Fluctuation Heat Capacity in Superconducting Thin Films of Amorphous BiSb*

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(Received 20 September 1971)

With a resolution of 10^{-10} J/°K the fluctuation heat capacity has been observed near T_c in thin films of $Bi_{0.4}Sb_{0.6}$. No indication of peaking was seen in the heat capacity near T_c. The heat-capacity transition when compared with the corrected resistivity transition is found to have approximately twice the width. This width is 3 times that predicted by Ferrell.

For a pure bulk superconductor near T_c the broadening of the heat-capacity jump due to thermodynamic fluctuations is less than 10^{-12} °K.[1] Such temperature resolution is experimentally impossible at the present time. However, in dirty superconductors in which the film thickness and a shortened coherence length have reduced the volume of a fluctuation, fluctuation phenomena can be experimentally observed. Paraconductivity near T_c was first noted by Glover[2] and measurements of it have now reached such a state of precision that depairing effects above T_c, first suggested by Maki,[3] can be studied.[4] The Aslamazov and Larkin theory (AL)[5] as interpreted by Ferrell[6] predicts for $T > T_c$ that the excess electrical conductivity σ' and the excess heat capacity C' in films where $\xi \gg d$ $[\xi = 0.86(l\xi_0)^{1/2}]$ are

$$\sigma'/\sigma = (1.85/k_F{}^2L)\epsilon^{-1}, \quad (1)$$

$$C'/\Delta C = (1.28/k_F{}^2L)\epsilon^{-1}, \quad (2)$$

where σ_n is the normal-state conductivity, k_F is the Fermi momentum, L is the film thickness, l is the electronic mean free path, ΔC is the classical jump in heat capacity, and ϵ is the reduced temperature $(T - T_c)/T_c$. Equation (2) predicts that the heat capacity due to fluctuations can rise above ΔC. Masker, Marčelja, and Parks[7] have predicted such a peaking of the heat capacity where the characteristic width of the peak is the same order of magnitude as the depression in T_c due to fluctuations. The quantity in parentheses will be called ϵ_{0R} for Eq. (1) and ϵ_{0C} for Eq. (2). One can calculate ϵ_{0R} from the resistance per square in the normal state: $\epsilon_{0R} = 1.52\times 10^{-5}R_\square{}^n$.

The major obstacle in making heat-capacity measurements of thin films is the small volume of the samples. In contrast to bulk measurements on several hundred grams of metal, high-resolution measurements must be performed on less than 1 mg of metal. The ac heat-capacity technique[8] is capable of such resolution if the background heat capacity is also small. In Fig. 1 an exploded view of the mount is shown. A total heat capacity of about 1 erg/°K is shared by a 1-mg germanium thermometer, a 2–5-μm thick Pyrex window, and the superconducting films. A heater drives temperature oscillation in the film at an angular frequency ω for which $\omega\tau \gg 1$, where τ is the thermal relaxation time of the experiment through the edge of the Pyrex window. The amplitude of the temperature oscillations is proportional to the inverse of the heat capacity of the combined system.

Powdered $Bi_{0.4}Sb_{0.6}$ was flash evaporated *in situ* on the Pyrex window. Superfluid helium at low pressure behind the window prevented it from heating up. $Bi_{0.4}Sb_{0.6}$ was chosen because it condenses in the amorphous state, producing an effective electronic mean free path of 0.8 Å.[8] It is stable against crystallization up to 100°K,[9] and it has a low transition temperature of approximately 2°K, thereby reducing the nonelectronic heat capacity compared to pure Bi. After the film was produced the helium was pumped away, thermally isolating the window. The most serious source of long-term drift of heat capacity was the varying submonolayer of helium atoms

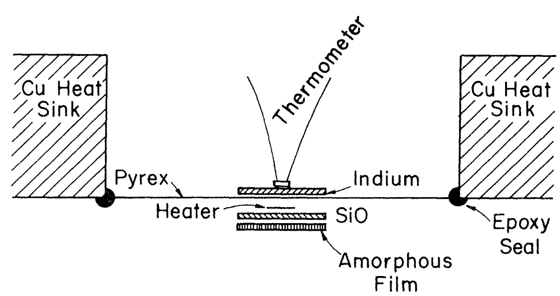

FIG. 1. Mount for measuring thin-film heat capacity. A 1-mg germanium thermometer measures the temperature of the system through a 3000-Å-thick indium dot. The Pyrex window is 2–5 μm thick. During evaporation of the amorphous film of $Bi_{0.4}Sb_{0.6}$, liquid helium at low pressure fills the space behind the window.

