

Melting of ^3He in a phase-separated solid ^3He – ^4He mixture

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The melting pressure of the ^3He -rich phase, formed after phase separation of a mixture of 0.6% ^3He in ^4He , has been studied in the temperature range 1–150 mK, below the phase-separation temperature T_{ps} , at pressures between 2.78 and 3.56 MPa. Measurements were made with the mixture confined in a silver sinter, and also in an open volume for comparison. An elevation of the melting pressure relative to pure ^3He of up to 60 kPa in the sinter cell and 20 kPa in the open-volume cell was observed. Hysteresis between the freezing and melting temperatures was found for both cells, similar to that observed for pure ^3He in small pores. The results of Schrenk et al. for heat capacity measurements on a similar system are discussed.

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1. Introduction

A homogeneous solid mixture of ^3He – ^4He decomposes into separate phases when cooled to the phase-separation temperature T_{ps} . For low ^3He concentrations, at temperatures well below T_{ps} , the ^4He -rich hcp matrix contains clusters or droplets of almost pure ^3He , see [1,2] and references therein. Schrenk et al. [1] have reported a depression of the melting pressure of the ^3He droplets relative to that of pure bulk ^3He . Furthermore, they have observed a history-dependent magnetic ordering in the droplets at pressures as low as 700 kPa below the melting pressure of pure ^3He [2]. A possible explanation for these results might be the confined-geometry effect of the small droplets. Pure ^3He in small glass pores has an elevated melting pressure [3], while a depression of the melting pressure has been reported for ^3He on a MgO substrate [4].

We have studied melting and freezing in a 0.6% ^3He mixture confined in a silver sinter cooled below T_{ps} (approximately 200 mK) at pressures from 2.78 to 3.56 MPa in order to determine the melting curve of the ^3He droplets [5]. We have also made measurements on the same mixture contained in an open volume in order to assess whether the silver sinter plays any role other than providing an effective means of cooling. Hysteresis and the effect of a thermal history on the transition were investigated in both cells. The implications of our observations

on the results of Schrenk et al. [2] are discussed, and possible explanations are given for some of the effects that they reported.

2. Experimental method

The sinter cell contains a thin disc of silver sinter of a particle size 500–1000 Å and packing fraction 50%. The disc of radius 25 mm and thickness 2.5 mm was packed in a silver cell with one wall forming the flexible diaphragm of a capacitive pressure transducer [6]. The open volume cell is similar in design, with the sample forming as a solid disc of radius 17 mm and thickness 1.3 mm. These geometries provide a short path for pressure transmission, thereby minimizing pressure gradients in the sample. The resolution of each cell is better than 1 Pa. The two cells were connected to the same fill-line, with a junction in the line at the experimental stage on which the cells were mounted.

Samples were formed at various pressures by the capillary-blocking technique, and it was intended that both the open-volume and sinter cells would contain samples at the same pressure, since they were connected to the same fill-line. However, the sinter cell samples consistently solidified at higher pressures than the open cell (by approximately 0.3 MPa). We attribute this to a larger degree of disorder in the sinter cell since there is a larger surface area on which a few atomic layers of amor-

phous solid ^4He form. After formation the samples were either quenched or annealed just below the solidification point. The phase separation in the sinter and open-volume cells was observed as an increase in the sample pressure of approximately 15 kPa with a time constant on the order of 10 h for the sinter cell and 20 h for the open-volume cell. The absence of a sinter in the open-volume cell did not significantly affect the cooling/warming rate of the sample. After the phase separation and further cooling, samples were then warmed through the freezing transition and cooled back through melting, taking care to keep $T < T_{ps}$. In some cases, several such cycles were performed. Temperatures were measured precisely with a ^3He melting pressure thermometer [7] mounted on the same experimental platform as the cells. The temperature was regulated by using the signal from the thermometer bridge to control the current to a heater on the experimental stage. All three strain gauges were calibrated with the same Paroscientific quartz transducer.

In order to ensure that the data were taken at equilibrium, the desired thermometer bridge value was set on the temperature control system, the samples cooled/warmed to the new temperature, and then held at that temperature until the pressure in the cells reached equilibrium. In the freezing transition of the open-volume cell, equilibration could take up to 20 h.

3. Results and discussion

In both the sinter and open-volume cells, melting of the ^3He droplets was observed at sample pressures from 3.13 to 3.45 MPa. At 3.48 MPa the ^3He remained solid down to the lowest temperature (1 mK), and at 2.96 MPa melting was not observed, presumably because the droplets formed as a liquid. Upon melting, the pressure of the sample in the sinter cell increased on the order of 1 kPa, and on the order of 5 kPa in the open-volume cell.

