proportional to $(bT_s)^2$, normalized at $I[H = 4$ kG, $(T/T_c) = 0.4]$. [At this temperature Eq. (2) holds for $0 \leqslant H \leqslant 4$kG.] It appears that Eq. (12), and hence Eq. (11), is reasonably well obeyed even for H considerably less than H_{c2}, as also concluded by Dubeck *et al.*[15] from an analysis of their high-field thermal conductivity measurements on In–3 at. % Bi.

ACKNOWLEDGMENTS

I wish to thank D. M. Sellman and H. Nadler for specimen preparation, C. G. Rhodes and P. C. Romo for micrographic and x-ray examinations, and K. Medeiros for computer programming. Valuable discussions with T. G. Berlincourt and H. B. Levine are acknowledged. This research was supported by the U. S. Atomic Energy Commission.

Discussion 17

MENDELSSOHN: Have you obtained a magnetization curve of your specimen?

HAKE: No, I haven't measured the magnetization.

MENDELSSOHN: What would you then consider to be the naive application of what you call the filamentary dislocation model?

HAKE: Well, I would suspect the naive application of the high-field filamentary-mesh model would tell that there is a great deal of flux trapped after cycling the field to 4 kG, and I would have expected this to have influenced the specific heat. Actually, field cycling had very little effect on the specific heat. [See Fig. 1, p. 125, this issue, and alsoK. Mendelssohn, Proc. Roy. Soc. (London) **A152**, 34 (1935).]

GORTER: In one of your earlier curves, the specific heat was measured in a field of 500 Oe and then between 0 and a 1000. In these fields, the specific heat would be the same as in zero field. Also, I didn't quite get your interpretation of the entropies. Is it your idea that in the mixed state there is a large entropy contribution from the normal part which is proportional to temperature?

HAKE: In answer to the first question, my interpretation was that in a field of 500 G the material should have been in the mixed state. I calculated a lower critical field of about 200 G so I think 500 G puts the specimen into the mixed state so that the specific heat is larger than that in zero field. In regard to the second question, I don't regard any part of the specimen as being normal in the mixed state, although this is always a possibility. I think it is reasonable to suppose that the energy gap, although everywhere finite, has been depressed somewhat (on the average) in the mixed state, and some of the order characteristic of the zero-field superconducting state no longer remains. As the field is increased there is a gradual increase of the entropy until the normal-state entropy is reached at the upper critical field.

GORTER: I got the impression from your curves that perhaps the process of heating up was not reversible, which might have a considerable influence on the derived entropy and apparent specific-heat curves. If there are irreversible processes when the sample is heating up, the specific heat which you measure is smaller than it should be.

HAKE: I don't think the present data indicate any significant irreversible processes. I cooled the specimen down in zero field and then started to apply the field. I took data at various fields up to 4 kG; then I took specific-heat data at various fields between 4 and 0 kG. There was no sign of any significant irreversibility.

Specific Heat Measurements and Proximity Effects in Tin–Lead Eutectic Alloys*

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I. INTRODUCTION

Recent experiments[1] indicate that superposed films of normal and superconducting metals display "proximity effects," that is, effects where the superconducting properties of one or both of the films are altered by contact with the other. This behavior has been explained[2] qualitatively in terms of the large coherence distance of the superconducting wave function which allows appreciable overlap of pairs into the normal region. An averaging of the electron–phonon interaction over both regions occurs which

* Research supported in part by the Advanced Research Projects Agency under Contract SD-90.

[1] P. Hilsch, Z. Physik **167**, 511 (1962), a historical survey and extensive bibliography is included in this reference.

[2] R. H. Parmenter, Phys. Rev. **118**, 1173 (1960); L. N. Cooper, Phys. Rev. Letters **6**, 689 (1961); D. H. Douglass, Jr., *ibid.* **9**, 155 (1962); P. G. DeGennes and E. Guyon, Phys. Letters **3**, 168 (1963).

alters the transition temperature. Some doubt has been cast on the interpretation of the evaporated film experiments by the work of Rose–Innes and Serin,[3] and recently by Van Gurp.[4] These authors show that diffusion and alloying effects can be very important factors in the behavior of superimposed evaporated films. In order to avoid these difficulties we have taken advantage of the layered two-phase structure which occurs in eutectic alloys. The object of the experiment is to compare the heat capacity of a suitable eutectic with the sum of the heat capacities of its parts measured in bulk form. We have chosen the lead–tin eutectic, commonly known as "soft-solder," and have made specific heat measurements on samples with compositions corresponding to various parts of the metallurgical phase diagram, as well as on a specimen with the eutectic composition. Figure 1 illustrates the laminar structure of this alloy. This is one of several microphotographs taken at various points on the surface of the specimen, which was a cylinder about $\frac{1}{2}$ in. in diameter by $3\frac{1}{2}$ in. long, solidified in vacuum in a traveling zone furnace. All the lamellas were found to run parallel to the rod

