PHYSICAL REVIEW B VOLUME 14, NUMBER 1 1 JULY 1976

Specific heat of composite superconductors in the proximity-effect regime*

A. J. Bevolo, E. D. Gibson, J. D. Verhoeven, and D. K. Finnemore
Ames Laboratory-ERDA and Department of Physics, Iowa State University, Ames, Iowa 50010

(Received 3 November 1975)

The specific heat of a series of Pb-Cd laminar composites with layer spacings ranging from 1000 to 85000 Å has been measured in order to study the superconducting proximity effect in bulk material. The jump in specific heat at the transition temperature is very sensitive to the spatial dependence of the superconducting order parameter and these measurements provide an estimate of this spatial distribution. Results show that the fourth moment of the order parameter is approximately 10% larger than the square of the second moment. The presence of the interleaved nonmagnetic normal-metal layers is not very detrimental to the superconductivity.

I. INTRODUCTION

A normal metal in close proximity to a superconductor can substantially alter the behavior of the superconductor near the boundary because the electrons flow from one metal to the other and are influenced by the potential in both regions.[1,2] This so-called proximity effect leads to a depression of the pair potential of the superconductor near the boundary and it also induces superconductivity in the normal metal. The spatial extent of these effects is typically a few hundred to a few thousand angstroms, values which are comparable to the penetration depth λ and the coherence distance ξ. In the design of a high stabilized critical current, superconducting wire, the efficient use of materials dictates that one should keep the dimensions of the superconducting filaments and the stabilizing normal metal comparable to λ. Hence the proximity effect is a very important aspect of the design and fabrication of composite materials for superconducting cables.

For the single-sandwich thin-film geometry, many aspects of the proximity effect are fairly well understood. Werthamer[3] and de Gennes[1,4] have provided a broad theoretical framework for the proximity effect and several aspects of the theory have been experimentally verified. Hauser[5,6] has made an extensive study of the transition temperatures of superimposed films and finds good agreement with the modified Werthamer–de Gennes model.[3,4] Adkins and co-workers[7,8] have studied the tunneling density of states near the gap edge and Lindenfeld and co-workers[9,10] have investigated the temperature dependence of the pair potential via thermal conductivity measurements. A general review of the subject is given by Deutscher and de Gennes.[2] Many qualitative aspects of theory agree with experiment but much remains to be done.

For bulk composites, there have been very few studies of the proximity effect because it is difficult to prepare suitable samples. Shiffman and co-workers[11,12] have measured the jump in specific heat, ΔC, at the transition temperature T_c for the directionally cooled Pb-Sn system and report a depression qualitatively similar to the ΔC predicted by Fulde and Moormann.[13] These results, however, were difficult to extend over a wide range because the Sn transition temperature was rather high and this interfers with the jump in specific heat at T_c.

We have recently made significant advances in the techniques for the fabrication of laminar composite materials by high-speed directional solidification and are now able to prepare Pb-Cd eutectics with a laminar repeat distance L as small 300 Å. We report here an extensive study of the jump in specific heat at T_c for these composites. The purpose of the experiment is to study the depression of T_c and ΔC with laminar spacing in order to gain insight into the spatial variation of the order parameter in the region of a superconductor–normal-metal boundary.

II. EXPERIMENTAL

Samples were prepared by a high-speed directional solidification technique. A molten sample of Pb-Cd encased in a stainless-steel (or glass) jacket is solidified by moving it at a carefully controlled rate through a steep temperature gradient which is provided by a furnace and appropriate jets of cold water. For Pb-Cd, the laminar repeat distance L is related to the solidification rate r by the relation $L=500\ r^{-1/2}$, where L is measured in angstroms and r is measured in cm/sec. A scanning-electron-microscope (SEM) picture for an $L=1000$-Å sample is shown in Fig. 1. SEM picutres taken shortly after solidification show an excellent laminar character with uniform plate thickness as shown in Fig. 1(a). After several days at room

