SPECIFIC HEAT OF SOLID $^4$HE

A Dissertation in

Physics

by

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ABSTRACT

Liquid $^4$He enters the superfluid state and flows without friction below 2.176 K at zero pressure limit. A similar phenomenon has been observed in solid $^4$He, in which a fraction of the solid seems to decouple from the motion of the surrounding lattice. This phenomenon was first observed in 2004 with torsional oscillator technique that detected the apparent presence of non-classical rotational inertia (NCRI), which can be associated with a new state of matter called a supersolid. There are many theoretical works carried out on this subject, but none of the present models can explain all of the experimental features. More experimental work is needed to understand the microscopic picture of NCRI.

If the apparent NCRI stems from a genuine transition between the normal solid and supersolid phases of $^4$He, it is interesting to consider whether there should be a heat capacity anomaly accompanying this phase change. This question motivated us to carry out high resolution measurements of the specific heat in solid helium.

To settle this issue we were required to address the primary problem limiting the sensitivity of previous heat capacity studies, i.e., a large addendum heat capacity of the calorimeter itself. We overcame this obstacle by constructing the calorimeter of silicon. In our study we found a broad peak in specific heat of solid $^4$He on top of the Debye $T^3$ term. The excess specific heat peaks at a temperature near the onset of NCRI, indicating the likelihood that we have observed the thermodynamic signature related to supersolidity.
Solid $^3$He-$^4$He mixtures were also studied. The specific heat peak was found to be independent of the $^3$He impurity concentration. With sufficient amounts of $^3$He, phase separation was observed below 150 mK, together with the specific heat peak, proving that the peak itself is not due to phase separation.
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Chapter 1

Introduction

1.1 Superfluidity

In 1938 Kapitza measured the viscosity of liquid helium below 2.176 K, later named the \( \lambda \)-point temperature, and found that helium possesses an abnormally low viscosity [Kapitza 1938]. In fact, Allen and Misener reported that its value at their lowest temperature of measurement was at least 1500 times smaller than that of the high temperature (> ~2 K) liquid [Allen 1938]. Even prior to these studies, extremely different behavior above and below the \( \lambda \)-point had been noted [Keesom 1933]. This ultimately led investigators to suspect the existence of two different “phases” of the liquid, designated helium I and helium II. We now know that these regions in the phase diagram are associated with an entirely normal fluid (I) and the presence of a superfluid component (II), which tends to 100% as the temperature goes to zero.

Superfluidity is usually associated with Bose-Einstein condensation (BEC). Cooling bosons to a very low temperature causes them to condense into their lowest accessible quantum state, resulting in extremely different macroscopic behavior. The predicted temperature below which ideal bosons start moving into the lowest energy level in helium is 3 K, only 30% higher than the \( \lambda \) temperature [London 1938]. Very soon Tisza proposed that the anomalous flow behavior in helium II phase could be qualitatively understood by a two-fluid model, in which the atoms undergoing BEC
behave completely without friction while the rest of liquid behaves like an ordinary liquid [Tisza 1938]. In 1941, Landau proposed a two-fluid hydrodynamic model [Landau 1941] and he identified the quasiparticle (an excitation of the system from the ground state) of a Bose liquid as one of two types: phonons and rotons [Landau 1947]. Although Landau rejected the view that BEC of an ideal gas might have something to do with the helium II, Bogoliubov proved that an excitation spectrum of the Landau quasiparticle is a natural consequence of condensation in a Bose system with weakly repulsive interactions [Bogoliubov 1947]. The liquid helium problem, instead of the dilute Bose gas, was treated by Feynman and Cohen [Feynman 1955]. The excitation spectrum of real liquid helium II that they predicted is consistent with neutron scattering experiments [Cowley 1971]. The current understanding of superfluidity is “a coherent amalgam of the ideas of London on the one hand, and Landau on the other, as refined and amplified by many subsequent workers” [Leggett 1999].

The relationship between superfluid $^4$He and BEC is not straightforward. Although BEC is not directly related to the appearance of a superfluid, the superfluid phase is characterized by a “generalized BEC” in modern theory of superfluidity [Leggett 1999]. If the assumptions of “generalized BEC” in reference [Leggett 1999] are applied, the entire superfluid component can be treated as a coherent phase and described by Eq. 1.1

$$\psi(r,t) = \psi_0(r,t) \exp[iS(r,t)]$$ (1.1)
where $\psi_0$ determines the superfluid density and $S$ is the phase. The superfluid velocity is defined from the momentum operator $-i\hbar \nabla$, shown in Eq. 1.2 if the superfluid density is uniform:

$$\tilde{v}_s = \frac{h}{m} \nabla S$$  \hspace{1cm} (1.2)

The definition of the velocity leads to an irrotational flow, $\nabla \times \tilde{v}_s = 0$ and implies that in a simply connected region the close contour integral is zero. However, experimental results found that superfluid helium can rotate with a finite $\nabla \times \tilde{v}_s$ [Osborne 1950]. Two-fluid theory was amended to account for this effect: $\nabla \times \tilde{v}_s = 0$ is still correct except at isolated singular lines in the fluid, placed on the axis of rotation. Such a singular line is called a vortex filament. The integral around a path that encloses such a vortex line can be calculated as Eq. 1.3:

$$\oint P_s \cdot d\bar{l} = nh, n = 0,1,2,...$$

$$\oint \tilde{v}_s \cdot d\bar{l} = nh / m$$  \hspace{1cm} (1.3)