Figure 1 shows typical cooling/warming cycles displaying the hysteresis seen in every sample in which melting occurred in the sinter cell. The numbers by the curves indicate the time sequence; curves 4 and 5 illustrate the effect of reversing the direction of temperature changes in the mid-cycle. Figure 2 shows a typical warming/cooling cycle in the open-volume cell, which also shows hysteretic behavior. In this figure the pressure in the cell is plotted relative to the pressure in the melting curve thermometer. Since the cells were calibrated against the same pressure standard, this eliminates uncertainty in the temperature and shows precisely the

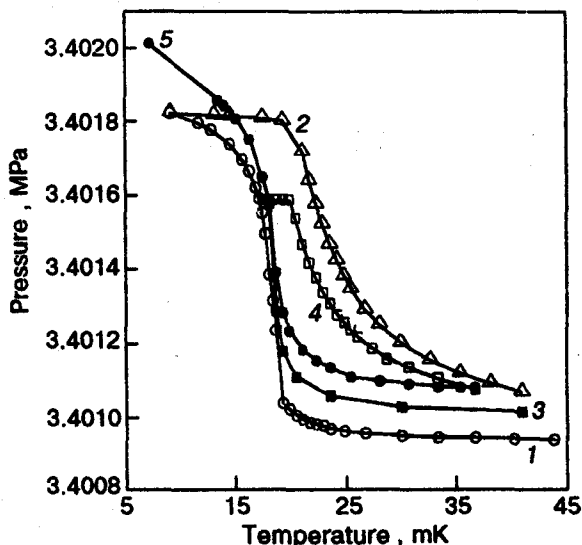


Fig. 1. Typical cooling (curves 1, 3, and 5) and warming (curves 2 and 4) cycles for the melting/freezing of ^3He in the droplets in the sinter cell, see text.

position of the transition relative to the bulk melting curve. Previously hysteresis was observed for pure helium in porous glasses and appears to be a characteristic of melting and freezing in confined geometries [3]. In that experiment the transitions occurred at pressures above that of the bulk melting curve, as one would expect for the homogeneous nucleation of a new phase in a confined geometry.

The temperatures for the sharp kinks in the cooling and warming curves such as in Fig. 1 are almost the same and the pressure differences are small. These are shown in Fig. 3 as single points for

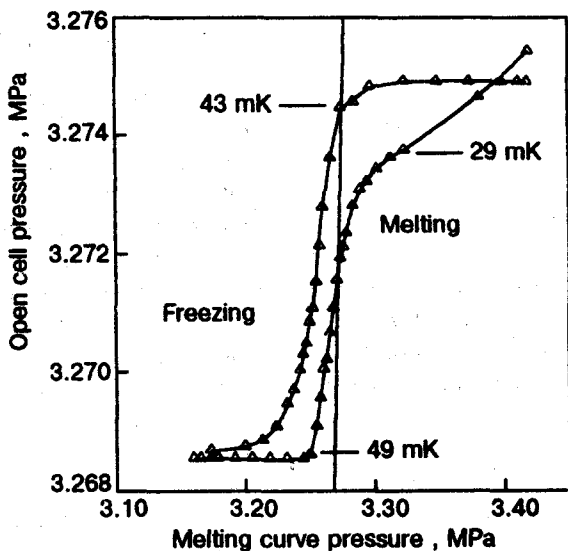


Fig. 2. Typical warming and cooling cycles for the freezing/melting of ^3He in the open-volume cell. The vertical solid line shows the melting pressure of bulk ^3He . Temperatures are given for the points indicated.

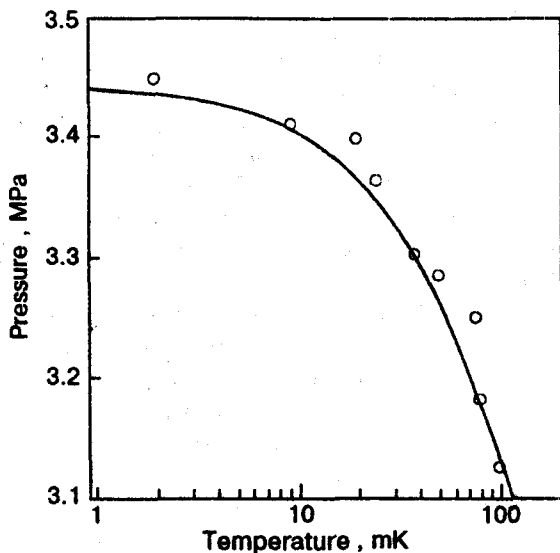


Fig. 3. The bulk ^3He melting curve (solid line) and the melting points of ^3He droplets, taken from sinter cell data.

samples formed at different pressures along with the pressure indicated by the pure ^3He melting pressure thermometer. For the sinter cell we found all melting transitions to be on or above the bulk melting pressure, elevated by as much as 60 kPa. The precision of the points in Fig. 3 is much better than would be indicated by the "scatter", which is possibly related to the thermal history of the sample and the droplet size [8]. However, we have not been able to correlate the size of the pressure elevation with the thermal history.

Also, we have measured the pressure minimum of essentially pure ^3He in the sinter plated with 1% ^4He as a substrate and find an elevation of the melting pressure in the sinter of 63.9 kPa.

