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# 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 $\mu$). 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. Theory[1-3] 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 work[4-6] 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] Hu[11] 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 reported[9] 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 Hu[11] 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 is[12]

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

where $\Delta$ 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 $\sigma_n$ is much smaller than the conductivity of the superconductor $\sigma_s$, 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 recently[14] there was no theoretical treatment of the case $T_{cn} \simeq T_{cs}$ and $\sigma_n \simeq \sigma_s$. Fink and Presson[14] 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 $\alpha$, defined by

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

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 $\alpha$ 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 as $\gamma \to 0$, 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).

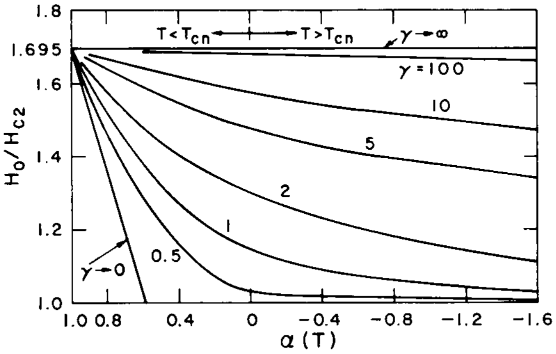

FIG. 1. Theoretical results obtained by Fink and Presson (Ref. 14) showing the nucleation field ratio as a function of $\alpha(T)$ for various $\gamma$ values.

## II. EXPERIMENTAL PROCEDURE

We have measured four Sn-In alloy samples of approximately 100 $\mu$ thickness with concentrations of 6-, 5.5-, 5-, and 4.7- at.% in (see Table I), six samples of 5.5- at.% In with thicknesses between 6 and 240 $\mu$ (see Table II), and five samples of In-Bi (2.9-at. % Bi) with thicknesses between 40 and 300 $\mu$ (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 regulator[16] 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 orientation[9] 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 $\mu$. 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 $\mu$, $T_{c2}$ 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 temperature[17] in Fig. 4. For the "thick" samples of 56, 100, and 240 $\mu$, $T_{c3}$ 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 | ($\mu$) | 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 | | | | |

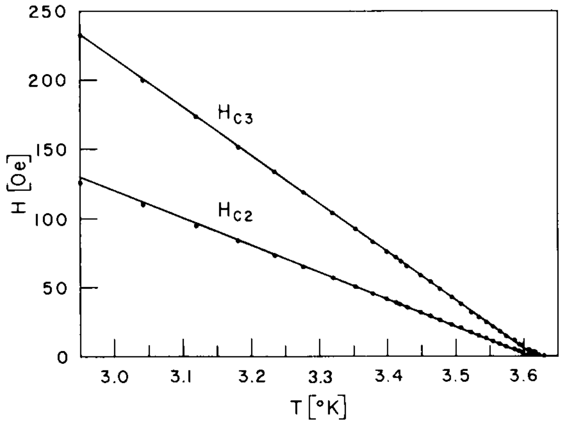

FIG. 2. $H_{c3}$ and $H_{c2}$ for a Sn-In (5.5-at.% In) sample 6 μ thick as a function of temperature.

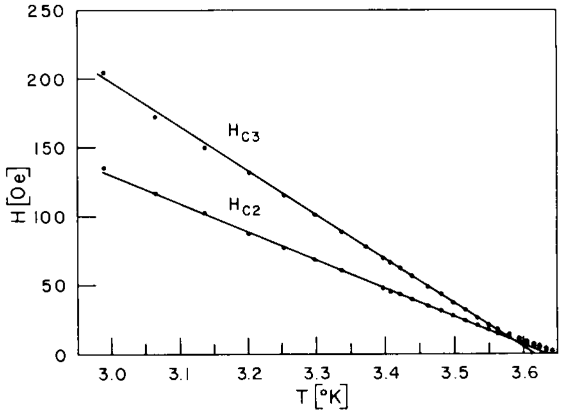

FIG. 3. $H_{c3}$ and $H_{c2}$ for a Sn-In (5.5-at.% In) sample 240 μ thick as a function of temperature.