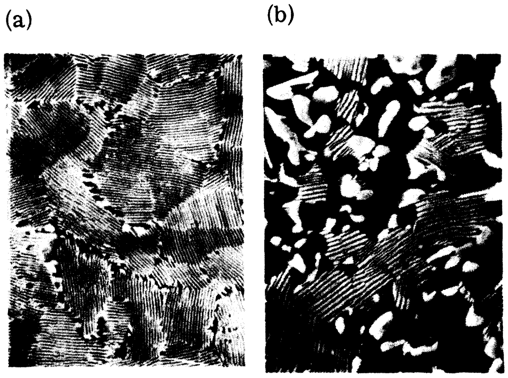

FIG. 1. (a) Scanning-electron-microscope (SEM) pictures of the Pb-Cd laminar composites taken after 2 h at room temperature. The repeat distance is 1000 Å. The dark regions are Pb rich and the light regions are Cd. The magnification is 7700×. (b) SEM picture after a sample has been allowed to coarsen at room temperature for 11 d. The magnification is 7000×.

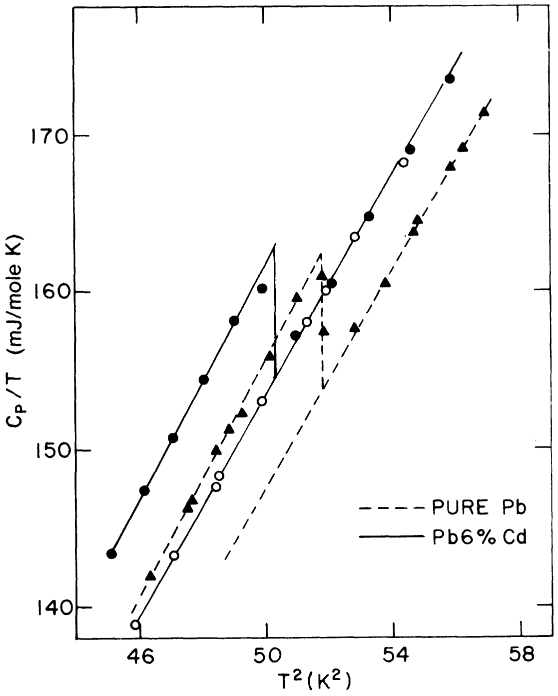

FIG. 2. Comparison of the specific heat of pure bulk Pb with that of a quenched 6-at.%-Cd alloy. Neither sample has any laminar structure.

temperature, however, the sample coarsens as shown in Fig. 1(b). This coarsening occurs for all samples with L less than 10 000 Å, so these samples were kept at 78 K from the time of solidification until they were mounted in the cryostat for measurement. They were at room temperature for less than 30 min before measurement. All of the samples reported here had the eutectic composition, so they were at 72-at.% Cd. Based on room-temperature density data, the volume fraction of Cd is approximately 19%. This means that a sample with $L = 1000$ Å would have a normal-metal thickness, d_n of 190 Å and a superconductor thickness d_s of 810 Å. Specific-heat measurements were taken by a standard pulse-heating method described elsewhere.[14]

III. RESULTS AND DISCUSSION

Pb-Cd composites fabricated by directional solidification will retain small amounts of Cd in solution in the Pb-rich lamina. From solubility studies[15] one would expect the amount to be 0.5%–1.5% but this still might significantly affect the superconducting properties. To investigate the magnitude of the changes in specific heat caused by alloying, a Pb-6-at.%-Cd alloy sample was quenched from the melt and measured. Specific-heat results from this alloy sample and for a sample of pure bulk Pb, shown on Fig. 2, indicate that the transition temperautre T_c is suppressed by 0.10 K, in agreement with the work of Nembach,[16] and the Debye temperature decreases with increasing Cd concentration as shown by the increase in specific heat. The qualitative features are similar to the Pb-In alloys reported by van der Hoeven and Keesom.[17] Indeed the pure-Pb data are in excellent agreement with the earlier work of Neighbor *et al.*[18] The most important aspect of these alloy data for this work is that the jump in specific heat at T_c is essentially unchanged by alloying. This means that the (0.5–1.5)% Cd retained in solution in the Pb-rich regions of the laminar samples will not significantly affect the magnitude of the jump in specific heat, ΔC.

Specific-heat results for the laminar samples are summarized on Fig. 3. For these data the ordinate has been shifted for clarity but there is no change in the abscissa. Values of the laminar repeat distance L are shown on Fig. 3 to identify the various samples. Corresponding values of the thickness of the Pb-rich region d_s, and the thickness of the Cd-rich region d_n, are given in Table I. A striking feature of Fig. 3 is the similarity of the specific-heat curves for a very wide range of L values. The magnitude of specific heat is nearly the same, the broadening of the transition remains constant at about 0.080 K, and the magnitude of the specific-heat jump is nearly constant. The most pronounced change is in the value of T_c.

To see the small changes in specific heat which arise from changes in laminar spacing, in more detail, it is helpful to plot the difference between the superconducting and normal-state specific heat as shown on Fig. 4 for three of the samples. On

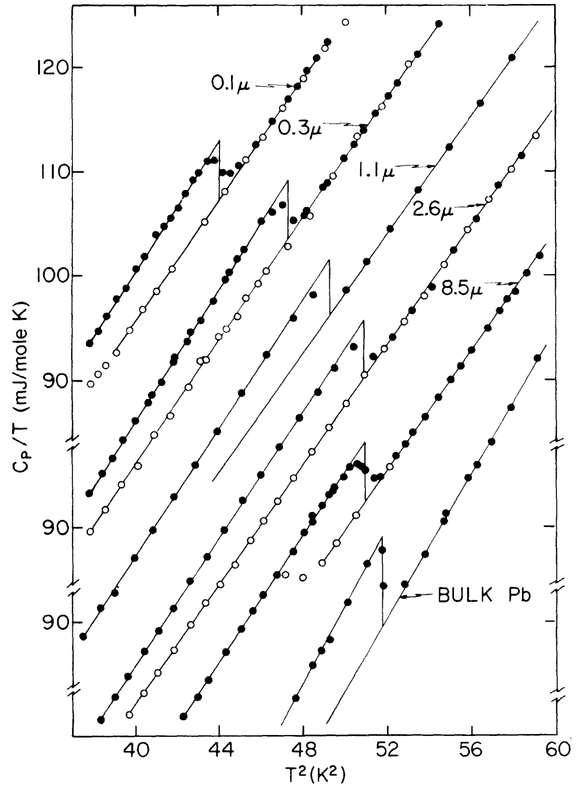

FIG. 3. Specific heat of Pb-Cd laminar composites for a wide range of repeat distances. The ordinate has been shifted so that all the curves would not lie on top of one another.

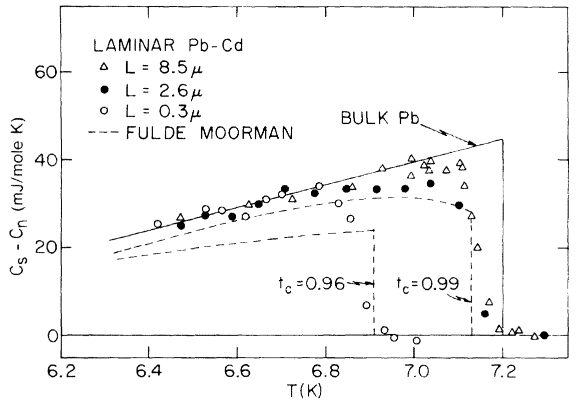

FIG. 4. Comparison of the measured jump in specific heat with the Fulde-Moormann prediction for a paramagnetic normal-metal region. For the Fulde-Moormann curves, $d_s/\xi = 13.3$ for the $t_c = 0.99$ curve.

this figure, the solid line represents the specific heat of bulk Pb normalized for the fact that only 81% of the laminar samples is Pb. There is considerable scatter on this type of plot because ΔC is a small fraction of the total specific heat. Nevertheless, the magnitude of the jump is known to about 10%. The dashed-line curves of Fig. 4 illustrate the predictions of the Fulde-Moormann theory[13] for composite alloys in which the normal metal contains paramagnetic impurities, so that the order parameter is forced to zero at the Pb-Cd boundary. This is the maximum possible suppression of ΔC which would be expected and the measured values show a significantly smaller depression of ΔC.

