SANS STUDY OF PHASE SEPARATION IN SOLID $^3\text{He}^-^4\text{He}$

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ABSTRACT

Small angle neutron scattering has been used to study phase separation in a quantum alloy, solid $^3\text{He}^-^4\text{He}_{1-x}$. The onset of phase separation is marked by a dramatic increase in the measured scattering. A simple interpretation of the results suggests that the late-stage phase separation kinetics are dominated by an increase in the concentration of $^3\text{He}$ atoms in pre-existing precipitate regions.

INTRODUCTION

The kinetics of phase separation is an important problem in materials science and technology as well as modern statistical physics. A particularly interesting regime is that in which atomic motions are dominated by quantum effects. In this paper we present preliminary results of a small angle neutron scattering (SANS) study of phase separation in the model quantum solid alloy, $^3\text{He}^-^4\text{He}_{1-x}$.

Solid He is the prototypical quantum solid, and its phase diagram has been studied in great detail [1]. At low pressures both $^4\text{He}$ and $^3\text{He}$ remain liquid down to $T=0$. Above $P=24$ atm., $^4\text{He}$ solidifies in the HCP structure for $T<1\text{K}$. Higher pressures are needed to solidify $^3\text{He}$, which has the BCC structure for $T<2\text{K}$, 35 atm. $<P<120$ atm., and the HCP structure at higher pressures. The binary alloy $^3\text{He}^-^4\text{He}_{1-x}$ phase separates at very low temperatures [2]. The coexistence curve is described well by regular solution theory for most values of x and is pressure dependent [3–5]. The maximum phase separation temperature, $T_{ps}$, is 380 mK for $P\sim 30$ atm. In general, $T_{ps}$ decreases both as the applied pressure increases and as x moves away from 0.5. Phase separation in a sample at constant volume is accompanied by a rise in pressure [3] and by an increase in the specific heat of the sample, indicating that the transition is always first order.

The characteristic times for completion of phase separation become large at high pressures resulting in observable changes over many hours [3]. The system is thus amenable to experimental investigation, and there have been many previous studies using a variety of techniques: specific heat[2], pressure measurements[3,4,7], thermal conductivity[6],
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NMR[8-10], acoustic waves[11], and wide angle x-ray diffraction [5]. The SANS method has the advantage of directly probing the domain sizes of precipitated regions. Unfortunately, the large neutron absorption cross-section of the $^3$He atom makes the experiment difficult. We have studied phase-separation in these mixtures at several $^3$He concentrations with $x < 0.03$. The present paper discusses results for $x=0.016$, which are representative of the results at other concentrations.

**EXPERIMENTAL DETAILS**

Differential pressure measurements were performed simultaneously with the SANS. This required a special sample cell made of copper, based on that used for previous pressure studies [3], modified for use with neutron scattering apparatus. The disk shaped cell (27 mm diameter, 1 mm thick) was mounted in an Oxford 200 dilution refrigerator and aligned in the sample position of the 30 meter SANS instrument at the High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory [11]. The dilution refrigerator was capable of cooling the sample to approximately 100 mK. Temperature measurement was accomplished with calibrated Ge and RuO$_2$ sensors. The pressure in the sample cell was measured using a BeCu diaphragm capacitance gauge coupled to a General Radio 1620 analog LC bridge.

Samples were prepared by introducing a $^3$He - $^4$He gas mixture of known concentration into the cell at 4.2K. Subsequently the cell was pressurized to a final pressure greater than 35 atm. where the mixture is still liquid. The SANS from the liquid was measured for several hours before cooling down further. The samples solidified in the hcp lattice structure between 1 and 3 Kelvin, depending on the applied pressure. When solidification starts a solid block forms first in the sample supply capillary which is thermally anchored to the mixing chamber, which is the coldest part of the fridge. This ensures that the amount of sample in the cell is constant. Since thermal contraction of the copper cell is negligible below 10 K this means that the average density of the sample also remains constant. The SANS measurements were carried out using a neutron wavelength $\lambda$ of 4.75 Å with $\Delta\lambda/\lambda \approx 5\%$. The sample to detector distance was 9.3 meters. The detector consists of 64 x 64 elements and is 64 cm x 64 cm in size. The data were corrected for instrumental backgrounds and detector efficiency on a pixel-by-pixel basis, and azimuthally averaged with an accessible wave-vector range of $0.06 < Q < 0.64$ nm$^{-1}$. Variations in the incident neutron flux were recorded with a monitor counter. The change in sample transmission with density was separately measured and accounted for.

The SANS signal in the homogeneous solid phase (HS) was recorded at several different temperatures, down to a temperature close to but above where phase-separation was expected to occur. There was little or no observable temperature dependence of the SANS in the homogeneous phase. Finally the sample was quenched to a final temperature below $T_{ps}$ at the
maximum cooling power of the dilution refrigerator. For the sample reported on here, at a nominal pressure of roughly 42 atm., the homogeneous solid formed at $T_m \approx 2$K and phase separation occurred at $T_{ps} \approx 170$ mK.

