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THE SPECIFIC HEAT OF $^3$He-$^4$He SOLID MIXTURES*

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Although the phase diagrams of pure $^3$He and pure $^4$He are fairly well known, and are relatively simple, the phase diagram of $^3$He-$^4$He mixtures is complicated at low temperatures by a separation of both the liquid and the solid into a $^4$He-rich and a $^3$He-rich phase. Edwards et al. reported in the article announcing the discovery of an isotopic separation in solid $^3$He-$^4$He mixtures that the temperature at which isotopic separation sets in is symmetric in $x$ and $(1 - x)$, where $x$ is the atomic fraction of $^2$He. Since their data were taken in the isotopic composition range of 82.4% $^4$He and 17.6% $^3$He to 0.03% $^4$He and 99.97% $^3$He, at the highest pressure of 35.8 atm, it was probable (according to the extrapolation of the phase diagrams of Vignos and Fairbank) that all the measurements of Edwards et al. were performed in the bcc phase.

The measurements reported here were performed to investigate the influence of the bcc-hcp crystalline phase transition, which comes at a lower $^3$He concentration and higher pressure than those at which the data of Edwards et al. on the isotopic phase separation were obtained.

The specific heat of $^3$He-$^4$He mixtures has been measured for $^3$He concentrations between 0 and 11.8%, in the temperature range between 0.06° and 0.7°K, at solidification pressures up to 63 atm.

The apparatus and method used in this measurement are similar to those described elsewhere. The specific heat was obtained by the pulse method, and measurements were carried out at constant volume, using the blocked capillary technique.

There are several things that one should bear in mind in considering these data. First, since there is no pressure-sensitive device inside the calorimeter, this pressure is known only at the time the capillary is blocked. The same pressurizing procedure as reported in detail by Zimmerman was followed here. Because the cooling through the solid-liquid transition was slow, and helium was observed to condense during the solidification, it can be assumed that the solidification took place at constant pressure rather than at constant volume on a $P-V$ diagram. Since the molar volumes of the solid $^3$He-$^4$He mixtures are unknown, only the solidification pressure and the volume of the calorimeter, which is 0.605 cc, can be given. The calorimeter volume was determined by observing the amount of $^4$He gas at standard temperature and pressure which condensed into it while the calorimeter was at 1.5°K, and then by correcting for the known volume of the capillary.

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Second, because one is dealing here with both crystallographic and isotopic phase transitions in the solid, one can expect a certain amount of supercooling and superheating. Such effects were indeed observed. At solidification pressures above 26 atm, the average time for the measurements of a specific heat point was about 10 min, while at a solidification pressure of 63 atm, it became as high as 45 min. At a particular isotopic composition and particular solidification pressure, there was an irreproducibility of data from one measurement to another which is attributed to superheating or supercooling. Because of the uncertainty in the data caused by the above effect, all the specific heat determinations reported here are a result of from 3 to 6 runs at each combination of isotopic composition and solidification pressure, with the lines drawn through points which have been validated by at least two determinations. It is hoped that this procedure will locate the specific heat maxima with an accuracy of plus or minus 0.005°K.

The quantity \( \Delta Q/\Delta T \), where \( \Delta Q \) is the heat added to the sample and \( \Delta T \) is the corresponding change in temperature, for samples of different isotopic composition at solidification pressure of 48 atm is plotted as a function of temperature in Fig. 1. The percentages denote the amount of \(^3\)He in the \(^3\)He-\(^4\)He mixture. The

![Graph](image-url)

Fig. 1. \( \Delta Q/\Delta T \) plotted against temperature for different compositions at solidification pressure of 48 atm.
crosses indicate the onset of phase separation as calculated from the equation given by Edwards et al.\(^2\) Going down in temperature, the crosses are for a \(^3\)He concentration of 11.8, 7.7, 3.12, 2.6, 1.18, and 0.58\%, respectively. At \(^3\)He concentration of 11.8 and 7.7\%, our agreement with the data of Edwards et al. is excellent except for the appearance of a secondary specific heat maximum at lower temperature which is smaller in magnitude than the high temperature one. At lower \(^3\)He concentrations—i.e., 3.12, 2.6, 1.18, and 0.58\%—the high temperature maxima come at a much higher temperature than those calculated by Edwards et al., but there is always a secondary specific heat maximum at the calculated temperature that might be due to passing first through a crystalline phase transition which is accompanied by a partial isotopic phase separation, and then through the nearly symmetric isotopic phase separation as temperature is decreased.

The 1.18\% \(^3\)He mixture and the 0.58\% \(^3\)He mixture exhibit three specific heat maxima. Two of these can be interpreted on the basis of passing through the hcp–bce transition and then at lower temperature encountering the almost symmetric isotopic phase transition. The third peak, the high temperature one in the

Fig. 2. \(\Delta Q/\Delta T\) plotted against temperature for isotopic composition of 2.6\% \(^3\)He and 97.4\% \(^4\)He at different solidification pressures.
The Specific Heat of $^3$He-$^4$He Solid Mixtures

Table I

<table>
<thead>
<tr>
<th>$^3$He concentration, %</th>
<th>Solidification pressure, atm</th>
<th>Temperature of maxima, °K</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.80</td>
<td>48</td>
<td>0.300, 0.095</td>
</tr>
<tr>
<td>7.70</td>
<td>48</td>
<td>0.260, 0.168</td>
</tr>
<tr>
<td>3.12</td>
<td>63.2</td>
<td>0.167</td>
</tr>
<tr>
<td>3.12</td>
<td>48</td>
<td>0.355, 0.195</td>
</tr>
<tr>
<td>3.12</td>
<td>27</td>
<td>0.376, 0.182</td>
</tr>
<tr>
<td>2.60</td>
<td>48</td>
<td>0.245, 0.145</td>
</tr>
<tr>
<td>2.60</td>
<td>26.5</td>
<td>0.260, 0.172</td>
</tr>
<tr>
<td>2.60</td>
<td>26.3</td>
<td>0.268, 0.170</td>
</tr>
<tr>
<td>2.60</td>
<td>26.0</td>
<td>0.282, 0.135</td>
</tr>
<tr>
<td>1.18</td>
<td>48</td>
<td>0.355, 0.227, 0.175</td>
</tr>
<tr>
<td>0.58</td>
<td>48</td>
<td>0.230, 0.147, 0.110</td>
</tr>
<tr>
<td>0.58</td>
<td>26.6</td>
<td>0.230, 0.137, 0.097</td>
</tr>
</tbody>
</table>

1.18% $^3$He mixture and middle one in the 0.58% $^3$He mixture, is possibly due to superheating effects.

This measurement would suggest that at a solidification pressure of 48 atm, the hcp-bcc line shifts to lower $^3$He concentrations on the $T$-$X$ diagram than that shown for 30 atm by Tedrow and Lee.7

In Fig. 2, $\Delta Q/\Delta T$ is plotted as a function of temperature for the mixture of 2.6% $^3$He and 97.4% $^4$He at different solidification pressures. The sample at solidification pressure of 25.3 atm is hitting the melting curve, while at higher solidification pressures the samples are solid in the temperature range of this measurement. At each of the isotopic compositions measured at different solidification pressures—i.e., 3.12, 2.6, and 0.58% of $^3$He—the common envelope on the high temperature side was observed. Another common feature was the increase in magnitude and decrease in temperature of the specific heat maxima as the pressure was raised.

At a solidification pressure of 63.2 atm and composition of 3.12% $^3$He, only one specific heat maximum was observed. This maximum has a value of $\Delta Q/\Delta T$ of $3.7 \times 10^6$ ergs/deg K, and comes at a temperature of 0.167°K. The data are summarized in Table I.

Acknowledgments

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References