PHYSICAL REVIEW B VOLUME 14, NUMBER 5 1 SEPTEMBER 1976

# Density of liquid $^4$He at freezing and entropy of solid $^4$He at low temperatures*

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(Received 8 January 1976)

The density of liquid $^4$He has been measured along the melting curve in the temperature range 0.1–0.82 K by observing the change with temperature of the resonant frequency of a superconducting microwave cavity immersed in the liquid. Relative changes in density as small as $4 \times 10^{-9}$ could be resolved. From the results the entropy of solid $^4$He was obtained by using the Clausius-Clapeyron equation in conjunction with values for the isobaric-thermal-expansion coefficient and entropy of the liquid calculated from other data. No evidence for an anomalous linear temperature term in the entropy of the solid was found. The data are shown to be in good agreement with published measurements of the Debye temperature of the solid by Gardner, Hoffer, and Phillips.

## I. INTRODUCTION

In this paper we report on an investigation of the entropy of solid $^4$He in the temperature range 0.1–0.82 K. Several studies of the entropy in this temperature range have been made previously.[1-6] An important problem that has remained unresolved is the limiting form of the specific heat at low temperatures. There have been a number of reports[2,4,6] of an anomalous linear term in the specific heat in addition to the expected $T^3$ contribution from phonons. Heltemes and Swenson[2] made measurements down to 0.3 K and obtained results which were consistent with a linear term of magnitude between $5\times10^{-3}$ and $10\times10^{-3}$ J mole$^{-1}$ K$^{-2}$ at low pressures. Franck[7] carried out similar experiments in the temperature range 1.3–4 K, and found a linear term of the same order of magnitude. However, he found that the size of the linear term could be considerably reduced by annealing. Thus this result suggested that the linear term was related to defects. More recent measurements have been made by Edwards and Pandorf[3] down to 0.3 K, by Ahlers[8] to 1.4 K, by Sample and Swenson[4] to 0.2 K, and by Gardner, Hoffer, and Phillips[5] to 0.3 K. In these experiments no linear term was observed, except by Sample and Swenson who observed a very small term that could possibly be attributed to an apparatus effect. The most recent measurements are by Castles and Adams.[6] They reported measurements down to about 0.14 K and found a linear term of the same order of magnitude as that found by Franck. They discussed a number of possible origins of this term, but also emphasized that more accurate measurements were necessary to prove that the linear term definitely existed.

The experiments we have carried out were designed to look for such a term. Traditional specific-heat experiments have the disadvantage that the calorimeter heat capacity $C_{\text{cal}}$ must be subtracted from the total measured heat capacity. $C_{\text{cal}}$ usually contains a large linear term, which must therefore be known accurately so that a spurious linear term does not appear in the final result. To avoid this difficulty we have measured instead the temperature dependence of the density of the liquid along the melting curve. The Clausius-Clapeyron equation is

$$\frac{dP_m}{dT} = \frac{S_L - S_S}{V_L - V_S}, \tag{1}$$

where $P_m$ is the melting pressure, $S_L$ and $S_S$ are the entropy per mole of liquid and solid, and $V_L$ and $V_S$ are the corresponding molar volumes. The density of the liquid is a function of temperature and pressure, so

$$\frac{1}{\rho}\frac{d\rho}{dT} = -\alpha + \kappa\frac{dP}{dT}, \tag{2}$$

where $\alpha$ is the isobaric thermal expansion and $\kappa$ is the isothermal compressibility of the liquid. Thus the temperature dependence of the liquid density along the melting curve is given by

$$\frac{1}{\rho}\frac{d\rho}{dT} = -\alpha + \kappa\frac{S_L - S_S}{V_L - V_S}. \tag{3}$$

