is broadened and the critical temperatures do not reproduce.

All the results shown were obtained using the same geometry between the pick-up field and the sample as the one described in Ref. 9, that is, the ac field was perpendicular to the surface. The results obtained for the parallel orientation are in good agreement with the ones reported here. With this orientation the effectiveness of the surface currents in shielding the ac magnetic field is considerably reduced. Consequently, the size of the signal decreases continuously from very small external fields until H_{c2} , making the definition of H_{c2} more difficult. The result is more dispersion in the H_{c2} data than we obtain with sharper transitions.⁹ We avoid this additional source of error in determining T_{c2} by using the perpendicular arrangement. To determine if internal inhomogeneities in the concentration were affecting the experimental data, several samples were annealed at yet higher temperatures and for up to 10 days and measured again.

TABLE III. Experimental data for the In-Bi (2.9-at. % Bi) samples of different thicknesses. T_{cn} for the thickest sample was determined from best theoretical fit (Ref. 14).

| Thickness | (μ) | 300 | 240 | 180 | 105 | 40 |
|---------------------------------|-----------------------|-------------------|-------------------|--------------------|--------------------|--------------------|
| Transition width | (m °K) | 35–65 | 15–20 | 20 | 25–35 | 35–45 |
| T_{c2} | (°K) | 4.156 | 4.117 | 4.124 | 4.119 | 4.116 |
| T_{c3} | (°K) | 4.131 | 4.116 | 4.129 | 4.125 | 4.123 |
| “Low-temperature” region begins | (reduced temperature) | 0.93 | 0.95 | 0.96 | 0.95 | 1 |
| $T_{c2} - T_{c3}$ | (°K) | 0.025 ± 0.003 | 0.001 ± 0.002 | -0.005 ± 0.001 | -0.006 ± 0.002 | -0.007 ± 0.003 |
| T_{cn} | (°K) | 4.121 ± 0.004 | | | | |

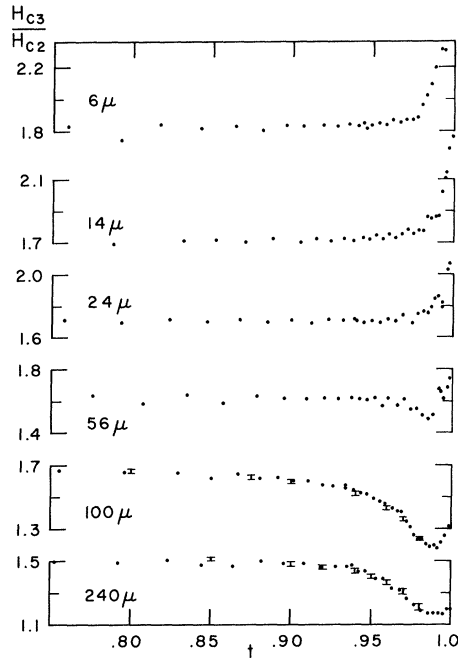


FIG. 4. Ratio H_{c3}/H_{c2} for the Sn-In (5.5-at.% In) samples of different thicknesses as a function of reduced temperature. Bars indicate the values obtained from the theory (Ref. 14) as explained in the text.

The results reproduced exactly. To avoid surface oxidation the samples had been carefully maintained in a He gas atmosphere. After measuring some of the samples, we exposed them to the air for several weeks and then remeasured them, again reproducing the original data.

We can summarize the properties that seem to characterize the Sn-In system: (a) The straight lines defined by the H_{c3} and H_{c2} data, at low temperatures, do not extrapolate to the same temperature. (b) The critical temperatures of the bulk coincide with T_{c2} and not with T_{c3} , as can be seen in Fig. 5. (c) The decrease in the value of the ratio H_{c3}/H_{c2} , at least until $t = 0.975$, can be expressed by the ratio of two straight lines having different extrapolations to the horizontal ($H = 0$) axis. (d) The temperature T_{c2} is a function of the thickness of the sample; T_{c3} is not. (e) The transition width at zero field is independent of the annealing time, the thickness of the sample, the time the sample is exposed to air, and the relative orientation of the ac pick-up field to the sample.