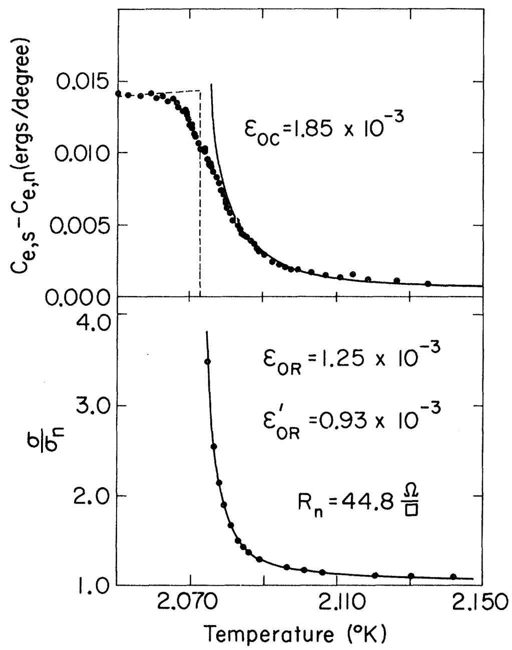

FIG. 2. The change in heat capacity and conductivity near T_c of a 1350-Å film of amorphous $Bi_{0.37}Sb_{0.63}$. Note the absence of a peak at T_c in the heat capacity for this dirty superconductor ($l_{eff}=1.0$ Å). The dashed line is predicted by mean field theory alone. The characteristic width, assuming an inverse temperature dependence, is ϵ_0.

remaining on the back of the Pyrex window.

The increase in heat capacity and conductivity, shown in Fig. 2 for a 1350-Å film of 63% Sb, is consistent with the ϵ^{-1} dependence predicted by AL. There is no peak observed in the heat capacity at T_c. Such a fit gives the same transition temperature to within 2 mdeg; $C_{e,s}-C_{e,n}=C_{tot}-C_{background}$, where $C_{background}$ was determined by a four-point fit above and below the transition such that $C_{es}-C_{en}$ went to zero for $T>T_c$ and followed mean-field theory for $T<T_c$. The points for this fit were at 2.050, 2.1031, 2.1185, and 2.1350°K. Another background subtraction can "sharpen" the heat-capacity transition approximately 50% only by destroying any power-law dependence of $C_{es}-C_{en}$ and causing it to go abruptly to zero at 2.10°K. Also, by choosing the appropriate background, one can create a peak in $C_{es}-C_{en}$ between 2.07 and 2.035°K rising approximately 10% of the total heat-capacity jump, but only at the cost of $C_{es}-C_{en}$ dropping nonphysically through zero 0.1°K below T_c. The 800- and 150-Å films were analyzed in the same manner. The normal-state resistance R_N was not used as an adjustable parameter for the 1350- and

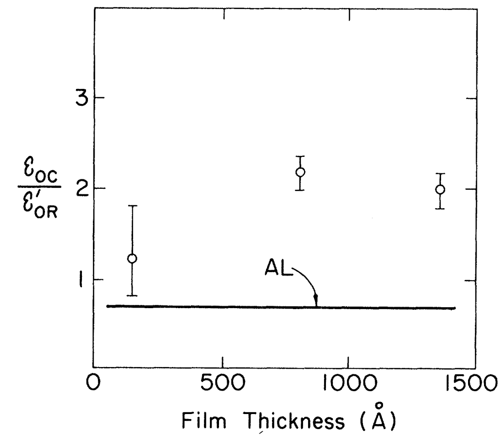

FIG. 3. Comparison of the ratio of heat-capacity transition width to resistive transition width with the AL value of 0.69. Three film thicknesses are shown and described in Table I.

