Materials Department of General Electric Corp., Schenectady, N.Y.

[24]GE RTV 102 silicone adhesive is manufactured by the Silicone Products Department of General Electric Corp., Waterford, N.Y.

[25]K. Schwidtal, Z. Physik 158, 563 (1960).

[26]J. E. Neighbor, Rev. Sci. Instr. 37, 497 (1966).

[27]A. W. Bjerkaas, Ph.D. thesis (University of Illinois, 1971) (unpublished).

[28]S. Tolansky, *Multiple-Beam Interferometry of Surfaces and Films*, (Oxford U.P., New York, 1948), p. 147.

[29]H. E. Bennett and J. M. Bennett, in *Physics of Thin Films*, edited by G. Hass and R. E. Thun (Academic, New York, 1967), Vol. 4, p. 1.

[30]D. M. Ginsberg and M. J. Melchner, Rev. Sci. Instr. 41, 122 (1970).

[31]K. R. Lyall and J. F. Cochran, Phys. Rev. 159, 517 (1967).

[32]K. H. Bennemann, Phys. Rev. Letters 17, 438 (1966).

[33]J. Keller and R. Benda, J. Low Temp. Phys. 2, 141 (1970).

[34]E. Muller-Hartmann and J. Zittartz, Phys. Rev. Letters 26, 428 (1971).

[35]K. H. Bennemann and F. M. Mueller, Phys. Rev. 176, 546 (1968).

[36]A. Griffin, in *Superconductivity*, edited by P. R. Wallace (Gordon and Breach, New York, 1969), Vol. 2, p. 577.

[37]V. Ambegaokar and J. Woo, Phys. Rev. 139, A1818 (1965).

[38]W. Bergmann, Z. Physik 228, 25 (1969).

PHYSICAL REVIEW B VOLUME 5, NUMBER 3 1 FEBRUARY 1972

Thermodynamics of the Proximity Effect: Specific-Heat Jumps in Lamellar Lead-Tin Eutectic Alloys*

Jon Lechevet, J. E. Neighbor, and C. A. Shiffman
Department of Physics, Northeastern University, Boston, Massachusetts 02115
(Received 6 July 1971)

The specific-heat jump at the critical temperature has been determined as a function of D_S, the thickness of the superconducting layers. For thick layers, the jump decreases rapidly as D_S decreases, approaching a limit of about one-half the bulk value. A second jump in the specific heat (associated with the transition in the "normal" layers) decreases rapidly as the normal-layer thickness decreases, and extrapolates to zero for $D_N \approx \frac{1}{4}\mu$.

Fulde and Moormann[1] have emphasized that the jump in the specific heat of a superconductor at the critical temperature should be a very sensitive measure of the proximity effect, even in cases where the associated shift of T_c itself is small. This paper presents calorimetric data for lamellar Pb-Sn eutectic alloys which support that conclusion. The measurements also yield interesting results concerning an additional specific-heat jump which occurs in these alloys below T_c, associated with the tin-rich lamellas (the "normal" regions in the layered structure). A full description of the temperature dependence of the specific heat and a discussion of analytic procedures involved in the present work will be given in a subsequent paper.

Cylindrical specimens were prepared by directional solidification[2] of melts with the eutectic proportions[3] of 99.9999% pure lead and tin. Photomicrographs of cross sections exhibited the typical grain structure for lamellar alloys. In particular, the lamellas within each grain always lay parallel to the specimen axis, but otherwise the orientation of grains was apparently random. The average lamellar period λ was determined directly from the photographs, but surface conditions did not permit accurate measurements of individual lamellar widths. The widths of the lead-rich [superconducting (S)] and tin-rich [normal (N)] layers (D_S and D_N, respectively[4]) were calculated from the concentration of tin in the lead-rich domains (see below) together with the observed value of λ, using the equilibrium phase diagram[3] to establish D_S/D_N as a function of concentration. Nine samples were prepared, spanning the range $0.64 \leq \lambda \leq 5.5\ \mu$. Specific heats were measured using the continuous-warming technique and apparatus described earlier.[5]