This equation was first proved by Onsager and later by Feynman [Feynman 1956]. The quantization of the contour integral and the concept of vortices have been experimentally observed [Vinen 1961] [Rayfield 1963].
1.2 Supersolidity

Shortly after London had proposed a relationship between BEC and superfluidity, Wolfke raised the possibility that a superfluid-like phase, later called a supersolid state, might also occur in solid helium [Wolfke 1939]. A number of more careful considerations were made in the 1970s, and now there are more than 100 publications on this subject. The early theoretical attempts spurred experimental efforts to look for the new phase in solid $^4$He. In 2004 the first probable observation of the supersolid phase was reported [Kim 2004] with a torsional oscillator (TO) technique. Three original reviews of experimental and theoretical work on this subject, as well as a perspective are recommended [Meisel 1992] [Prokof'ev 2007] [Balibar 2008] [Chan 2008]. The mechanism behind the possible superfluidity of solid helium is still under debate. In this section a summary of theoretical and experimental papers on the subject is briefly reviewed.

1.2.1 Theoretical background

Bose-Einstein condensation was first thought to be prohibited in perfect crystal by Penrose and Onsager, [Penrose 1956] and later Chester pointed out that the proof of Penrose fails if defects are considered [Chester 1970]. “Perfect” or sometimes called commensurate here means that each particle is localized on a lattice site and each site is occupied by a particle. Chester also pointed out that there exist systems of interacting bosons which exhibit both crystalline order and superfluidity; such a quantum solid might
not be a perfect crystal in its ground state. In 1970 Leggett suggested to look for non classical rotational inertia (NCRI) as evidence of the supersolid phase [Leggett 1970]. In his work the solid can be either crystalline or amorphous, but the calculated superfluid fraction will be very small (less than $10^{-4}$ for solid helium at zero temperature). In 1976, Saslow extended Leggett’s theory and found the supersolid fraction to be between 0.05 and 0.2 at zero temperature for crystalline helium [Saslow 1976].

The relationship between the ground state of a solid and BEC (or supersolid) is an interesting question. There are some theoretical and numerical results similar to the conclusion of Penrose. Shi showed that there is no NCRI in absence of defects [Shi 2005]. Prokof’ev and Svistunov proposed that defects are necessary for supersolid [Prokof'ev 2005]. Ceperley, Bernu and Clark also showed that there is no NCRI and BEC in a perfect solid [Ceperley 2004] [Clark 2006b]. Boninsegni et al. suggested that a commensurate crystal is insulating [Boninsegni 2006].

There are also studies that showed NCRI or BEC is possible in perfect crystals. Galli et al. found that in a perfect crystal at least up to 54 bars the condensate fraction in the hcp solid is $5 \times 10^{-6}$ [Galli 2005] but Galli and Reatto suggested a vacancy induced BEC later [Galli 2006]. Zhai and Wu proposed a wave function that describes supersolidity in a perfect crystal [Zhai 2005]. Cazorla and Boronat found a supersolid fraction of about 0.08 at zero temperature for a commensurate solid by studying the localization of liquid $^4$He [Cazorla 2006]. With similar method as Cazorla and Boronat, Saslow and Jolad also found NCRI is possible in a defect-free crystal [Saslow 2006].

The ground state of solid helium is another interesting question. Anderson and Huse suggested that ground state of solid helium is incommensurate with zero point
vacancies, based on X-ray results [Anderson 2005], although the X-ray result might not be necessarily sensitive enough and span enough temperature range to support their idea [Fraass 1989]. Besides vacancies, dislocations and grain boundaries are well known defects in crystals. We are going to organize the theoretical and numerical results by different kinds of defects.

1.2.1.1 Point defects

The condensation of point defects like vacancies was the first microscopic mechanism proposed for the subject of supersolidity. Andreev and Lifshitz suggested that zero point defects (called defectons by the authors) exist at T=0 and do not violate crystal periodicity [Andreev 1969]. At low temperature these localized defects convert to excitations that move freely through a lattice [Andreev 1969]. Guyer also considered the presence of vacancies as a possible mechanism for the mobility of $^4$He particles and predicted the supersolid transition happens below 0.1 mK with a superfluidity density $\sim10^{-6}$ [Guyer 1971]. By using a quantum lattice gas model, Cheng concluded that there is no supersolid without vacancies and the transition temperature in a real solid is about 10 to 100 mK [Cheng 1976]. Later Cheng predicted the excitation spectrum of solid helium and encouraged experimentalist to detect supersolid phase with neutron scattering [Cheng 1981]. After the observation of apparent NCRI in 2004, there were more theoretical studies attending to explain NCRI by point defects [Prokof'ev 2005] [Dai 2005] [Galli 2006].
The experimental results of the vacancy concentration are a little confusing. Burns and Goodkind concluded that data from X-ray, NMR and acoustic measurements indicated the presence of vacancies while the melting curve and pressure measurement in solid could be explained with only lattice vibrations [Burns 1994]. However, the experiments against the existence of vacancy condensation generally have higher sensitivity. For example, X-ray diffraction set an upper limit of 0.1% based on the temperature dependence of the lattice constant [Fraass 1989], while pressure measurement set an upper limit of $4 \times 10^{-5}$ for the solid near the melting curve [van de Haar 1992]. The vacancy density limit from experiments is much smaller than the non-classical rotational inertia fraction (NCFIF) observed (see 1.2.2.1) if the superflow is a direct result of the condensation of point defects.