150-Å film, but was adjusted for the 800-Å film because of the low quality of the resistance measurements for this film. Although pure amorphous Sb is semiconducting, the normal-state resistance of amorphous $Bi_{0.4}Sb_{0.6}$ is well behaved, decreasing less than 20% up to 100°K.[9] We have measured R_N between 0.7 and 1.0°K above T_c in our films.

ϵ_{0R} and ϵ_{0C} characterize the width of the transitions. To compare ϵ_{0R} with ϵ_{0C}, the contribution of the Maki term to ϵ_{0R} must be removed.[10] The depairing parameter δ is not known for $Bi_{0.4}Sb_{0.6}$, but a reasonable choice consistent with other materials is $\delta=0.005+(5\times10^{-4}R_\square{}^n)$.[11] Applying Maki correction to ϵ_{0R} we obtain ϵ_{0R}'. Both ϵ_{0R}' and ϵ_{0C} could also be corrected for thick-film effects; however their ratio should not be directly affected, and can therefore be compared directly with the AL theory. From Eqs. (1) and (2) we obtain

$$(\epsilon_{0C}/\epsilon_{0R})_{AL}=0.69. \tag{3}$$

By use of this analysis, the measurements produce an average ratio of 2 as shown in Fig. 3 for three film thicknesses. 150 Å was the thinnest film we could study. The resolution achieved in this measurement corresponds to the heat capacity of less than one monolayer of metal atoms at 2°K. Table I lists all the experimental parameters.

Without any corrections to the resistive transition, the widths of the heat-capacity transition and corresponding resistive transition are close enough to be called the same. Although heat capacity is an equilibrium property we must de-

TABLE I. Experimental parameters for the amorphous film of $Bi_{1-x}Sb_x$.

d [a] (Å)	χ	$R_\square^n$ (Ω)	T_c (°K)	ΔC_{expt} [b] (erg/deg)	ϵ_{0C} (10^{-3})	ϵ_{0R} (10^{-3})	ϵ_{0R}' [c] (10^{-3})	$\epsilon_{0C}/\epsilon_{0R}'$ [d]
1350	0.63	44.8±0.2	2.075	0.0143± 5%	1.85±10%	1.25±10%	0.93±10%	1.99±15%
800	0.60	55.1	2.298	0.011 ± 5%	1.5 ±10%	1.3 ±10%	0.70±10%	2.14±15%
150	0.60	260.0±0.2	2.100	0.0015±15%	5.0 ±10%	7.7 ±10%	4.2 ±10%	1.19±50%

[a] Film thickness measured by using an optical-interference technique after warmup.

[b] Values are within 10% of mean-field-theory calculation using free-electron model and assuming Sb does not contribute any electrons to $N(0)$. Pure amorphous Sb films are semiconducting and are practically insulators at low temperatures.

[c] Maki contribution is removed. ϵ_{0R}' cannot be compared directly with AL theory until the finite thickness compared to ξ is considered. A reasonable choice of ξ (≈ 80 Å) produces agreement.

[d] AL theory predicts this quantity to be 0.69.

termine in future measurements if the normal-state resistivity alone is enough to determine the width of the heat-capacity transition. Perhaps depairing can also alter the heat capacity. The absence of a peak in the heat capacity of the magnitude predicted[7] is quite insensitive to our analysis. Gunther and Gruenberg[12] have suggested that

$$C'/\Delta C = [1 + (k_F{}^2 Ll)\epsilon]^{-1}, \quad (4)$$

which is much closer to our experimental results. The nondivergence of Eq. (4) is due to a "saturation" of the order-parameter fluctuations near T_c. This is a natural result of the Hartree approximation used to derive Eq. (4).

In conclusion, there is no indication of a peak in the heat capacity at T_c in these dirty superconducting films. A superconducting film in which $l_{eff} \geq L$ has yet to be studied. The fluctuation heat capacity is much like the fluctuation conductivity above T_c but with twice the width, in disagreement with Eq. (3). The experimental techniques developed for these measurements can be improved by a factor of 10, and have general application for many other thin-film experiments and two-dimensional thermodynamical investigations.

We would like to thank Professor R. A. Ferrell for early encouragement to do these measurements. One of us (J.M.) wishes to thank Professor R. Parks and Dr. S. Marčelja for a fruitful discussion.

*Work supported in part by the Advanced Research Projects Agency under Contract No. HC 15-67-C-0221.

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