At low temperatures where rotons are unimportant one expects that, to lowest order in $T$, $\alpha$ and $S_L$ will be proportional to $T^3$, and that $\kappa$ and $V_L - V_S$ will be constants. Thus if there is a linear term in the specific heat of the solid we have in the limit of low temperature

$$\frac{1}{\rho}\frac{d\rho}{dT} \propto T, \tag{4}$$

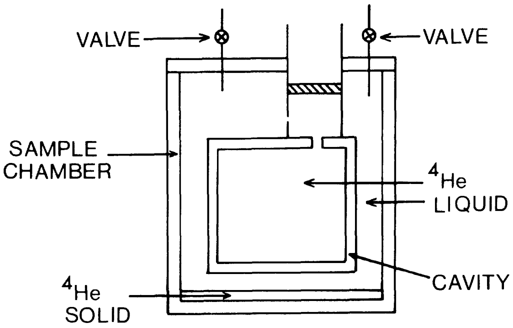

FIG. 1. Experimental arrangement.

whereas if there is no such term,

$$\frac{1}{\rho}\frac{d\rho}{dT}\propto T^3. \tag{5}$$

## II. EXPERIMENTAL

The density of the liquid helium was measured using the same superconducting microwave cavity as described in the preceding paper[9] hereafter referred to as I. The experimental arrangement was as shown schematically in Fig. 1. The sample chamber was completely filled with liquid helium at about 1.4 K, and was pressurized to 25 atm. Both of the superfluid-tight low-temperature valves at the top of the sample chamber were then closed. The sample was cooled and at about 1.3 K solid began to form. Because the density of the liquid at the temperature at which solid first began to form was greater than at any lower temperature, the sample always remained on the melting curve as it was cooled. At the lowest temperature (100 mK) it was calculated that about 3%, or 3 cm$^3$, of the sample chamber volume was occupied by solid.

At each temperature the density of the liquid in the cavity was determined by the measurement of the resonant frequency of the cavity using the Clausius-Mossotti relation as discussed in I. The temperature determination was also the same as in I.

The results were consistent with the assumption that no solid formed *inside* the cavity. Had an appreciable amount of solid formed within the cavity, it would have caused a large shift in resonant frequency since the density of $^4$He increases by nearly 10% upon solidification. Further evidence for the absence of solid formation in the cavity was obtained by warming until the entire sample melted and then recooling to the lowest temperature. The temperature dependence of the data obtained in this way was reproducible to within the accuracy of the measurement of the cavity resonant frequency (about 1 Hz in $10^{10}$ Hz). This reproducibility persisted even if after melting the entire sample, the pressure was increased by a small amount so that on subsequent cooling the first solid was formed at a slightly higher temperature. Had there been solid formation in the cavity, not only would the same amount of solid have had to form, but it would have had to form in the same place so as to affect the frequency change upon cooling in the same way each time. This is very unlikely.

The final data were taken by cooling the sample to near 0.1 K and then warming it by applying heat to the mixing chamber of the dilution refrigerator. As the temperature drifted up slowly the frequency and temperature of the cavity were monitored. The frequency shift $\Delta\nu$ was then related to a density change $\Delta\rho$ using the formula (see I)

$$\Delta\nu/\nu = -[(\epsilon-1)(\epsilon+2)/6\epsilon]\Delta\rho/\rho, \tag{6}$$

where $\epsilon$ is the dielectric constant of liquid helium on the melting curve at $T=0$ K. Using the value of $\epsilon$ found by I gives

$$\Delta\rho/\rho = -(30.550\pm0.001)\Delta\nu/\nu. \tag{7}$$

The uncertainty in $\Delta\rho/\rho$ due to the uncertainty in $\epsilon$ is thus negligible compared to the other errors. There is also a small correction to $\Delta\rho/\rho$ which occurs because as the pressure changes along the melting curve the size of the cavity varies. This gives a frequency shift relative to zero temperature of

$$\Delta\nu/\nu = \tfrac{1}{3}\Delta P(T)\kappa_{\mathrm{Nb}},$$

where $\kappa_{\mathrm{Nb}}$ is the compressibility of niobium. The correction to the density change from this effect is very small compared to the uncertainty arising from the thermometer calibration, and thus may be neglected at all temperatures except near the density minimum. At this temperature the correction is equivalent to a density change of 0.03 ppm. This was calculated using the method discussed in Sec. III of I.