There are qualitative similarities between these Pb-Cd results and the Pb-Sn results reported by Shiffman and co-workers[11,12] but the Pb-Cd system shows a much smaller depression in ΔC than reported for Pb-Sn. For the case of Pb-Sn, ΔC values are as small as 50% of that of pure Pb, ΔC_0, whereas the Pb-Cd ΔC values in a corresponding range are about 85% of ΔC_0. A very clear example of the difference between the laminar sample and the alloy sample is illustrated by the $L = 1000$-Å data. After the specific-heat for the laminar sample was complete, the sample was allowed to coarsen at room temperature for 15 d and the specific heat was remeasured. ΔC in-

TABLE I. Sample characteristics.

L (Å)	1000	3000	11 000	26 000	85 000
d_s (Å)	810	2430	8 900	21 000	69 000
d_n (Å)	190	570	2 100	4 900	16 000
l_s (Å)	300	190	550	550	420
ξ (Å)	280	230	370	370	340
T_c (K)	6.70	6.85	7.02	7.12	7.13
T_c/T_{c0}	0.932	0.955	0.976	0.991	0.993
ΔC (mJ/mol K)	37	38	37	39	41
$\Delta C/\Delta C_0$	0.85	0.88	0.85	0.90	0.95
β	1.02	1.08	1.14	1.10	1.04

creased from 37 to 42 mJ/mol K, about a 14% increase.

To make a more-detailed comparison with the Fulde-Moormann theory,[13] it is necessary to evaluate the mean free path l_s and the coherence distance ξ_s. Values of l_s were determined as follows: The upper critical field of the sample, H_{c2}, was measured. Kappa was evaluated from $\kappa = H_{c2}/\sqrt{2}\,H_c$. The resistivity ρ was determined from $\kappa = \kappa_0 + (7.53\times10^3)\rho\gamma^{1/2}$, where[19] $\kappa_0 = 0.38$, ρ is measured in Ω cm and the specific-heat coefficient γ is measured in ergs/cm^3. l_s was then determined from the anomalous-skin-effect[20] result $\rho l = 1.1\times10^{-11}$ Ω cm. Direct measurements of the resistivity lead to approximately the same result. The coherence distance was then calculated from the dirty-limit formula,[2] $\xi = (\frac{1}{3}\xi_0 l)^{1/2}$. Values of these characteristic lengths are given in Table I.

From the values of the ξ and the d_s one can calculate the Fulde-Moormann depairing parameter $\rho_c = \frac{1}{8}\pi^2(\xi^2/d_s^2)$ for substitution into the jump-in-specific-heat formula

$$\Delta C/\Delta C_0 = (1/\beta)(1 - 0.472\,\rho_c)(T_c/T_{cs}) ,$$

where

$$\beta = \frac{\langle \Delta^4(x)\rangle}{\langle \Delta^2(x)\rangle^2}$$

and $\Delta(x)$ is the spatial dependence of the order parameter.

Values of β are all about 1.1, as indicated in Table I. There is a systematic variation of β with thickness which indicates a peak near the $L = 1.1$-μm sample as shown on Fig. 5. This would seem to indicate that the order parameter is very uniform for samples with $L < 2000$ Å. This is supported by tunneling measurements on the Cd side of Pb-Cd tunnel junctions as well.[21]

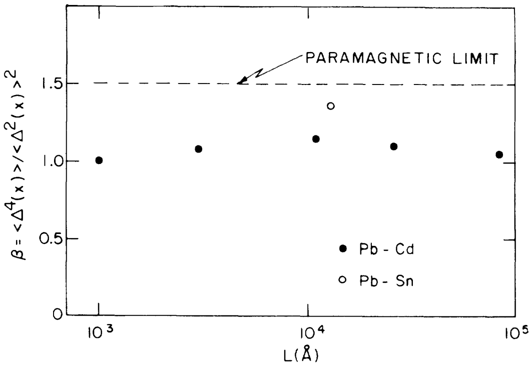

FIG. 5. Thickness dependence of the fourth moment of the order parameter as derived from the measured jump in specific heat.