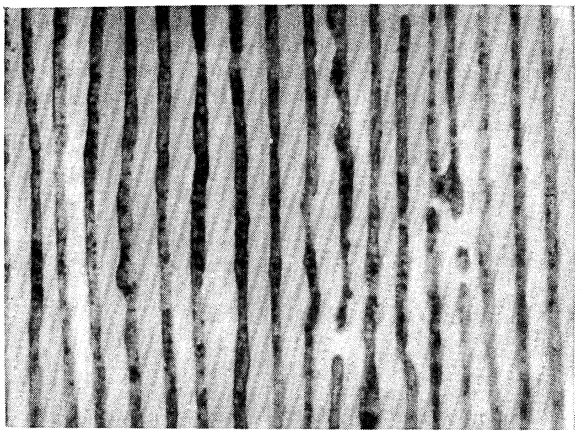


FIG. 1. Photomicrograph of the surface of the eutectic specimen. (Eutectic No. 3 about 2 months after solidification.) The light lamellas are the tin-rich phase. On the average these are 1.8 μ thick.

axis and were quite uniformly spaced. The lamellas were not all parallel to a common plane, but were grouped in large colonies whose orientations were more or less random. The area shown in the photograph represents a small fraction of a colony. The dark regions are the lead-rich lamellas and these are about 0.75μ thick on the average, with a variation of 25% or so over the sample. It is noted that there is considerable precipitate within these lamellas. This is probably an excess of the tin-rich phase which comes out of the solid solution on cooling as a result of the strong temperature dependence of the solid solubility limit. It is interesting that this precipitation seemed to be incomplete even a month after solidification. The measurements of the specific heat were made 2 months after solidification but there is clearly no guarantee that the lead-rich lamellas had reached their low-temperature equilibrium concentration even then. The light regions in the photo are the tin-rich phase. These are about 1.8μ ± 25% thick, averaged over the specimen. Both lamellas thicknesses are substantially larger than ξ_0, the coherence distance in either pure lead or pure tin, which are 0.083μ and 0.23μ, respectively.[5] In addition, the lamellas are not pure, but contain roughly 2% tin on the one hand and 1% lead on the other. We therefore expect the coherence distances to be smaller in the alloys than in the pure metals. The mean free paths l, can be estimated from the resistivity data of Lynton *et al.*[6] and of Livingston,[7] using Chambers' data[8] for l in terms of resistivity. We get $l = 0.1\mu$ for the lead-rich regions and $l = 0.33\mu$ in the tin-rich lamellas. Applying the Pippard[9] relation for ξ, the coherence distance in the alloy,

$$1/\xi = 1/\xi_0 + 1/l$$

we find $\xi(\mathrm{Pb}') = 0.05\mu$ and $l(\mathrm{Sn}') = 0.14\mu$. (The designations Pb′ and Sn′ refer to the alloys in the lamellas.) The various dimensions involved in our measurements are summarized in Table I.

TABLE I. Comparison of laminar dimensions with mean free paths and coherence distances.[a]

domain	l	ξ	d	d/ξ	d/l
Lead-rich lamellas	0.1	0.05	0.75	15	7.5
Tin-rich lamellas	0.33	0.14	1.80	13	5.4

[a] l = mean free path; ξ = coherence length, d = domain width (all dimensions are in microns).

[3] A. C. Rose-Innes and B. Serin, Phys. Rev. Letters **7**, 278 (1961).
[4] G. J. Van Gurp, Phys. Letters **5**, 303 (1963).
[5] Tabulated by Bardeen and Schrieffer in *Progress in Low Temperature Physics* (North Holland Publishing Company, Amsterdam, 1961), Vol. 3, p. 243.
[6] E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957).
[7] J. D. Livingston, Phys. Rev. **129**, 1943 (1963).
[8] R. G. Chambers, Proc. Roy. Soc. (London) **A215**, 481 (1952).
[9] A. B. Pippard, Physica **19**, 765 (1953).

It turns out that the domain thicknesses are in the inverse ratio as are the coherence lengths, so that both types of lamellas are about 14 times thicker than their respective coherence lengths.

II. RESULTS AND DISCUSSION

The specific heat of the specimen just described was measured from 1.8° to 8°K in zero field giving C_s, and in a field of 1450 G, giving C_n. The measured specific heat is overwhelmingly dominated by the lattice contribution. Therefore we show in Fig. 2 the difference $\Delta C = (C_n - C_s)$ rather than C vs T. The observed behavior is shown by the curve with the circled points. It was obtained by fitting high-order polynomials to the specific heat data by the method of least squares and subtracting C_s from C_n analytically. On the same figure, we have included the specific heat difference calculated on the assumption that the tin-rich and lead-rich lamellas are completely independent of each other. This curve is simply the linear combination of ΔC for lead with ΔC for tin in the proportions which are determined by the metallurgical phase diagram. The disagreement between various measurements of the phase diagram constants causes an uncertainty of several percent in the values of the proportions of the phases in the eutectic. We have used the proportions 0.597 tin-rich phase to 0.403 lead-rich phase which we determined from earlier specific heat measurements on this alloy system.[10] The specific heat differences for the separate lamellas were calculated from the critical field curves of pure lead and tin after demonstrating that the specific heats of bulk tin-rich and lead-rich single phase alloys at their solubility limits are essentially the same as those of the pure materials.

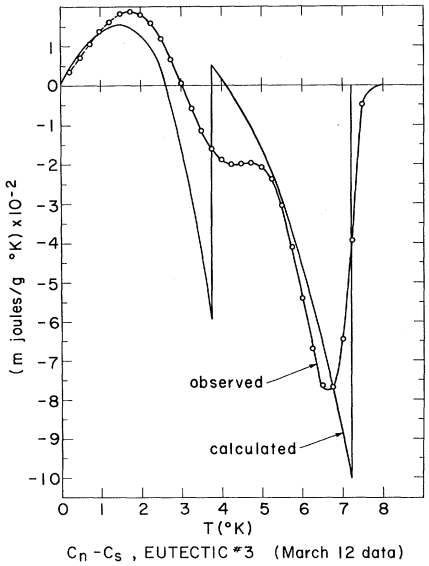


FIG. 2. The difference between the normal and superconducting state specific heats vs temperature. Circled points represent measured values. The solid curve represents the behavior of the alloy calculated on the assumption that the lamellas are independent of each other.

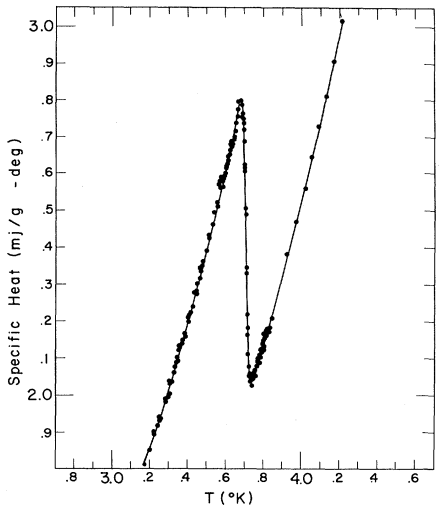


FIG. 3. The specific heat of a tin plus 2% lead alloy in zero field near its transition temperature.

The two almost discontinuous drops in the calculated ΔC curve represent the usual specific heat jump at the transition temperature. From the observed behavior it is clear that the eutectic undergoes a reasonable facsimile of the lead transition near 7.2°K, although the observed transition is broader than was expected from the behavior of the bulk lead-rich phase. A lead plus 5% tin alloy had a transition width of only 0.1°K compared to the value 0.8°K observed here. Near 5°K the observed ΔC departs from the calculated curve and this departure persists down to the lowest temperatures in our range of measurement. This effect is much larger than any error in the experimental procedure. We have examined several tin-rich alloys with up to 2.8% lead and it is quite clear that no effect of this magnitude exists in the single phase alloys. The specific heat of a 2% lead–in–tin specimen is shown in Fig. 3 as an example of an alloy corresponding to the tin-rich lamellas. The transition width is only 0.02°K and the specific heat jump is equal to the jump in pure tin. The scatter in the data in Fig. 3 is also typical of the eutectic results.

[10] C. A. Shiffman, M. Garber, J. F. Cochran, E. Maxwell, and G. W. Pearsall, Bull. Am. Phys. Soc. 8, 66 (1963).

