PHYSICAL REVIEW B VOLUME 2, NUMBER 1 1 JULY 1970

Anomalous H_{c3}/H_{c2} near T_c in Pb-In and Critical Phenomena in the Superconducting Sheath*

R. W. Rollins, R. L. Cappelletti, and J. H. Fearday

Ohio University, Athens, Ohio 45701

(Received 25 June 1969; revised manuscript received 10 October 1969)

The measured ratio of the critical field for the sheath state to that for the vortex state H_{c3}/H_{c2} increases sharply above the Saint James-de Gennes value of 1.695 near T_c in Pb-8.7 at. % In alloy samples with several surface preparations. The sudden increase beginning at temperatures above $0.96T_c$ for the relatively short mean free path Pb-In alloy is in sharp contrast to the precipitous drop of H_{c3}/H_{c2} beginning at about 0.85 T_c which has been observed by others in pure Nb and V. The Nb experiment was interpreted in terms of a critical phenomenon. Our observations of anomalous behavior over a narrower reduced temperature interval in the dirty Pb-In alloy than that in clean Nb and V is used (i) to argue that an interpretation of both effects based solely on a critical phenomenon is not valid and (ii) to suggest that neither effect is solely a critical phenomenon. A model recently advanced by Hu which does not appeal to critical phenomena at all may be used to describe both sets of results. In terms of Hu's parameters, the results in Pb-In correspond to $\delta V/V_0 \simeq 10^{-4}$ and $D \geqslant 17\xi(0)$. A simple description of the Pb-In results consistent with Hu's model is that the "critical temperature" of the surface is enhanced by 0.1% relative to that of the bulk.

I. INTRODUCTION

In this paper we report measurements of an anomalous rapid rise in the ratio of the surface to bulk critical magnetic fields H_{c3}/H_{c2} beginning at about 0.96 T_c and continuing as T_c is approached in Pb-In alloys. The work was undertaken to investigate the generality of the anomalous sharp decrease of the same ratio recently observed[1] in very pure Nb. The precipitous drop of H_{c3}/H_{c2} from the Saint James-de Gennes[2] (SJdG) value of 1.695 in Nb, beginning at about 0.85 T_c and continuing as T_c is approached was interpreted as a critical phenomenon. With this in mind, we chose the system Pb-In for a number of reasons. First, the range of temperature over which critical fluctuations are important is estimated to be greater by at least a factor of 25 in these short electron mean free path alloys than in pure Nb. Thus, if the anomalous behavior were a critical phenomenon one would expect it to occur over a broader reduced temperature interval in the alloys than in pure Nb. Second, the Pb alloys differ in many properties from pure Nb and so provide a good test of the generality of the anomalous behavior. Third, we were able to prepare homogenous samples with very narrow transitions so that measurements could be made quite close to T_c.

The general results of these measurements are that H_{c3}/H_{c2} increases sharply (as opposed to the decrease reported in Nb) beyond the SJdG value of 1.695 as T_c is approached and that the increase occurs within a narrower reduced temperature interval than the corresponding decrease in pure Nb. These results suggest strongly that an interpretation based on a critical phenomenon alone is not generally valid and an alternative explanation should be sought.

EXPERIMENT

Cylindrical specimens of Pb-5 wt% In were prepared by melting the 99.999% pure starting ingredients[3] in sealed evacuated Pyrex tubes, mixing the melt for about two days, then quenching the vials in water. The specimens were extruded to a length of 2 in. and a diameter of $\frac{1}{8}$ in., chemically polished in an acetic-acid–hydrogen-peroxide mixture, sealed in evacuated Pyrex tubes, and annealed at about 10 °C below the melting point for a week. Measurements were made on samples with freshly annealed, chemically polished, and electropolished surfaces.

The critical temperatures were obtained in "zero" dc magnetic field by measuring the in-phase ac permeability μ' of the sample with a lock-in amplifier at 206 Hz using an ac field of 4-mOe amplitude parallel to the sample. No attempt was made to compensate for the earth's field. The width of the μ' transition was about 0.002 K or about $0.0003T_c$ in all cases. The temperature at the center of a transition was taken as the critical temperature. Such a narrow transition width is usually indicative of a high degree of sample homogeneity. Our critical field measurements were made to within $0.004T_c$, well outside the zero-field transition and yet close enough to T_c to see a significant effect in H_{c3}/H_{c2}. Throughout all measurements, the temperature was controlled to a precision of less than 0.5 mK and measured with an accuracy of 0.01 K using a calibrated germanium resistance thermometer.