1.2.1.2 Dislocations

Dislocations were also considered as a possible explanation of superfluidity in solid $^4$He. Boninsegni et al. proposed that screw dislocations in $^4$He possess a superfluid core at zero temperature, while the same dislocations in H$_2$ are insulating [Boninsegni 2007].

Recent experimental results support that the $^3$He dependence of NCRI detected with a TO is correlated to the condensation of $^3$He atoms onto the dislocation network in solid $^4$He [Kim 2008]. Dislocation lines in solid $^4$He form a random three-dimensional network, where the lines can intersect with each other to form nodes. $^3$He atoms condense
onto dislocations and inhibit their motion. An important parameter characterizing the dislocation network is the length between fixed points, which is either limited by the dislocation segment length between nodes or between $^3$He impurities [Iwasa 1980].

There is a characteristic temperature when the distance between two neighboring $^3$He atoms is shorter than the dislocation line segment between nodes. The transition temperature of NCRI as a function of $^3$He concentration was found to track this characteristic temperature associated with the condensation of $^3$He onto the dislocation network [Kim 2008].

An increase in the shear modulus has been observed, which shares the same temperature and $^3$He concentration dependence as that of NCRI [Day 2007]. The shear modulus behavior was explained in terms of a dislocation network that is pinned by $^3$He at the lowest temperatures but becomes mobile above 100 mK. It is difficult to believe there is no relationship between the shear modulus anomaly and NCRI, but how the two phenomena are related is still not clear. It has been suggested that a rigid dislocation network is required by the long range phase coherence in supersolidity [Day 2007]. The role of the dislocation network in NCRI found in porous materials [Kim 2004] [Kim 2005], especially the 7 nm dimension limit in Vycor glass, is not understood.

The results of shear modulus and NCRI could also be qualitatively connected without supersolidity. If the TO and the solid $^4$He are treated as a whole system, the stiffening of solid $^4$He will cause an increase of the total rigidity of the system and therefore lower the resonant period. Simulations by our group with finite element method (FEM) of some cells used in TO studies indicate that the reduction in the calculated resonant period drop due to the shear modulus increase is quantitatively inconsistent with
experiments. Those results listed in Table 1-1 have been presented in references [Clark 2008] [Clark 2008b].

Table 1-1: Summary of the finite element calculation. Similar calculation has been done in the Vycor cell described in reference [Kim 2004]. The $C_{44}$ of Vycor is 500 times larger than of solid $^4$He. If $^4$He and Vycor are treated together, the total shear modulus is determined by that of Vycor. FEM calculation shows that a 6% of shear modulus change in Vycor-helium system is needed to be responded for the NCRI signal, which is not seen by Suzuki and collaborators [Kobayashi 2008].

* For two cells used in [Kim 2004b], the calculated $\delta f/f$ is almost unchanged with and without the barrier in the simulations [Clark 2008b]. The difference in $\delta f/f$ between two cells is mainly due to the different amount of Be-Cu used.

<table>
<thead>
<tr>
<th>Label</th>
<th>Helium space (mm) (diameter/height/width)</th>
<th>$\delta f/f$, calculated “Beamish” effect [for $\Delta c_{44}/c_{44} = 20%$] (ppm)</th>
<th>measured $\delta f/f$, (ppm)</th>
<th>NCRIF</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Clark 2007] Be-Cu cell</td>
<td>Cylinder 9(d); 5(h)</td>
<td>1.98</td>
<td>11.2</td>
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<tr>
<td>[Clark 2007] AgCu cell</td>
<td>Cylinder 10(d); 6(h)</td>
<td>1.38</td>
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<tr>
<td>[Aoki 2007]</td>
<td>Cylinder 10(d); 7(h)</td>
<td>High Frequency 0.065</td>
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<tr>
<td></td>
<td></td>
<td>Low Frequency 0.43</td>
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<td>0.1%</td>
</tr>
<tr>
<td>[Kim 2004b]</td>
<td>Annulus 10(d); 5(h); 1(w)</td>
<td>0.38*</td>
<td>38</td>
<td>~1%</td>
</tr>
<tr>
<td>[Kim 2004b]</td>
<td>Blocked annulus 15(d); 5(h); 1(w)</td>
<td>0.08*</td>
<td>~1</td>
<td>0.02%</td>
</tr>
</tbody>
</table>

In summary, dislocation network seems to be strongly related to the apparent NCRI from the $^3$He impurities dependence. