

## Pressure dependence of the isotopic phase separation temperature in solid $^3\text{He}$ - $^4\text{He}$ mixtures

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(Received 22 October 1979)

The isotopic phase separation temperature of solid mixtures of  $^4\text{He}$  in  $^3\text{He}$  has been measured as a function of pressure ( $31 \text{ atm} \leq P \leq 42 \text{ atm}$ ) for  $^3\text{He}$  mole fractions  $x$  greater than 0.900. The phase separation temperature was found to increase with decreasing pressure, as predicted by Mullin. The results are compared with other experiments and with theoretical calculations.

### I. INTRODUCTION

In 1962, Edwards, McWilliams, and Daunt<sup>1</sup> (EMD) began a systematic study of the specific heat of solid  $^3\text{He}$ . As was common at that time, their sample gas contained small amounts of  $^4\text{He}$ . They observed that, at temperatures depending on the impurity concentration, there was a large anomaly in the specific heat. By extending their work,<sup>2</sup> they were able to conclude that they were witnessing an isotopic phase separation in these mixtures. In 1964 Zimmerman<sup>3</sup> noticed that the phase separation temperature  $T_{ps}$  decreased with increasing pressure but was unable to obtain a quantitative measurement, and in 1968 Panczyk, Scribner, Gonano, and Adams<sup>4</sup> (PSGA) were able to deduce the pressure derivative  $dT_c/dP$  from their measurements of the total pressure change upon complete phase separation.  $T_c$  is the critical temperature, namely, the highest temperature at which phase separation can occur.

In order to explain the phase separation theoretically, EMD relied on classical thermodynamics. In such a treatment, one discusses various excess quantities which are defined as the increase in that thermodynamic parameter upon phase mixing. For mixtures such as those of solid  $^4\text{He}$ - $^3\text{He}$ , the important thermodynamic quantity is the Gibbs free energy, which is a constant for reversible processes occurring at constant temperature and pressure. EMD found that solid  $^4\text{He}$ - $^3\text{He}$  mixtures form regular solutions,<sup>5</sup> in which case the excess Gibbs energy per mole has the form

$$g^E = x(1-x)\Delta E(P) \quad (1)$$

where  $x$  is the  $^3\text{He}$  mole fraction and  $\Delta E(P)$  is the energy of mixing. This leads to a critical temperature of

$$T_c = \Delta E/2R \quad (2)$$

and a phase separation curve given by

$$T_{ps} = \frac{2(1-2x)}{\ln[(1-x)/x]} T_c \quad (3)$$

In 1968 Mullin<sup>6</sup> presented a microscopic treatment of phase separation in solid  $^4\text{He}$ - $^3\text{He}$  mixtures in which he showed that there should be slight deviations from regular solution theory. In particular he predicted that the phase separation curve should not be symmetric with respect to  $x = \frac{1}{2}$  as indicated by Eq. (3). This was confirmed by PSGA.<sup>4</sup> Mullin also estimated that the critical temperature should decrease with increasing pressure at the rate of about 1 mK/atm. The measurements of PSGA indicated a somewhat higher value of about 2 mK/atm.<sup>4</sup>

In the work reported here we have obtained direct measurements of the phase separation temperature as a function of pressure for several values of  $^3\text{He}$  mole fraction. First we shall describe the experimental techniques used and then we shall discuss the results in the context of previous work.

### II. EXPERIMENTAL

The sample cell, which was cooled by means of a dilution refrigerator, had incorporated into its design a capacitive strain gauge with a sensitivity of  $10^{-4}$  atm. Construction details of such a strain gauge have been presented in other works.<sup>7</sup> Since we used a blocked capillary technique to form the solid sample, all of our measurements were made at constant volume. We thus employed the strain gauge to detect the onset of the phase separation by means of the accompanying pressure rise upon cooling through  $T_{ps}$ . During each run the strain gauge was calibrated at 4.2 K against a Heise gauge which had previously been calibrated by the manufacturer.<sup>8</sup>

The temperature of the sample was determined by measuring the nuclear magnetic susceptibility of the  $^3\text{He}$  in the sample using continuous-wave NMR. The magnetic susceptibility of dilute solid mixtures of  $^4\text{He}$  in  $^3\text{He}$  has been shown to obey a Curie-Weiss law with a Weiss constant  $\Theta$ , essentially the same as that of pure solid  $^3\text{He}$ .<sup>9,10</sup> We have assumed  $\Theta = -2.0$  mK.<sup>11,12</sup> The Curie constant was obtained by mea-

suring nuclear susceptibility in the temperature range  $0.3 \leq T \leq 0.5$  K where a calibrated carbon resistance thermometer was available for temperature measurement. This method of thermometry avoids any problems that might arise from the Kapitza boundary resistance at lower temperatures.

The values of  $^3\text{He}$  mole fraction were determined with a Veeco MS9AB leak detector which has been modified to sense  $^3\text{He}$  as well as  $^4\text{He}$ . Two carefully prepared mixtures were used to calibrate this machine and corrections for differing sensitivities to the two helium isotopes were made.

All phase separation temperatures were measured while the sample was cooling. By adjusting the dilution refrigerator still power, the cooling rate was set at 2–3 mK/min. In order to locate the phase separation, the output of the capacitance bridge was monitored on a chart recorder. When the pressure in the cell began to rise, an NMR trace was taken, thus yielding the phase separation temperature. The heater on the mixing chamber of the refrigerator was turned on, and the output of the pressure transducer was used to determine when the sample had completely phase mixed. The heater was then turned off and the sample was allowed to cool through the phase separation again. This process was repeated a minimum of four times per sample. The high sensitivity of the strain gauge meant that the uncertainty in locating the point of the pressure rise was much less than other temperature measurement uncertainties.