H_{c2} and H_{c3} were determined from the in-phase and out-of-phase permeabilities μ' and μ'' measured in the presence of a coaxial dc magnetic field produced by a compensated solenoid having a field homogeneity in the sample region of 0.03%. This field was aligned with the sample axis to within ±15 min by adding the adjustable field produced by a Helmholtz pair. The determination of H_{c2} and H_{c3} from this type of data has been extensively discussed elsewhere.[4] Both $(1-\mu')$ and μ'' approach zero smoothly as the dc field approaches H_{c3}. The value of H_{c3} could be taken as that dc field at which either $(1-\mu')$ or μ'' reaches zero. However, we have observed that the values of H_{c3} obtained from the $(1-\mu')$ curves are consistently lower than those obtained from the μ'' curves. Also, both curves lead to an H_{c3} value which depends on ac field amplitude for large amplitudes. These observations are consistent with the critical current model of the sheath,[4,5] and suggest that the best value of H_{c3} is determined from a μ'' curve. We have determined H_{c3} from μ'' curves taken with ac field amplitudes less than $10^{-4}\,H_{c2}$. The rounding of these curves gives rise to an uncertainty in the choice of H_{c3} of a few percent and the values of H_{c3} reported represent a lower-bound estimate. The choice of H_{c2} is made easy by the occurence of a discontinuity in the slope of both μ' and μ'' (but especially the former) at the value of H_{c2} as determined by dc magnetization measurements.[4] This break in slope occurs for ac field amplitudes large enough to penetrate the sheath (generally about $10^{-3}H_{c2}$), but otherwise there is no ac field dependence in the determination of H_{c2}. The H_{c2} values so determined are precise within better than 1%.

RESULTS AND DISCUSSION

H_{c3} and H_{c2} data obtained for three samples with different surface preparations are shown in Fig. 1. All samples and preparations show the same general behavior. Below $t \equiv T/T_c \sim 0.96$, the ratio $H_{c3}/H_{c2} = 1.68 \pm 0.02$, in agreement with the SJdG prediction. The corrections to SJdG due to Ebneth and Tewordt[6] are negligible for these "dirty" samples.[7,8] Above this temperature, H_{c3}/H_{c2} begins to increase rapidly above the SJdG prediction. The reduced temperature corresponding to the onset of the increase in H_{c3}/H_{c2} depends somewhat on the surface preparation. In the case of the freshly annealed sample, H_{c3}/H_{c2} remains near the mean field-theory value of 1.695 until $t \sim 0.99$ where the ratio starts to rise sharply. These results are in contrast to the behavior of pure Nb (solid curve labeled O-F in Fig. 1) where a sharp decrease in the ratio is observed,[1] beginning at

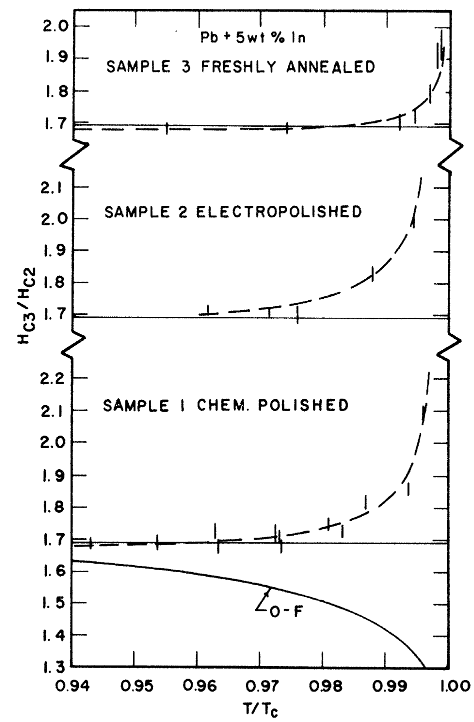

FIG. 1. Temperature dependence of H_{c3}/H_{c2} near T_c. The bars are the Pb-In data. The lowest dashed curve is the ratio of the straight lines in Fig. 2. The other dashed curves are from similar plots. The solid line $H_{c3}/H_{c2} = 1.695$ represents the mean field prediction for the alloy and the curve labeled O-F represents the pure Nb data of Ref. 1.

about $t \sim 0.85$. In both cases, the SJdG extension of the Ginzberg-Landau[9] theory is violated. Moreover, *the departure from* SJdG *occurs in a narrower temperature interval in the dirty* Pb-In *alloys than in the clean* Nb. *This is the reverse of what is to be expected if the anomalous behavior in both cases were a critical phenomenon.* In short, a critical phenomenon interpretation valid for both the Nb and Pb-In alloy data would have to describe both positive and negative deviations from the SJdG prediction. It would also have to explain the much narrower "critical region" of the dirty alloy in comparison to the clean Nb.