Apart from D_S and D_N, the most important parameters required for comparisons with theory are the electron mean free paths, l_S and l_N, in the S and N layers. In general, lamellar specimens are not equilibrium structures, so l_S and l_N cannot be inferred from concentrations given by the alloy phase diagram. We derive the concentrations from measurements of the normal-state specific heat, using the assumption that the low-temperature lattice contribution to the molar specific heat of lead is not changed by addition of moderate amounts of the lower-mass tin solute. Values for the mean free paths (and also for slight shifts in the bulk transition temperature due to the dissolved tin) are calculated using known dependences on concentration.[6]

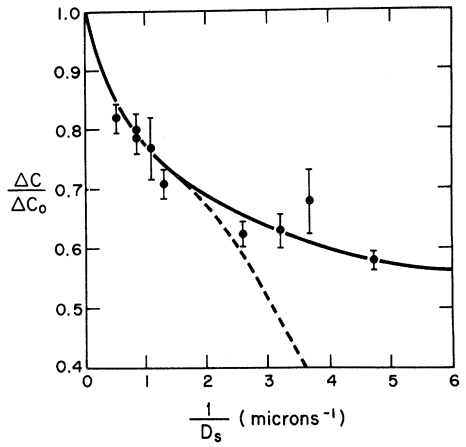

FIG. 1. Normalized jump in the specific heat at T_c, as a function of inverse thickness of the S layers. This corresponds to the superconductive transition in the lead-rich phase of the alloys. The dashed line represents the behavior of Eq. (1) of the text, while the solid line is an *ad hoc* curve chosen to represent the behavior of the data. The two curves merge below $D_S^{-1} \approx 2\ \mu^{-1}$.

We have checked this procedure by measuring the Ginzburg-Landau parameter,[7] κ, near 7 °K for specimens with large λ (i.e., in the regime of small proximity effect).

We find excellent agreement with values of κ calculated from the concentrations derived for the lead-rich lamellas.

The "thickness" and "dirtiness" criteria for the samples can be summarized by the inequalities[8]

$$0.98 \leq \xi_{0,S}/l_S \leq 2.02, \quad 0.39 \leq \xi_{0,N}/l_N \leq 0.82,$$

$$2.2 \leq D_S/2\xi_S \leq 22, \quad 1.0 \leq D_N/2\xi_N \leq 9.2,$$

where ξ_0 is the BCS coherence distance, and $\xi^2 = \frac{1}{3}\xi_0 l$.[7]

The specific-heat curve for each alloy exhibits two distinct "jumps," one at a temperature (T_c) near 7 °K, corresponding to the superconducting transition in the lead-rich phase, and the other near 4 °K, corresponding to the transition in the tin-rich phase. Instead of the sharp discontinuity characteristic of pure unstrained materials, we find a broadened jump in the specific heat in each case. For the transition at T_c, the half-width varies from 0.15 °K (for $\lambda = 5.5\ \mu$) to 0.40 °K (for $\lambda = 0.64\ \mu$). For specimens with small λ, much of the transition width can be attributed to variations of layer thicknesses within a sample. Calculations based on a Gaussian distribution of individual thicknesses, taking into account the dependence of T_c and the specific heat on D_S, give reasonable agreement with the observed broadening. For specimens with large λ, on the other hand, T_c and the specific heat are much less sensitive to variations in D_S, and the observed breadths probably cannot be explained in these terms. We have found that single-phase Pb-$Sn_{0.05}$ alloys have transition half-widths of roughly 0.05 °K, so it is perhaps not surprising that the lamellar alloys, whose lead-rich layers contain from 8 to 18 at.% tin, should exhibit half-widths of the order of 0.10 °K. This "residual" width, in specimens with large λ, may well be caused by inhomogeneous impurity concentration and to a lesser extent by strains.[9]

We define the jump at T_c, labeled ΔC, by extrapolation to the midpoint of the transition region. The calculations based on variations of D_S within a sample show that ΔC defined in this way is not very sensitive to the width or form of the distribution. For example, if D_S is allowed to vary by 10% about a mean value of 0.2 μ, ΔC will differ from the value for a sharp distribution by only 2%.