B. In-Bi

As we have cited, for the Sn-In system there is a certain "characteristic" thickness, below which the ratio H_{c3}/H_{c2} increases as T_c is approached. We studied the In-Bi system to determine whether the

ratio increase reported in Ref. 9 was an intrinsic property of this alloy, or if the samples in Ref. 9 were thinner than some characteristic thickness for the In-Bi system. Five samples of 2.9-at.% Bi with thicknesses of 300, 240, 180, 105, and 40 μ were investigated. Figures 6 and 7 show H_{c3} and H_{c2} as a function of temperature for the thinnest and the thickest samples. The relevant experimental data for all five samples are shown in Table III. The ratio increase was found to diminish as the thickness of the samples was increased; and a marked decrease in the ratio near T_c occurred for the 300- μ sample, as can be seen in Fig. 8. For this sample T_{c3} is lower than T_{c2} .

Both the magnetic transition and the zero-field transition are wider than those of the Sn-In system. We attempted without success to reduce the transition width by enhancing the annealing procedure beyond the 24 h (at room temperature) necessary for data reproducibility.

Both T_{c3} and T_{c2} varied somewhat from sample to sample, and it cannot be said as in the case of Sn-In, that T_{c3} is constant and T_{c2} is shifting systematically with sample thickness. Nevertheless, the difference $T_{c2} - T_{c3}$ is a function of thickness.

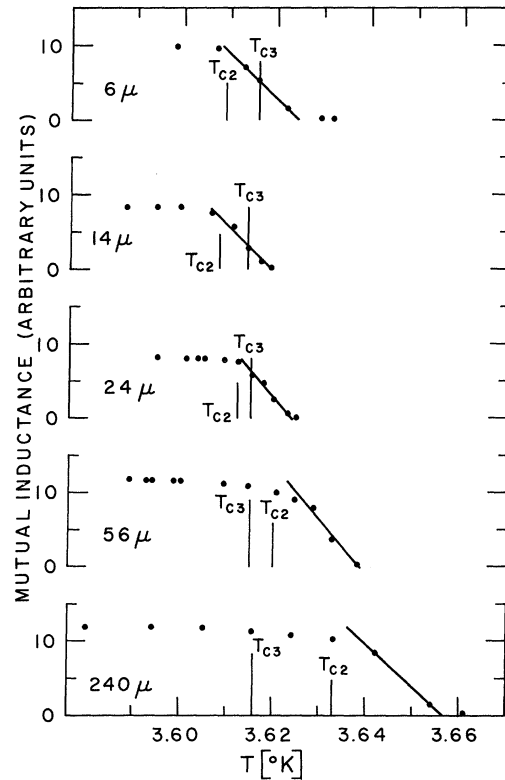


FIG. 5. Transition width at zero field for Sn-In (5.5-at.% In) samples of several thicknesses.

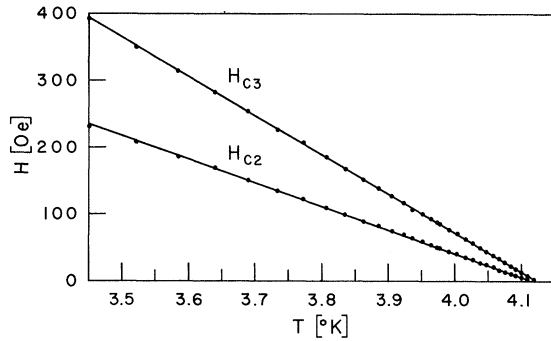


FIG. 6. H_{c3} and H_{c2} for an In-Bi (2.9-at.% Bi) sample 40 μ thick as a function of temperature.

Also, the variation of the ratio H_{c3}/H_{c2} near T_c behaves very similarly to that of Sn-In (Fig. 4) as the sample thickness is changed.

For the 300- μ sample, the low-temperature value of the ratio was measured to be 1.35, somewhat lower than that of the other samples (between 40 and 240 μ). The unusually high slope of the H_{c2} -versus- T line can be attributed to the inordinate thickness of the sample. When the dc field H is perpendicular to the sample (parallel to the primary of the mutual inductance), and larger than H_{c2} , there might still be some shielding of the ac field from that component of the sample parallel to H , namely, the edges of 300- μ depth.

IV. DISCUSSION

It is not possible to explain these results by assuming that some part of the bulk of the sample remains superconducting at a higher temperature than the rest. If this were so, T_{c2} should be higher than T_{c3} , and T_{c3} should correspond to the critical temperature of the main part of the sample. Moreover, the decrease in T_{c2} with thickness could be attributed to an increase in homogeneity for thinner samples. If T_{c3} is the critical temperature then the transition at zero field must be fixed by this temperature. Also, if the thinner samples are more homogeneous the transition width would decrease with the thickness of the sample. But as can be seen in Fig. 5, the transition width is independent of thickness. Furthermore, the transition at zero field for different samples changes in accordance with the variation of T_{c2} . Thus, the assumption of internal inhomogeneities of higher critical temperature is inadequate.

The theoretical treatments mentioned in the Introduction^{11,14} concern semi-infinite superconductors. For our thicker samples we expect that a comparison with results for semi-infinite layers is possible, but we must bear in mind that the surface layer of our model is likely to be thin. To ally our

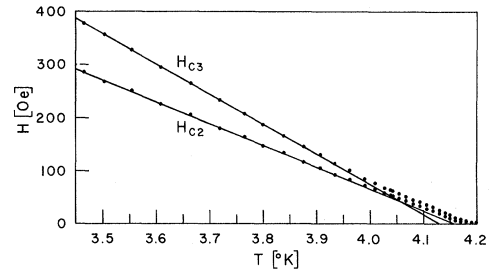


FIG. 7. H_{c3} and H_{c2} for an In-Bi (2.9-at.% Bi) sample 300 μ thick as a function of temperature.

measurements with the model of Hu,¹¹ we assume that the experimental value obtained for H_{c3} depends upon the surface properties of the sample, and that H_{c2} is determined (except for a small perturbation) by the bulk. Then the experimental data indicate that the surface of the sample has a lower critical temperature T_{c3} than the one that corresponds to the bulk, T_{c2} . From Figs. 3 and 7 we know that there is qualitative agreement between the experiment in the low-temperature region and the results of the theory¹¹ in region A. But a careful review renders incorrect the association of Hu's calculated H_{c3} with our measured H_{c3} , and the theory cannot be applied. Let us assume that we are in the low-temperature region and we begin to increase the magnetic field (oriented parallel to the surface). When the external magnetic field reaches the value calculated by Hu¹¹ the superconductivity is destroyed in the surface layer. But owing to the stronger interaction in the bulk, "surface" superconductivity will remain in the bulk of the sample (at the interface between the bulk and the surface layer). The effective surface critical field of the sample should be fixed by the bulk interaction, and slightly depressed by the proximity effect of the weaker-interaction region in the surface. Now, the region of the sample in which the interaction is depressed, D , is expected to be of the order of magnitude of the

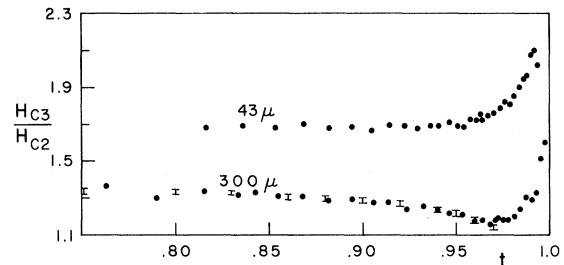


FIG. 8. Ratio H_{c3}/H_{c2} for the 40- and 300- μ samples of the In-Bi alloy as a function of reduced temperature. Bars indicate the theoretical values (Ref. 14).

coherence length at zero temperature. But since the variation of the mutual inductance of the coils at the transition is proportional to the volume of the sample that is shielded, the variation due to the destruction of superconductivity in the region of weaker interaction cannot be detected with our sensitivity. Then the experimental H_{c3} should be the surface critical field of the bulk, modified by the proximity effect of a material with lower critical temperature.