### III. RESULTS AND CONCLUSIONS

The results that show the pressure dependence  $T_{ps}$  are shown in Fig. 1. Each point represents an average of four or more passages through the phase separation temperature and the error bars are one standard deviation. The solid lines are the best linear regression fits to the data and the slopes give values for  $dT_{ps}/dP$  of  $-2.6 \pm 0.4$ ,  $-3.0 \pm 0.4$ , and  $-3.2 \pm 0.2$  mK/atm for  $x = 0.987$ ,  $0.968$ , and  $0.900$ , respectively.

The values of  $dT_{ps}/dP$  given above can be used to estimate  $dT_c/dP$  using regular solution theory. This can be done by differentiating Eq. (3) and solving for  $dT_c/dP$  to get

$$\frac{dT_c}{dP} = \frac{\ln(1-x)/x}{2(1-2x)} \frac{dT_{ps}}{dP} \quad (4)$$

A fit of our data to Eq. (4) results in a value of  $dT_c/dP$  of  $-4.7 \pm 1.0$  mK/atm, or about twice that obtained by PSGA.<sup>4</sup> The error quoted in our value is the standard deviation in the slope of a linear regression fit to the values of  $dT_{ps}/dP$  quoted above and does not take into account the errors in the individual values of  $dT_{ps}/dP$ . This, added to the fact that only three points were used in the fit, means that our

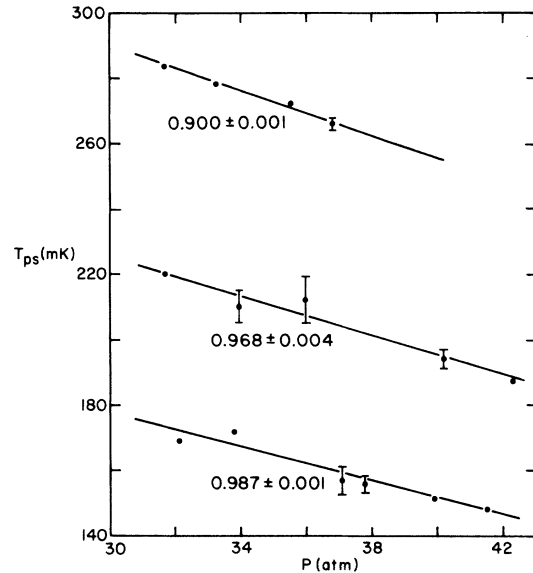


FIG. 1. Isotopic phase separation temperature as a function of pressure. The curves are labeled by  $^3\text{He}$  mole fraction.

quoted error overestimates the precision of our value for  $dT_c/dP$ . Because of this we feel that anything more than a qualitative comparison with the results of PSGA is unwarranted. Also PSGA do not give estimates of the precision of their values of  $dT_c/dP$ . Our results fit Eq. (4) marginally, at best, which may indicate that solid  $^4\text{He}$ - $^3\text{He}$  solutions deviate from regular solution theory even for large values of  $x$ .

Figure 2 shows the phase separation curve for  $P = 35.8$  atm in the region of  $x$  covered by these ex-

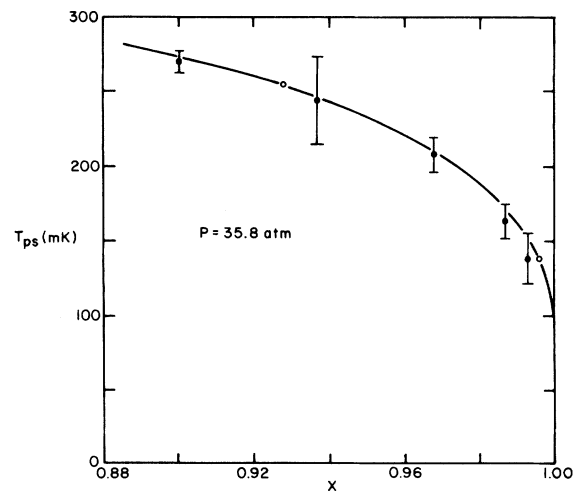


FIG. 2. Isotopic phase separation temperature as a function of  $^3\text{He}$  mole fraction for  $P = 35.8$  atm. The closed circles are our results and the open circles are those of PSGA. The curve is regular solution theory.

periments. The points for  $x = 0.900$ ,  $0.968$ , and  $0.987$  were taken from Fig. 1 and the points for  $x = 0.937$  and  $0.993$  are the results of measurements made at those values of mole fraction but over too small a pressure range to yield a value for  $dT_{ps}/dP$ . It is clear that our data for the phase separation curve agree quite well with other experiments and with regular solution theory.

In conclusion, we have obtained the first direct measurements of the pressure dependence of the phase separation temperature of solid  $^4\text{He}$ - $^3\text{He}$  mix-

tures. Our results confirm indications of previous experiments<sup>3,4</sup> and microscopic theory<sup>6</sup> that the phase separation temperature should increase with decreasing pressure.

#### ACKNOWLEDGMENTS

We would like to thank Dr. J. U. Free for many valuable discussions of this work. One of us (P.B.P.) was partially supported by the Alfred P. Sloan Research Foundation.

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