Figure 1 shows $\Delta C/\Delta C_0$ as a function of D_S^{-1}. Here, ΔC_0 is the jump at T_c expected in the absence of any proximity effect.[10] We note that for $D_S \approx 2\ \mu$, ΔC is reduced to about 80% of ΔC_0, while the depression of T_c due to the proximity effect is found to be only $\frac{1}{2}$%. This supports the general conclusion of Fulde and Moormann, although a quantitative comparison with their theory cannot be made until numerical solutions of their equations are available. An approximate calculation can be performed in the following way. The expression for the free-energy difference appropriate to the proximity effect,[11]

$$\Delta F = -\frac{N(0) f_1(\rho) \langle \Delta^4(x) \rangle}{16(\pi T)^2},$$

can be differentiated twice, yielding[1]

$$\frac{\Delta C}{\Delta C_0} = \frac{Tc}{T_{cS}} \frac{[1 - \rho_c g(\rho_c)]^2}{\beta} \frac{f_1(0)}{f_1(\rho_c)} \tag{1}$$

if the temperature dependence of ρ and β are neglected. In this expression, ρ is essentially $[D_S/2\xi_S(T)]^{-2}$, $\rho_c = \rho(T_c)$, $\langle \cdots \rangle$ indicates spatial averaging, $\beta = \langle \Delta^4(x) \rangle / \langle \Delta^2(x) \rangle^2$, f and g are functions related to the digamma function, and T_{cS} is the bulk transition temperature of the lead-rich phase. This expression will not be valid when the "pair-breaking parameter," ρ, is large; one indication of this is that the formula for $\Delta C/\Delta C_0$ clearly breaks down when $\rho_c g(\rho_c)$ approaches unity (i.e., when $D_S/2\xi_S \approx 1.5$). Errors due to the neglect of the temperature dependence of ρ and β will probably be serious for still larger $D_S/2\xi_S$. We have evaluated β using the spatial dependence of the gap function appropriate to T_c: $\Delta_S(x) \propto \cos[k_S(x - \frac{1}{2}D_S)]$.[12] The value of k_S was derived from Moormann's theory[13] (using, however, the observed values of T_c). The normalized specific-heat jump calculated in this manner is shown in Fig. 1 as a dashed curve,

which merges, for $D_S^{-1} < 2\ \mu^{-1}$, with the solid curve representing the experimental results. Considering the experimental uncertainties and the approximations in the theory, the agreement with the data is remarkably good.

We should remark that choosing the simple cosine form for $\Delta_S(x)$ ignores a central feature of Fulde and Moormann's work. They point out that for $T < T_c$, the Ginzburg-Landau equation requires that $\Delta_S(x)$ be a Jacobi function rather than a cosine. When the shift in T_c is small, as in a very thick S layer, the Jacobi function takes its limiting form as a hyperbolic tangent for all temperatures except those extremely close to T_c. $\Delta_S(x)$ is then large throughout most of the S layer, and $\Delta C \approx \Delta C_0$. Conversely, at T_c the Jacobi function takes the limiting form of a cosine, and if the change from cosine to hyperbolic tangent proceeds slowly as T is reduced, $\Delta C/\Delta C_0$ will be small. The agreement between our data and the calculation just outlined can therefore be interpreted, in the framework of the theory, as an example of this second type of behavior. Fulde and Moormann give explicit expressions for $\Delta C/\Delta C_0$ only for cases involving paramagnetic normal layers, for which $\Delta_S(x=0) = 0$ (i.e., $k_S d_S = \frac{1}{2}\pi$). It is interesting to note that they find that $C_S(T)$ exceeds $C_{S0}(T)$ for T substantially less than T_c, if the change from cosine to hyperbolic tangent is slow. We find just this behavior for all of our specimens, although $\Delta_S(x=0)$ is of the order of $0.4\Delta_S$ ($x = \frac{1}{2}D_S$).