Pictured this way, our experiment will appropriately be compared with the results obtained by Fink and Presson.¹⁴ No theory at zero field is available for the case in which b is a function of temperature. The thickness dependence of T_{c2} can be associated with proximity effects. Due to the small variation of T_{c2} in the range of thickness in which the measurements were done, the sensitivity was not enough to determine an exact functional relationship between thickness and the bulk critical temperature. The variation of T_{c2} with thickness is not considered by Fink and Presson,¹⁴ and consequently, it is not possible to expect from the theory a change in sign for $T_{c2} - T_{c3}$ for the thin samples. Nevertheless, the proposed N - S sandwich model affords a qualitative explanation of these results. As we have mentioned, T_{c2} corresponds to the critical temperature of the bulk S . If a proximity effect is present, T_{c2} should be a function of the thickness of S , and this would account for the observed shift in T_{c2} . The surface critical field extrapolation that we defined as T_{c3} would have no physical meaning. Near $H = H_{c3}$ the sample is in the normal state except for the surface superconducting region of the order of the coherence length. Then it is reasonable to expect that as long as the samples remain much thicker than the coherence length, changing the thickness will not change the proximity effect on H_{c3} . That is, T_{c3} should be independent of thickness over our range of sample thicknesses.

To make a comparison between our experiment and the theoretical results¹⁴ shown in Fig. 1, it is necessary to know σ_s , σ_n , n_n , n_s , and T_{cn} . This is quite possible in a standard proximity effect experiment in which two different metals are in contact. In our case a determination of most of these parameters is impossible. Nevertheless, considering the sample preparation we can think that γ should be very close to unity and $n_s \approx n_n$. Using $\gamma = 1$ and $n_s = n_n$ we found reasonable agreement with the data for thicker samples. The results are shown in Figs. 4 and 8. The T_{cn} values were determined as those best fitting the data for fixed γ and n_n/n_s . The values obtained for T_{cn} are shown in Tables I–III. Except for the critical temperature irregularities with In-Bi, all the T_{cn} 's are lower than the lowest T_{c2} obtained from the thinnest sample, as should be expected. The choice of γ , n_s , and n_n is not unique and other values can fit the experimental data as well, but we have no physical arguments to choose them. For all the samples the ratio H_{c3}/H_{c2} is constant¹⁹ at low temperatures (below $t \sim 0.85$); to compare with theory, the experimental data were normalized by this constant value.

We have shown that the anomalous values of H_{c3}/H_{c2} can be explained if a perturbation decreasing the critical temperature in a surface layer is introduced. This assumption with the results of the proximity effect theory¹⁴ gives a good picture of the phenomena for temperatures at least as close to T_c as $t = 0.98$. Nevertheless, for temperatures closer to T_c the experimental data remain unexplained. It can be seen that the ratio H_{c3}/H_{c2} , for all the thick samples, reaches a minimum value at about $t = 0.99$ and at higher temperatures has a tendency to increase. Over this region of temperatures very close to T_c all the plotted data correspond to temperatures below the transition width region (the sample is fully superconducting in zero field, as measured with the mutual inductance bridge).

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¹⁵H. J. Fink and A. G. Presson, Phys. Rev. (to be published).

¹⁶As explained in Ref. 9, the critical field definition has no significant effect on the results obtained.

¹⁷P. G. Strelkov and E. J. Walker, Rev. Sci. Instr.

30, 834 (1959).