For the open-volume cell, it is clear from Fig. 2 that the onset of melting in the droplets is elevated above the bulk melting curve (by 20 kPa), and that the melting/freezing transition is broadened relative to a bulk ^3He isochore. We attribute this to differences in the droplet size between the sinter cell and the open cell. In the open volume cell, we suggest that the ^3He forms in a range of different-sized clusters, up to a size on the order of 1 μm [8]. In the sinter cell, the pore size of approximately 100 nm limits the size of a cluster which can grow from the ^3He contained inside the pore. Thus the larger droplets in the open-volume cell contain ^3He which is less confined and one would, therefore, expect a smaller elevation of the melting pressure. This accounts for the melting transition observed for the open cell being broadened, with the onset for smaller droplets at a high elevation. In comparison, the sinter cell melting transitions are sharper

and more elevated, suggesting that a high percentage of the ^3He in a pore is contained in a single cluster, limited in size only by the ^3He available within that pore. The cluster size would be approximately 20 nm if it contained all the ^3He within a pore.

The fractional change in volume in the droplets on melting $\Delta v/v$ can be calculated from the change in pressure on melting such as that shown in Figs. 1 and 2 (assuming that the molar volume change of ^3He in the droplets is the same as in bulk). We find this to be only about 8% of that for pure ^3He in a typical sinter cell measurement, and 40% in the open-volume cell. This indicates that a large fraction of the ^3He remains solid at pressures well below the bulk melting curve. A volume change less than for bulk ^3He would be expected if surface layers of the ^3He droplets do not melt because of the influence of the adjacent higher-density hcp ^4He . As a result of the van der Waals attraction to the ^4He surface, the density of the solid in the droplet would be higher at the interface than in the interior. The higher-density ^3He solid layers will melt at progressively colder temperatures. Evidence for these density gradients can be found in data such as that shown in Fig. 1, curve 5, where the pressure continues to increase upon cooling well below the sharp melting transition. The initial pronounced increase in pressure would then be due to material in the center of the droplets, indicating that the high-density hcp ^4He affects only the outer layers of the ^3He in the cluster. The larger fractional volume change in the open-volume cell reinforces the assertion that it contains larger droplets, so that a lower proportion of the ^3He is directly affected by its proximity to the ^4He matrix. It should be emphasized that this continued pressure increase is not owing to the continued phase separation as the sample was held at a temperature below T_{ps} and above the melting transition temperature until the pressure remained constant for a further temperature decrease, before the onset of melting (Fig. 1, curve 1).

The existence of density gradients in the outer layers of the droplets can account for effects reported by Schrenk et. al [2] relating to magnetic ordering of ^3He droplets in solid ^4He contained in a silver sinter. Their observations, based on the heat capacity, include higher magnetic ordering temperatures, T_N , at pressures as low as 2.8 MPa, 700 kPa below the melting pressure of pure ^3He , and a history-dependent transition temperature. As discussed above, the existence of solid ^3He at pressures below the bulk melting curve appears to be a

consequence of confining the droplets within a higher density ^4He matrix. The history dependence of T_N they report is that samples cooled to lower minimum starting temperatures, T_{\min} , appear to give lower transition temperatures in the heat capacity data taken whilst warming. The transitions that they observe show no latent heat and are much broader than those measured by Greywall and Busch [9] in bulk ^3He . These are well-known effects of density gradients in the sample. The peak that they observe does indeed appear at a higher temperature if T_{\min} is higher, although it is not clear that this peak actually indicates T_N . In fact, the broadening of the peak owing to density gradients means that the samples with higher values of T_{\min} are not cooled all the way through the ordering transition, so that for successively higher values of T_{\min} , less of the solid ^3He contributes to the heat capacity. If the droplets were cooled all the way through the ordering temperature then there would be a decrease in entropy (extrapolated to $T = 0$) of $R \ln 2$, where R is the gas constant. Their data for a sample at 3.4 MPa with $T_N = 0.92$ mK actually shows a greater contribution to the entropy reduction in cooling from 2 mK to just above T_N than that found by Greywall and Busch in bulk, probably indicative of a broadening of the transition in the droplets. Greywall and Busch report an entropy reduction of $0.41 R \ln 2$ in going through the transition alone. However, even including contributions from 2 mK down to T_{\min} , the entropy reduction of Schrenk et al. is only $0.32 R \ln 2$ for $T_{\min} = 783 \mu\text{K}$ and $0.22 R \ln 2$ for $T_{\min} = 837 \mu\text{K}$. This suggests strongly that all of the solid in the droplets was not cooled through T_N , as would occur for a transition broadened by density gradients.

4. Conclusions

Melting of ^3He droplets contained in a matrix of ^4He occurs at higher pressures than bulk ^3He and has a hysteresis characteristic of melting in confined geometries. The small volume change on melting indicates that much of the ^3He in the droplets does not undergo melting, and remains solid at pressures below the bulk melting curve owing to interaction with the surrounding hcp solid ^4He . Comparison with a mixture in an open-volume indicates that containing the solid in a sinter has the effect of limiting the size of the ^3He clusters, and the smaller droplets give rise to a larger elevation of the melting pressure. We intend to use NMR to measure the droplet size, the relative amounts of liquid and solid, and to study solid ordering.

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