Figure 2 shows $\Delta C'$, the specific-heat jump associated with the tin-rich lamellas,[14] normalized by the jump expected for an appropriate amount of bulk tin. These transitions are also broad, and their midpoints lie between 3.8 and 4.5 °K. $\Delta C'$ appears to extrapolate to zero at a value of D_N^{-1} in the range 3–4 μ^{-1}. This corresponds to values of λ only slightly less than the smallest we were able to achieve while maintaining regular lamellar structure. Indeed, for the specimen with $D_N^{-1} \approx 2.2\ \mu^{-1}$ the jump is already so small that the

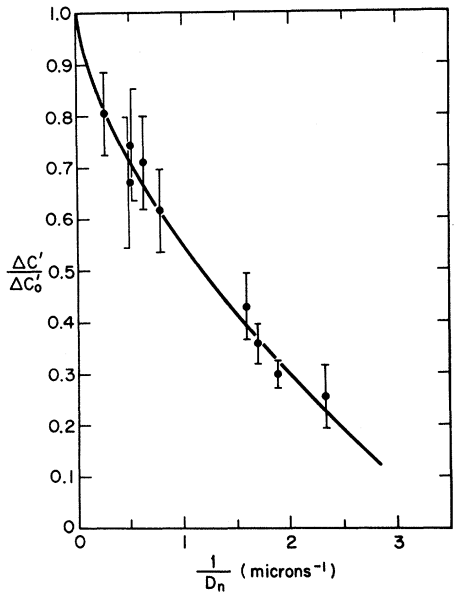

FIG. 2. Normalized jump in the specific heat *below* T_c, as a function of inverse thickness of the N layers. This corresponds to the superconductive transition in the tin-rich phase of the alloys. The solid line is an *ad hoc* curve chosen to represent the behavior of the data.

entropy-temperature curve shows essentially no evidence of a separate transition associated with the tin-rich lamellas. A comparison of Figs. 1 and 2 suggests that in these alloys the jump at T_c becomes independent of λ roughly when $\Delta C'$ goes to zero, and that no dramatic changes will occur at smaller λ. Since in these alloys D_S/D_N is roughly constant, the over-all behavior at small λ is reminiscent of the Cooper limit,[15] in which the effective interaction strength depends on D_S and D_N only through their ratio. However, $k_S D_S \approx 1$ for these specimens, so they certainly fail to satisfy the criteria for the Cooper limit in the ordinary sense.

---

*Work supported by the U. S. Atomic Energy Commission [AEC Contract No. AT(30-1)-3972].

[1]P. Fulde and W. Moormann, Physik Kondensierten Materie 6, 403 (1967).

[2]G. A. Chadwick, Progr. Mater. Sci. 12, 99 (1963).

[3]M. Hansen, *Constitution of Binary Alloys*, 2nd ed. (McGraw-Hill, New York, 1958), p. 1106.

[4]The lead-rich layers are regarded as the "superconductive" component (S) and the tin-rich layers as the "normal" component (N). In our notation, $D_S + D_N = \lambda$.

[5]J. F. Cochran, C. A. Shiffman, and J. E. Neighbor, Rev. Sci. Instr. 37, 499 (1966).

[6]See, e.g., E. Nembach, J. Phys. Chem. Solids 29, 1205 (1968); also B. N. Aleksandrov, Zh. Eksperim. i Teor. Fiz. 43, 399 (1962) [Sov. Phys. JETP 16, 286 (1963)].

[7]P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966), pp. 220–227.

[8]The occurrence of $\frac{1}{2}D_S$ (rather than D_S) is a consequence of the periodic structure. See O. S. Lutes and D. A. Clayton, Phys. Rev. 145, 218 (1966).

[9]Unpublished measurements by J. F. Cochran and C. A. Shiffman show that strain effects are very small. By measuring the shift in transition temperature of thin foils of $Sn\text{-}Pb_{0.02}$ encapsulated in various Epoxy resins, they show that the tin-rich lamellas cannot support the forces required to induce shifts of more than a few tens of millidegrees in the critical temperature of the lead-rich lamellas.

[10]ΔC_0 takes into account the variations of D_S/D_N from one sample to another connected with variations in the composition of the S and N layers. However, there were

no corrections for possible changes in the molar specific-heat jump of the bulk lead-rich phase due to the varying tin concentrations. Direct measurements on a number of quenched single-phase alloys indicate that such corrections would amount to less than 5% in the present study. (A precise determination was precluded by unavoidable precipitation of excess tin from the more concentrated alloys.)

[11]P. Fulde and K. Maki, Physik Kondensierten Materie 5, 380 (1966).

[12]See, e.g., Ref. 1. We have verified that the contribution to β from $\Delta_N(x)$ at T_c is negligible.

[13]W. Moormann, Z. Physik 197, 136 (1966). The measured values of T_c agree with Moormann's theory for all but the smallest D_S.

[14]The use of the word "jump" for $\Delta C'$ requires some comment for the samples with the thinnest lamellas. Although the "tin transition" is clearly discernible, the specific-heat curve is monotone below T_c, and the "jump," $\Delta C'$, only appears upon extrapolation to the midpoint of the transition region.

[15]See, e.g., P. G. de Gennes, Rev. Mod. Phys. 36, 225 (1964). The transition temperature in these alloys also seems to be approaching a constant value for specimens with the smallest values of λ. [Jon Lechevet, thesis, (Northeastern University, 1971) (unpublished).] Our calculations show, however, that the temperature which should be labeled "T_c" is rather sensitive to details of the thickness variations in a specimen.

PHYSICAL REVIEW B VOLUME 5, NUMBER 3 1 FEBRUARY 1972

Fluctuation Effects on the Superconducting Transition of Tin Whisker Crystals*

R. S. Newbower, M. R. Beasley, and M. Tinkham
Division of Engineering and Applied Physics, Harvard University, Cambridge, Massachusetts 02138
(Received 21 June 1971)

We report the results of measurements of the resistive transitions of clean one-dimensional superconductors (pure tin whiskers) at currents of $\sim 10^{-7}$ A. Comparison with the McCumber-Halperin theory, including consideration of the current-dependent terms necessary at these current levels, yields good agreement with no adjustment of the attempt frequency. We conjecture, however, that precise conclusions concerning the magnitude of the attempt frequency cannot yet be drawn. Rather, we present arguments which suggest that a meaningful fit to the data in the top portion of the transition must await an improved theory, and that adjustments of the attempt frequency such as those used by Lukens, Warburton, and Webb (in fitting lower-current data) may not be meaningful.

In the last few years fluctuations in one-dimensional superconductors have been studied with a variety of techniques.[1-4] Recently very sensitive measurements of the resistive transition in tin whisker crystals were obtained by Lukens, Warburton, and Webb[5] (LWW) using superconducting instrumentation. The shape of the observed transition lent strong support to the McCumber-Halperin[6] modification of the Langer-Ambegaokar[7] theory of such fluctuation effects (LA-MH). The LA-MH theory predicts resistance-producing thermally activated phase-slippage events in such samples, with an energy barrier approximately equal to $A\xi(T)H_c^2(T)/8\pi$, where A is the cross-sectional area of the sample, $\xi(T)$ is the Ginzburg-Landau coherence length, and $H_c(T)$ is the thermodynamic critical field. The predicted attempt frequency is approximately $[L/\xi(T)]\tau^{-1}$, where L is the length of the sample and τ is the relaxation time of the time-dependent Ginzburg-Landau equation. One may visualize fluctuations occurring in $L/\xi(T)$ independent systems, each $\xi(T)$ in length.

A conclusion presented by LWW is that their data from tin samples can be fit best with an adjustment of the attempt frequency by a factor ranging from 1 to 100, with the cleaner samples requiring the greater adjustments. Their data were taken at currents $I \lesssim I_1 \cong 2.5\times10^{-8}$ A, where I_1 is a characteristic current of the theory, defined below.

We report here the results of a similar study taken at somewhat higher currents ($\sim 10^{-7}$ A). Our data, like those of LWW, support the LA-MH theory. Since the higher currents at which the present data were taken exceed the characteristic current I_1, the resistance is nonlinear. This made it necessary to take account of the full current dependence of the LA-MH theory and also to treat carefully the addition of the parallel conductance of the normal and superconducting electrons. We found that no adjustment of the attempt frequency was required to fit the 10^{-7}-A data. We conjecture, however, that precise conclusions concerning the magnitude of the attempt frequency cannot yet be drawn. Rather, we present arguments which suggest that a meaningful fit to data in the top portion of the transition must await an improved theory, perhaps one based on departures from the normal state, as is that of Tucker and Halperin.[8]

Our data were taken with a specially constructed