Clem[10] first suggested to us that a difference of a few mdeg between the critical temperature characteristic of the surface and that characteristic of the bulk might lead to a description of the anomalous results. The thickness of the superconducting sheath is proportional to $[T_c/(T_c - T)]^{1/2}$ and thus at temperatures not too close to T_c the sheath critical field H_{c3} would depend on the properties of the material near the surface. If these properties are characterized by a "critical temperature" T_{c3}, then not too close to T_c we may expect $H_{c3} = H'_{c3}\,(T_{c3} - T)$ where H'_{c3} is a constant. H_{c2}, of course, depends on the properties of the bulk of the sample, which, if different from those of the surface, could be characterized by the critical temperature T_{c2} and $H_{c2}=H'_{c2}(T_{c2}-T)$ where H'_{c2} is constant. Accordingly, the ratio H_{c3}/H_{c2} would be greater or less than 1.695 as the critical temperature of the surface is greater or less than that of the bulk. Very close to T_c the sheath spreads deeply into the specimen and samples the properties of the bulk material as well as the surface region. Consequently, the parameters T_{c2} and T_{c3} must be functions of temperature very near T_c where they merge toward T_c. So it is expected that very near T_c the above cited linear behavior of the H_{c2} and H_{c3} in which T_{c2} and T_{c3} are treated as constants would give way to a more complicated nonlinear behavior.

The critical-field data of the chemically polished sample are plotted versus temperature in Fig. 2. The straight lines are least-squares fits. As seen in Fig. 2, the intercepts on the temperature axis of these lines, $T_{c3}=(7.042\pm0.001)$ K and $T_{c2}=(7.035\pm0.001)$ K. The uncertainties are plus and minus one standard deviation. T_{c2} was found to agree within the limits of error with the measured zero-field transition temperature T_c. This might be expected since at T_c the distinction between sheath and bulk disappears and the probing ac field measures those properties characterized by T_{c2}. Using the straight-line fits, and similar plots for the other samples, we have calculated curves of H_{c3}/H_{c2} versus T/T_c and compared them with our data. These are the dashed lines of Fig. 1 which are seen to fit the data well.

This very slight (0.1%) enhancement of the critical temperature of the surface may be due to contamination, irregularities, or inhomogenities at or near the surface, or it may be due to inherent differences in surface properties from those of the bulk. Any concentration gradient introduced by chemical polishing should be negligible for the freshly annealed sample since the Pb atoms diffuse an average distance equal to the sample radius during the anneal.

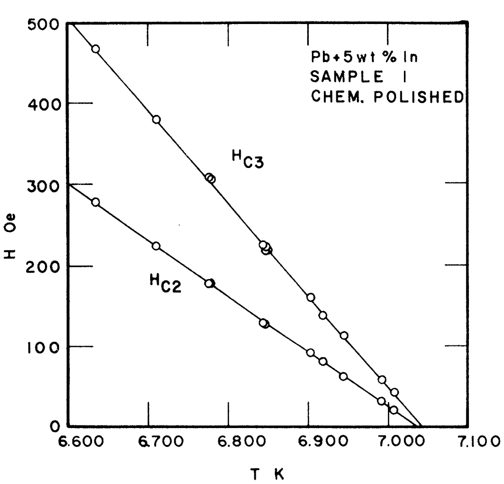

FIG. 2. Temperature dependence of H_{c2} and H_{c3} near T_c for the first sample. The straight lines are least-squares fits and extrapolate to $T_{c2}=7.035\pm0.001$ K and $T_{c3}=7.042\pm0.001$ K, respectively.

Hu[11] has proposed a model which does not appeal to critical phenomena to describe results of this kind. In this model, the BCS[12] coupling parameter V_0 is altered by a step δV within a layer of thickness D near the surface. Three regimes are important: $\xi(T)\ll D$, $\xi(T)\simeq D$, $\xi(T)\gg D$. In the first regime, the behavior of the critical fields is of the linear type cited above. The temperature dependence of H_{c3} in the other regimes is nonlinear. Apparently our experiment was done entirely within the first regime, since we see no noticeable departure from linearity. In the first regime the thickness of the sheath, $\simeq\xi(T)$, is less than D and $\delta T/T_c=(T_{c3}-T_{c2})/T_c$ is related to $\delta V/V_0$ by simply differentiating the BCS relation for T_c, giving

$$\delta T/T_c=[1/N(0)V_0]\delta V/V_0 \quad .$$

We observe $\delta T\simeq 2$–7 mK, and using $N(0)V_0\simeq 0.35$,[13] as for pure Pb, we find $\delta V/V_0\simeq(1-4)\times10^{-4}$. To obtain a lower-bound estimate of D, we may assume that our highest-temperature measurements are at the edge of the second regime. For our Pb-In alloy, Hu's equation would give $D\geqslant 1.185\times\xi(T_{max})$ for this estimate. In the dirty limit[14] $\xi(T)=0.85\,(\xi_0 l)^{1/2}\,\epsilon^{-1/2}$ where ξ_0 is the BCS coherence length, l is the electron mean free path, and $\epsilon=(T_c-T)/T_c$. Using $l=120$ Å obtained from our resistivity measurements and $\xi_0=1000$ Å we find for $T_{max}/T_c=0.995$ that $\xi(T_{max})=4190$ Å. Thus, $D\geqslant 4965$ Å or about 17 $\xi(0)$. This value of D is surprisingly large and indicates that refinements of the model may be necessary to describe these Pb-In results. Finnemore and Ostenson[15] have recently reported measurements on pure V showing behavior much like their pure Nb near T_c. They analyze the data for both these pure materials according to the Hu model, and obtain values for D: $\simeq 0.5\,\xi_0$ for V and $\simeq 2\,\xi_0$ for Nb.