The specific heat differences shown in Fig. 2 have been integrated to yield the entropy differences. $\Delta S = S_n - S_s$ represents the degree of superconductive ordering (Fig. 4). Again, the solid curve represents the calculated values and the curve with the

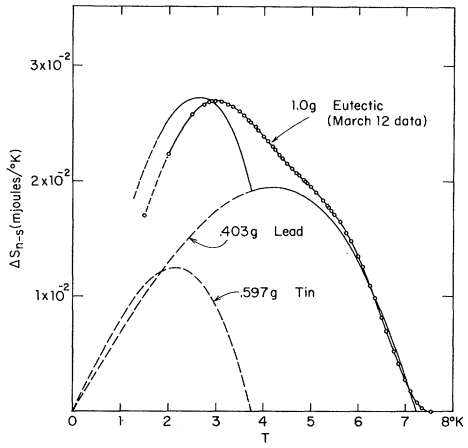


FIG. 4. The entropy difference $\Delta S = S_n - S_s$ vs temperature for the eutectic (circled points) and for the sum of its parts taken independently (solid curve).

circled points represents the observed behavior. It is interesting to note that above 6°K the eutectic entropy difference is virtually equal to the calculated value despite the observed broadening of the specific heat transition. Below 6°K there is a progressive departure from the simple calculation, which becomes largest at about 3.8°K, diminishing to zero and changing sign at just under 3°K. This is a large effect. At 3.8°K the difference between the observed and calculated curves is one-half the maximum ΔS which would be found in the tin lamellas in the absence of a proximity effect.

III. DISCUSSION

We conclude from this analysis that there is a genuine proximity effect in the eutectic alloy. At first sight it would appear that the lead-rich lamellas are unaffected by the tin-rich regions, while the tin lamellas have their transition temperature shifted upwards by the presence of lead neighbors. Of course, we know only that there is an excess of ordering from 3° to 5.5°K in the alloy over what would be found if the entropies of the lamellas were simply additive, but this cannot be localized in one set of domains or the other by a specific heat measurement. It should be borne in mind that there are two basic differences between this experiment and most of the evaporated film measurements which have shown proximity effects. First, we deal with an effect between two superconductors, rather than with one normal metal and one superconductor. (If one takes the point of view of de Gennes and Guyon,[11] however, this difference is a difference in degree rather than in kind.) Secondly, in our case both metals have mean free paths and coherence lengths which are much smaller than the thicknesses of the layers, while in the evaporated film experiments the reverse has usually been true. Referring to the last two columns Table I, one would expect no proximity effect at all between domains which are so large compared with l and ξ. On the other hand, it is interesting to note that the only two dimensions which are comparable are the thickness of the lead lamellas and the mean free path in the tin lamellas. This suggests that as the temperature is lowered the effective thickness of the lead region is gradually increased by one "tin mean free path." This picture is consistent with the hypothesis that the lead pairs which cross the boundary have wave functions which are governed by the coherence length or mean free path appropriate to the tin region and that the proximity effect occurs only in the immediate neighborhood of the boundary between the two regions in alloys of this type.

We are indebted to Professor E. Maxwell for suggesting this problem to us and for many stimulating and helpful discussions.

[11] See Ref. 2.

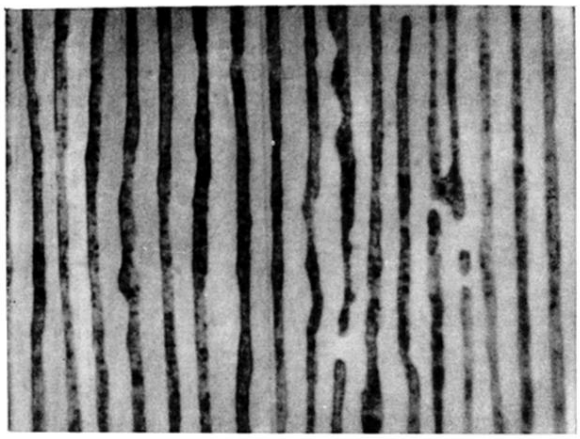
Discussion 18

PIPPARD: It seems to me possible that the lamellae are in a state of considerable shear because the thermal contraction of the materials is quite different. There is an old result showing that, when you put tin into shear by sticking it with durafix to a glass sheet, you can raise the transition temperature strongly. I wonder in fact whether this gives an explanation of the high transition temperature of the tin layers.

C. A. SHIFFMAN, *Massachusetts Institute of Technology:* This is possible, but I don't know why it doesn't happen equally well to the lead, for one is squeezing the other.

PIPPARD: Lead is cubic and tin is not—lead is probably much less sensitive to shear than tin.

SHIFFMAN: Minnigerode has shown that massive nonhomogeneous plastic deformation at low temperatures produces shifts in the (resistive) transition of at most 0.2° or 0.3°K.



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