IV. SUMMARY

Laminar Pb-Cd composite superconductors of very high regularity can be produced by directional solidification. The jump is specific heat at T_c for these alloys does not show the dramatic depression of ΔC which has been reported for the Pb-Sn system, but the measured ΔC values are clearly smaller than predicted for bulk alloys. The fourth moment of the order parameter calculated from the data using the Fulde-Moormann ideas shows a maximum of about $\beta = 1.15$ for laminar repeat distances of about 10 000 Å and the moment decreases for both larger and smaller thicknesses.

---

*Work performed for the U. S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

[1] P. G. de Gennes, Rev. Mod. Phys. 36, 225 (1964).

[2] G. Deutscher and P. G. de Gennes, in *Superconductivity*, edited by R. D. Parks (Dekker, New York, 1969).

[3] N. R. Werthamer, Phys. Rev. 132, 2440 (1963).

[4] P. G. de Gennes and E. Guyon, Phys. Lett. 3, 168 (1963).

[5] J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. 136, A637 (1964).

[6] J. J. Hauser and H. C. Theuerer, Phys. Lett. 14, 270 (1965).

[7] J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. 142, 118 (1966).

[8] B. W. Kington and C. J. Adkins, Philos. Mag. 13, 971 (1966).

[9] G. Deutscher, P. Lindenfeld, and R. D. McConnell, Phys. Rev. Lett. 21, 79 (1968).

[10] G. Deutscher, P. Lindenfeld, and S. Wolf, Phys. Rev. Lett. 23, 1102 (1969).

[11] C. A. Shiffman, J. F. Cochran, and M. Garber, Rev. Mod. Phys. 36, 127 (1964).

[12] J. Lechevet, J. E. Neighbor, and C. A. Shiffman, Phys. Rev. B 5, 861 (1972).

[13] P. Fulde and W. Moormann, Phys. Kondens. Mater. 6, 403 (1967).

[14] A. J. Bevolo, H. R. Shanks, and D. Eckels, Phys. Rev. B (to be published).

[15] M. Hansen, *Constitution of Binary Alloys*, 2nd ed. (McGraw-Hill, New York, 1958).

[16] E. Nembach, J. Phys. Chem. Solids 29, 1205 (1968).

[17] B. J. C. van der Hoeven, Jr. and P. H. Keesom, Phys. Rev. 137, A103 (1965).

[18] J. E. Neighbor, J. F. Cochran, and C. A. Shiffman, Phys. Rev. 155, 384 (1967).

[19] M. Strongin, A. Paskin, and D. G. Sweitzer, Phys. Rev. Lett. 12, 442 (1964).

[20] R. G. Chambers, Proc. R. Soc. Lond. 215, 481 (1952).

[21] J. Toplicar (private communications).

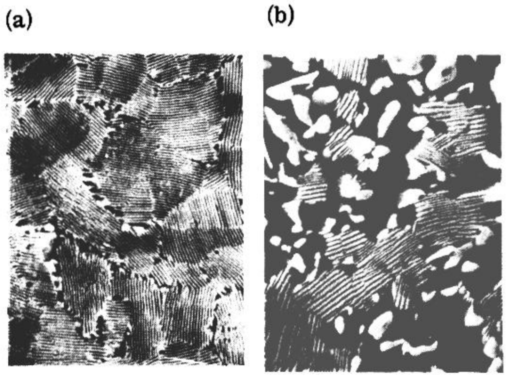

FIG. 1. (a) Scanning-electron-microscope (SEM) pictures of the Pb-Cd laminar composites taken after 2 h at room temperature. The repeat distance is 1000 Å. The dark regions are Pb rich and the light regions are Cd. The magnification is 7700×. (b) SEM picture after a sample has been allowed to coarsen at room temperature for 11 d. The magnification is 7000×.