SUMMARY

In summary, an explanation of the results in Pb-In and in pure Nb and V based solely on critical phenomena clearly meets with severe difficulties. There remain three other possibilities: (i) The effect in Nb and/or V is a critical phenomenon; (ii) the effect in Pb-In is a critical phenomenon; and (iii) neither effect is solely a critical phenomenon. Possibility (i) does not rule out a critical phenomenon in Pb-In, but it would imply that we are reporting for Pb-In the result of a competition between a critical phenomenon and an effect of a different nature such that the temperature variation of H_{c3}/H_{c2} is compensated except very near T_c. The likelihood of such a cancellation resulting from totally different phenomena, occurring over an extended temperature range, in our three specimens each of which has a different surface preparation, seems remote. The second possibility would imply that the effect in Nb and V cannot be a critical phenomenon because the anomaly occurs over a broader temperature interval in these pure materials than in the dirtier Pb-In. The explanation of the Nb and V data would have to be sought elsewhere; perhaps, as has been done,[15] in the spatial variation of the BCS coupling parameter of which Hu's model[11] is an example. But the fact that the Pb-In data also find a simple description in these terms, as discussed above, renders unnecessary a critical phenomenon interpretation based on the present experimental evidence. Thus, we are led to suggest that the third possibility is valid: Neither the effect in Pb-In nor that in Nb or V is solely a critical phenomenon. This possibility allows for ruling out the operation of critical phenomena entirely, and the results in all three materials can be described without reference to critical phenomena at all.

ACKNOWLEDEMENTS

We wish to acknowledge useful discussions with D. K. Finnemore and Chia-Ren Hu who also kindly supplied us with a preprint of his work. Lavern Clune gave us valuable suggestions in designing the apparatus and Jerome Wagner prepared the samples.

---

*Work supported by a National Science Foundation Departmental Science Development Grant No. NSF-GU 2603.

[1]J. E. Ostenson and D. K. Finnemore, Phys. Rev. Letters, 22, 188 (1969).

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

[3]American Smelting and Refining Co., South Plainfield, N. J.

[4]R. W. Rollins and J. Silcox, Phys. Rev. 155, 404 (1967).

[5]The critical current model of the surface sheath leads to the expressions: $(1-\mu') \propto (J_c/h_0)^{3/2}$; $\mu'' \propto J_c/h_0$ near H_{c3} where $(4\pi J_c/ch_0) \ll 1$. Here J_c is the critical current of the sheath, and h_o is the ac field amplitude. Previous measurements of J_c near H_{c3} on similar samples show $J_c \propto [(H-H_{c3})/H_{c3}]^n$ with $n>2$. Thus, both $(1-\mu')$ and μ'' are expected to approach zero as some higher power of $(H - H_{c3})/H_{c3}$ and μ'' is expected to give a more sensitive measurement of H_{c3}.

[6]G. Ebneth and L. Tewordt, Z. Physik 185, 421 (1965).

[7]Ebneth and Tewordt show that if $t > 0.9$ the deviation of H_{c3}/H_{c2} from 1.695 is less than 0.1% when the Gor'kov impurity parameter $\rho = 0.88\xi_0/l \gtrsim 10$, where ξ_0 represents the coherence length for $l \to \infty$ and l is the average electron mean free path. Measurements on similar Pb-In alloys (Ref. 8) indicate that $\rho \simeq 7$ for the sample under discussion.

[8]D. E. Farrell, B. S. Chandrasekhar, and Harvey V. Culbert, Phys. Rev. 177, 694 (1969).

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

[10]J. R. Clem (private communication).

[11]Chia-Ren Hu, Phys. Rev. 187, 575 (1969).

[12]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[13]T. P. Sheahen, Phys. Rev. 149, 370 (1966).

[14]P. G. de Gennes, *Superconductivity of Metals and Alloys*, translated by P. A. Pincus (Benjamin, New York, 1966), p. 225.

[15]D. K. Finnemore and J. E. Ostenson, *Proceedings of the International Conference on the Science of Superconductivity, Stanford*, 1969 (North-Holland, Amsterdam, to be published).