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 | | | | |

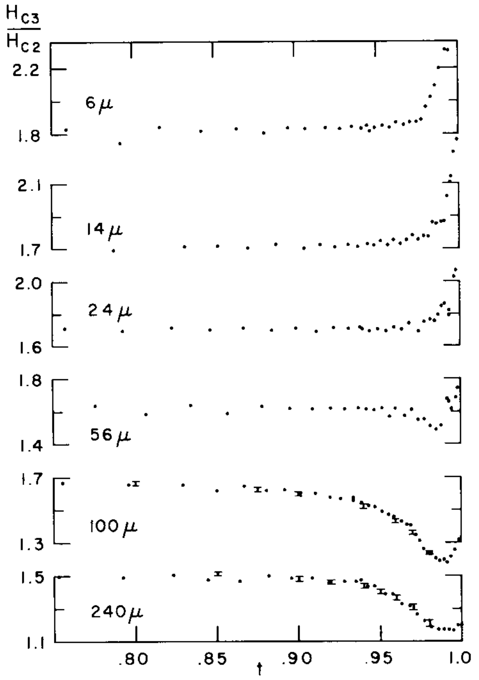

FIG. 4. Ratio $H_{c3}/H_{c2}$ for the Sn-In (5.5-at.% In) samples of different thicknesses as a function of reduced temperature. Bars indicate the values obtained from the theory (Ref. 14) as explained in the text.

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.

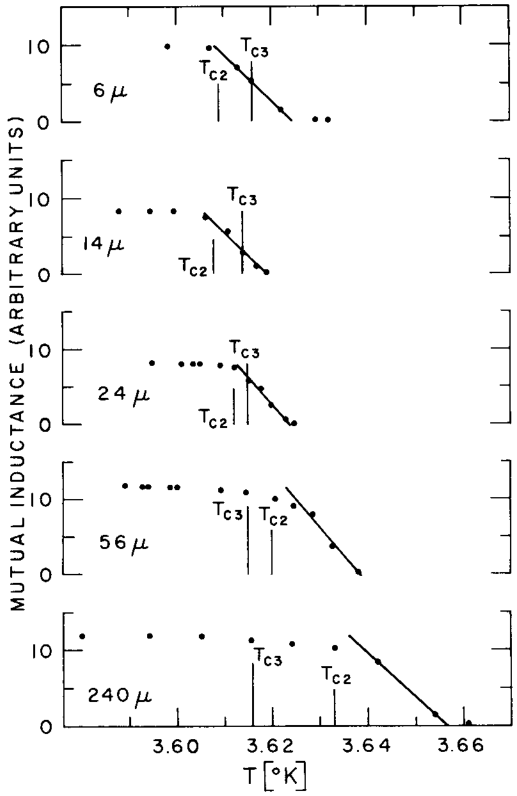

FIG. 5. Transition width at zero field for Sn-In (5.5-at.% In) samples of several thicknesses.

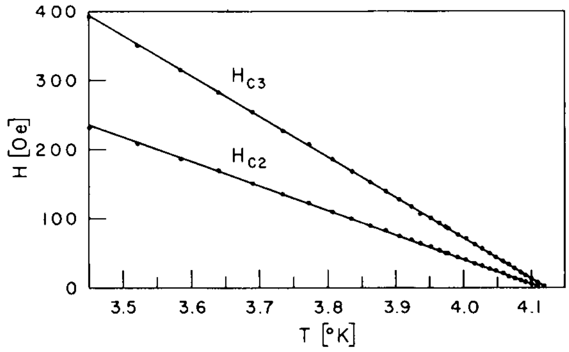

FIG. 6. $H_{c3}$ and $H_{c2}$ for an In-Bi (2.9-at.% Bi) sample 40 μ thick as a function of temperature.

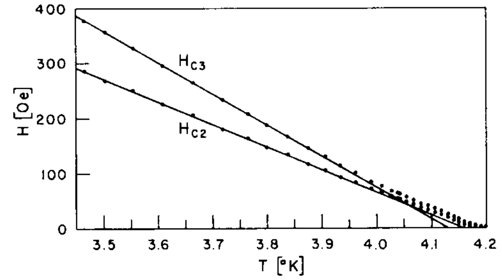

FIG. 7. $H_{c3}$ and $H_{c2}$ for an In-Bi (2.9-at.% Bi) sample 300 μ thick as a function of temperature.

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 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 theory[11] 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 Hu[11] 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

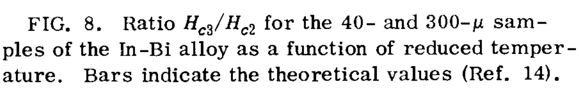

FIG. 8. Ratio $H_{c3}/H_{c2}$ for the 40- and 300-μ samples of the In-Bi alloy as a function of reduced temperature. Bars indicate the theoretical values (Ref. 14).

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 results[14] shown in Fig. 1, it is necessary to know $\sigma_s$, $\sigma_n$, $n_n$, $n_s$, 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 $\gamma$ should be very close to unity and $n_s \simeq n_n$. 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 $\gamma$ 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 $\gamma$, $n_s$, 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 constant[19] 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 theory[14] 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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