## III. RESULTS AND DISCUSSION

### A. Density measurements below 0.5 K

Figure 2 shows results for the quantity

$$(\rho_T-\rho_0)/\rho_0 T^2$$

plotted versus $T^2$. The uncertainty in the data is too small to show on the figure. Below 200 mK the principal error comes from the 1-Hz uncertainty in the measurement of the resonant frequency of the cavity. This gave a resolution of $\pm 4\times10^{-9}$ for changes in fractional density. Above about 250 mK the density change was large enough so that the uncertainty in resonant frequency was no longer

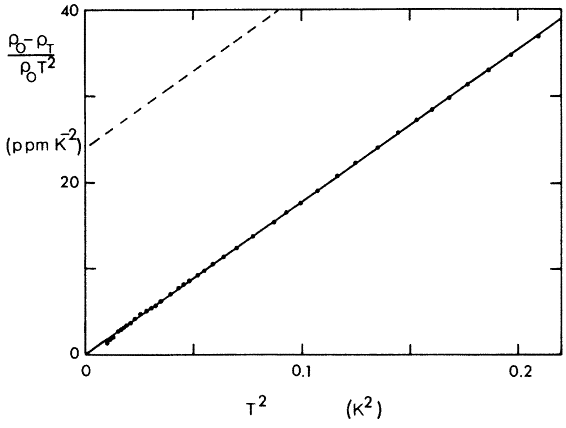

FIG. 2. Temperature dependence of the density of liquid $^4$He at the melting curve for $T < 0.47$ K. The solid straight line passing through the origin has a slope $1.77\times10^{-4}$ $K^{-4}$. The dashed line has the same slope, but has the intercept that would be expected if the entropy of the solid contained a linear term of the magnitude found in Ref. 6.

important. From this temperature upwards the principal uncertainty was from the thermometry errors. As discussed in I these were ±0.2%.

### *1. Linear term in specific heat of solid*

It is clear from Fig. 2 that to a very good approximation the density change is proportional to $T^4$. Thus the thermal expansion coefficient is proportional to $T^3$, and so by the argument given in the Introduction the linear term in the specific heat must be very small. To obtain a better idea of the limits imposed on the linear term by our results we have made a least-squares fit of

$$(\rho_T - \rho_0)/\rho_0$$

to the function $AT^2 + BT^4$. The result was

$$A = -6.3\times10^{-8}\ \mathrm{K}^{-2}, \tag{8}$$

$$B = 1.77\times10^{-4}\ \mathrm{K}^{-4}. \tag{9}$$

We can now use Eq. (3) to calculate the size of the linear term $A'T$ in the specific heat of the solid. To do this we calculate the compressibility $\kappa$ of the liquid from the sound-velocity measurements of Abraham *et al.*[10] ($c = 3.663\times10^4$ cm/sec) and the density measurements of Grilly[11] ($\rho = 0.1729$ g/cm$^3$). The molar volume change on melting[11] is 2.165 cm$^3$/mole. Equation (3) then gives a linear term in the specific heat

$$A'T = 6.3\times10^{-6}T\ \mathrm{J\,mole^{-1}\,K^{-1}}. \tag{10}$$

The uncertainty in the coefficient $A'$ is $\pm6.3\times10^{-6}$ J mole$^{-1}$ K$^{-2}$ at the 70% confidence level and is $\pm16.2\times10^{-6}$ J mole$^{-1}$ K$^{-2}$ at the 99% confidence level. Thus the results give no clear indication of a linear term in the specific heat, and show that any such term must have a coefficient no larger than about $10^{-5}$ J mole$^{-1}$ K$^{-2}$.

For a 20.59 cm$^3$/mole$^{-1}$ sample Castles and Adams[6] found a linear term with coefficient $A' \simeq 2.4\times10^{-3}$ J mole$^{-1}$ K$^{-2}$. The density change expected if the solid specific heat contained a linear term of this magnitude is shown by the dashed line in Fig. 2. This is clearly inconsistent with our data.

### *2. Possible contribution from $^3$He impurities*

The actual $^3$He concentration in the $^4$He sample was not measured. However, a typical $^3$He concentration for $^4$He which has been extracted from natural gas wells is $10^{-7}$. At temperatures in the range of interest here a concentration of $^3$He atoms of this order of magnitude will obey classical statistics. Also the $^3$He concentration in the solid can be neglected. Under these conditions the contribution of $^3$He to the temperature dependence of the melting pressure is[12]

$$\left(\frac{dP}{dT}\right)_3 = \frac{Rx}{V_L - V_S}, \tag{11}$$

where $R$ is the gas constant and $x$ is mole fraction $^3$He. The $^3$He contribution to the thermal-expansion coefficient is[13]

$$\alpha_3 = x n_4 k_B \kappa(1 + \tfrac{3}{2}\beta^*), \tag{12}$$

where $n_4$ is the $^4$He number density, $k_B$ is Boltzmann's constant, and

$$\beta^* = -\frac{\partial \ln m^*}{\partial \ln \rho_4}. \tag{13}$$

$m^*$ is the effective mass of a $^3$He quasiparticle in a dilute solution with $^4$He density $\rho_4$. It is known that $\beta^* \approx -1$, and using Eq. (3) we obtain

$$(\rho_T - \rho_0)/\rho_0 \approx -0.17xT. \tag{14}$$

Thus at 0.1 K the fractional change in density is $1.7\times10^{-9}$. This is slightly less than our sensitivity.

### *3. Calculation of the entropy of solid $^4$He*

The data can be used to calculate the entropy of solid $^4$He on the melting curve if the isobaric thermal expansion and the entropy of the liquid are known. The isobaric thermal expansion $\alpha$ is given by

$$\alpha = (2\pi^2 k_B^4/15\hbar^3\rho c^5)(u + \tfrac{1}{3})T^3, \tag{15}$$

where $c$ is the sound velocity at $T = 0$ K and $u$ is the Grüneisen constant

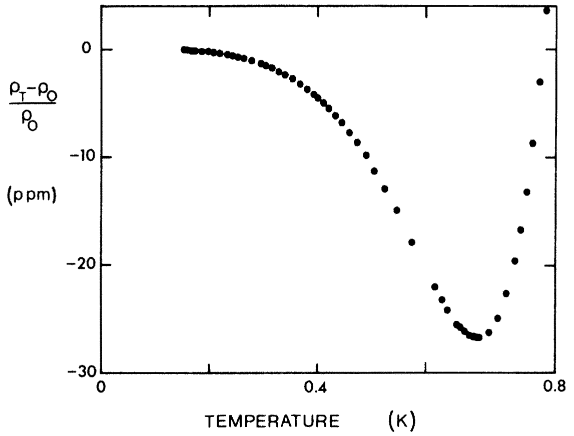

FIG. 3. Temperature dependence of the density of liquid $^4$He at the melting curve for temperatures up to 0.82 K.

$$u=\frac{\partial \ln c}{\partial \ln \rho}. \qquad (16)$$

Equation (16) assumes that the temperature is sufficiently low that only long-wavelength phonons need be considered. Using[10] $u = 2.21$ we obtain

$$\alpha = 9.09\times 10^{-5} T^3 \text{ K}^{-1}. \qquad (17)$$

If we use this value for $\alpha$ in Eq. (2) together with our experimental result for the $T^3$ term in $\partial\rho/\partial T$ [see Eq. (9)], we find

$$\frac{dP}{dT} = -0.141 T^3 \text{ atm/K}. \qquad (18)$$

In the same low-temperature approximation the molar entropy of the liquid is

$$S_L = (2\pi^2 k_B^4 V_L / 45\hbar^3 c^3) T^3 = 6.40\times 10^{-3} T^3 \text{ J mole}^{-1}\text{ K}^{-1}. \qquad (19)$$

Use of Eqs. (1) and (19) then gives (neglecting the possibility of a linear term in the entropy)

$$S_S = 3.74\times 10^{-2} T^3 \text{ J mole}^{-1}\text{ K}^{-1}. \qquad (20)$$

Hence the specific heat of the solid is

$$C_S = 0.112 T^3 \text{ J mole}^{-1}\text{ K}^{-1}. \qquad (21)$$

The Debye temperature calculated from this specific heat is 25.9 K with an estimated error from all sources of ±0.3%. Gardner, Hoffer, and Phillips[5] have measured the specific heat of hcp $^4$He at several molar volumes from 20.456 to 20.960 cm$^3$/mole[1] obtaining values of the Debye temperature $\Theta_D$ ranging from 27.921 to 26.074 K. They fit their data by

$$\Theta_D = 2340 V_S^{-0.8114} e^{-0.0969 V_S}. \qquad (22)$$

This gives a Debye temperature of 25.92 K at melting, in excellent agreement with our value.

### B. Density measurements above 0.5 K

The fractional density change of liquid $^4$He at melting for temperatures up to 0.82 K is shown in Fig. 3. A minimum of depth 26.77 ± 0.01 ppm occurs at 0.697 K ± 0.35%. Grilly[11] has also observed a maximum in the molar volume of liquid $^4$He near 0.7 K, but was not able to obtain an accurate numerical value for the magnitude. From an analysis of heat-capacity measurements of the liquid and solid phases in the vicinity of the transition Hoffer *et al.*[14] calculated that the molar volume of the liquid at freezing reaches a maximum at 0.701 K in good agreement with the results of these measurements. Furthermore, as seen in Eq. (2) if $d\rho/dT = 0$ then $\alpha = \kappa dP/dT$. From the data of Grilly,[11] Abraham *et al.*,[10] and Straty and Adams[15] the temperature of the density maximum is calculated in this manner to be 0.700 K.

The minimum in density occurs because above about 0.6 K the entropy of the liquid increases rapidly due to the excitation of rotons. If it is assumed that the dispersion relation for rotons is given by the Landau approximation

$$\epsilon = \Delta + (p - p_0)^2 / 2\mu, \qquad (23)$$

and if it is assumed that phonons have a linear dispersion relation, it is straightforward to calculate the temperature dependence of the liquid density along the melting curve. The expression for the liquid density involves the molar volumes of the solid and liquid, the roton parameters $\Delta$, $p_0$, $\mu$, and their derivatives with respect to density. Despite the good accuracy of the data it

TABLE I. Temperature dependence of the density of liquid $^4$He at the melting curve for temperatures between 0.458 and 0.821 K. The uncertainties in these data are discussed in the text.

| $T$ (K) | $\frac{\rho_0-\rho_T}{\rho_0}$ (ppm) | $T$ (K) | $\frac{\rho_0-\rho_T}{\rho_0}$ (ppm) |
|---|---|---|---|
| 0.458 | +7.77 | 0.683 | 26.58 |
| 0.471 | 8.70 | 0.687 | 26.67 |
| 0.487 | 9.90 | 0.691 | 26.72 |
| 0.504 | 11.27 | 0.695 | 26.75 |
| 0.523 | 12.94 | 0.697 | 26.77 |
| 0.544 | 14.91 | 0.699 | 26.73 |
| 0.574 | 17.82 | 0.716 | 26.23 |
| 0.616 | 22.02 | 0.732 | 24.98 |
| 0.628 | 23.14 | 0.749 | 22.71 |
| 0.639 | 24.10 | 0.764 | 19.64 |
| 0.656 | 25.38 | 0.775 | 16.75 |
| 0.664 | 25.80 | 0.786 | 13.24 |
| 0.671 | 26.17 | 0.797 | 8.74 |
| 0.676 | 26.38 | 0.809 | +3.07 |
| 0.681 | 26.52 | 0.821 | −3.61 |

was not possible to make a definite determination of any of the roton parameters in this way. The problem was that the data could be fitted by a rather wide range of choices of the roton parameters. However, when accurate specific-heat measurements in the liquid become available it should be possible to combine these with the present data to give very accurate values of the roton parameters. For this reason we include in Table I values for $\rho_0 - \rho_T$. The uncertainty in these results arises almost entirely from errors in temperature which are estimated to be ±0.2% up to 0.6 K, ±0.35% at 0.7 K, and 0.4% at 0.8 K. This error is of course in addition to possible errors associated with the $^3$He vapor-pressure scale itself.

## IV. SUMMARY

We have made precise measurements of the density change in liquid $^4$He along the melting curve. From these and other data it is possible to determine the entropy of the solid phase. No evidence is found for an anomalous linear term in the entropy of the solid. The Debye temperature obtained for the solid is in excellent agreement with the earlier result of Gardner *et al.*[5]

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*Work supported in part by the National Science Foundation through the Materials Research Laboratory at Brown University and through Grant Nos. DMR 75-14761 and DMR 73-07493.

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