RESULTS

Results of a typical run are displayed in figure 1. Quantities are plotted vs. time in minutes relative to an arbitrary time at which the sample was in the HS phase. The lowest panel shows

Figure 1. Integrated Counts (top), differential pressure (middle) and temperature (bottom) as a function of time during phase separation as discussed in the text.
the temperature. The middle panel is the pressure differential, which shows a clear rise as T drops below 150 mK. The upper panel is the total scattering in the detector, summed over the measured Q range, and normalized to the monitor count. This quantity is essentially constant in the HS phase, but jumps dramatically at the onset of phase separation. The increase in the SANS signal is visible before the increase in pressure becomes evident. Clearly SANS is very sensitive to phase separation in the $^3$He$_x$-$^4$He$_{1-x}$ system. The decrease in the signal at late times is not understood, but it may arise from a systematic error if much of the true scattering is at Q values too small to be observed directly in the experiment.

Figure 2 shows representative azimuthally averaged scattering profiles in the phase-separated regime, expressed in absolute units of cm$^{-1}$. A background, taken as the scattering observed in the HS phase, has been subtracted from the data. The measurement times are identical to those plotted in figure 1. Phase separation is characterized by a pronounced increase in the scattering at small Q.

**DISCUSSION**

The scattering intensity $I_Q$ from a sample with precipitates is $I_Q \propto V_p C_p (\rho_p - \rho_m)^2 P(Q)$ where $V_p$ is the total volume in the precipitate phase, $C_p$ is the volume fraction of particles in the precipitate, and the contrast $(\rho_p - \rho_m)^2$ is determined by the difference between the neutron
scattering length densities $\rho_p$ in the precipitate phase and $\rho_m$ in the matrix phase [13]. $P(Q)$ is the precipitate single particle structure factor ($P(0)=1$).

In the Guinier approximation [14], valid for precipitate domain sizes $L$ where $QL << 1$, the single particle structure factor can be written as $P(Q) = \exp\left(-Q^2 R_G^2 / 3\right)$, where $R_G$ is the radius of gyration of a particle. The inset of figure 2 shows a Guinier plot ($\ln(I_Q)$ vs. $Q^2$) for the SANS data at 1014 minutes. The solid line is a least squares fit to the small $Q$ range of the data. The slope of the line can be used to estimate $R_G$, and the intercept at $Q=0$ is the prefactor in $I_Q$ above. The results of Guinier fits to several spectra spanning the observed time range are given in Table I. Interestingly, $R_G$ changes very little over the entire time during which extra SANS is visible. The typical value of 25 nm is comparable to the finite size of crystallites inferred from measured widths of x-ray bragg peaks in the phase separated region [5]. Those experiments probed much larger values of $x$, and since the starting HS crystals generally have a crystallite size large compared to 25 nm there is not an obvious reason why the precipitate domain size and crystallite size should be similar. Magnetic resonance measurements have been reported at lower pressures where the $^3$He forms liquid bubbles in a solid $^4$He matrix [8]. There the typical bubble size is several microns, much larger than the estimate obtained in the present work.

One problem apparent from the present analysis is that the measured $Q$ range does not have much overlap with the $Q$ range where the Guinier analysis is valid for $R_G$=25 nm. Clearly there is a need for more data at lower $Q$.

Both the scattering extrapolated to $Q=0$ (see Table I) and the total scattering integrated over the detector (Figure 1) do change markedly with time. The reason for the continued increase in intensity is not completely clear. Two limiting possibilities come to mind: (1) Over time there is continued creation of small $^3$He rich domains with approximately the same size, and little domain growth. The intensity grows because the total volume fraction in the precipitate phase, $C_p$, is increasing. (2) At early times many similarly sized $^3$He rich domains are created, however the concentration, $c_p^3$ of $^3$He in such a domain changes drastically over time from an initially small value to one approaching 1. In this picture the change in contrast between the domains and the matrix is responsible for the growth in intensity. This occurs because of $^3$He atoms from outside the domain exchanging with $^4$He atoms inside it. The values of $c_p^3$ necessary to match the Guinier fits under these assumptions are shown in Table I.

Table I. Results of Guinier Fits (see text).

<table>
<thead>
<tr>
<th>time (min)</th>
<th>$R_G$ (nm)</th>
<th>$I_0 / I_0^{\infty}$</th>
<th>$c_p^3$</th>
</tr>
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<tbody>
<tr>
<td>535</td>
<td>24</td>
<td>0.1</td>
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<td>0.78</td>
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<td>856</td>
<td>25</td>
<td>0.58</td>
<td>0.85</td>
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<tr>
<td>935</td>
<td>26</td>
<td>0.70</td>
<td>0.90</td>
</tr>
<tr>
<td>1014</td>
<td>27</td>
<td>1.0</td>
<td>1</td>
</tr>
</tbody>
</table>
The same values also match the measured integrated intensity. If the late time scattering is
examined, and the precipitates assumed to be monodispersed spheres of essentially pure $^3$He,
the number of such spheres needed to match the measured intensity extrapolated to $Q=0$ is equal
within error to the number of domains calculated from the known value of $x$. The consistency of
the estimates of the sphere sizes with the absolute intensity measurements is strong evidence that
the Guinier analysis is reasonable [14].

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