¹⁷For the cases in which $T_{c3} < T_{c2}$, we defined the reduced temperature $t = T/T_{c2}$. For $T_{c2} < T_{c3}$, we defined $t = T/T_{c3}$.

¹⁸S. L. Wipf, *Cryogenics* **3**, 225 (1963).

¹⁹The increase in the ratio H_{c3}/H_{c2} predicted in Refs. 1–3 was found to be zero within experimental error (1–2%). To check for this our samples were measured down to $t = 0.5$ for the Sn-In system, and $t = 0.3$ for the In-Bi system.

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Superconducting Penetration Depth of Lead[†]

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The temperature dependence of the change in the superconducting penetration depth λ from its value at absolute zero has been measured in polycrystalline and single-crystal specimens of lead, using radio-frequency fields at about 80 MHz. In the polycrystalline material, it has been found that the temperature dependence is the same as that of a weak coupling superconductor with Δ_T/Δ_0 given by the BCS theory and with an energy gap $2\Delta_0 = 3.75kT_c$, rather than $2\Delta_0 = 4.3kT_c$, the value found from tunneling measurements. Near the transition temperature T_c , $d\lambda/dy = 418 \pm 9 \text{ \AA}$, where $y = (1 - t^4)^{-1/2}$ and $t = T/T_c$. A full comparison with Nam's general formulation of the electromagnetic properties of superconductors (which encompasses strong coupling effects) awaits more detailed theoretical work on lead. Among the single crystals, there is a small anisotropy in the values of $d\lambda/dy$ near T_c , and at lower temperatures a slight anisotropy in the form of the temperature dependence of λ . A review of all the relevant experiments on lead gives the following consistent values for the coherence length and London penetration depth of lead: $\xi_0 = 960 \text{ \AA}$, $\lambda_L(0) = 305 \text{ \AA}$.

I. INTRODUCTION

Lead differs from the other extensively studied superconductors in that it cannot be regarded as a close approximation to the so-called weak coupling superconductors of the Bardeen-Cooper-Schrieffer theory,¹ hereafter referred to as BCS superconductors. The first indications of this were deviations from the predicted temperature dependence of the critical field² and an energy gap found from infrared measurements³ much larger than predicted for a superconductor with $T_c = 7.2 \text{ K}$. Then followed the more detailed results of tunneling experiments⁴ supported at the same time by theoretical studies of the effects of strong coupling between the electrons and phonons in superconductors.⁵ There still remained the question as to the effect of the strong coupling on the low-frequency electromagnetic properties, which are closely related to one of the most fundamental properties of superconductors – the Meissner effect.⁶

Some measurements of the penetration of radio-frequency fields by Maxfield⁷ using the “active” resonator method⁸ had shown an anomalous increase in the penetration as the lead was cooled through its superconducting transition, followed, at low temperatures, by the expected decrease. This anomaly was later observed by Gasparovic⁹ using the “passive” resonator technique¹⁰ which is more readily analyzed

in cases where there is doubt about what is actually being measured. At about this time, theoretical work by Scalapino and Wada¹¹ had shown that the gap function would vanish for low frequencies (of the order of the ones being used in the experiments). However, detailed calculations by Wada¹² showed that this had an insignificant effect on the commonly measured properties of lead. Further experimental studies of the anomalous penetration of radio-frequency fields at T_c showed that the effect was due to using too large an amplitude of oscillating field, which irreversibly forced the transition and thus produced a highly nonlinear response. Similar effects causing an apparent shift of the transition temperature had been observed by others,¹³ but it seems that in lead greater precautions are needed than in other superconductors studied previously.

The results reported here were obtained from further measurements carried out to see if there were any real strong coupling effects on the penetration of radio-frequency fields into lead. During the course of this work, the theory of the electromagnetic properties of superconductors was extended by Nam.¹⁴ His formulation is sufficiently general to include, among other things, the effects of strong coupling. This work has recently been compared with the measurements of the infrared absorption by Palmer and Tinkham¹⁵ and is compared with the results of the present work later in this paper. The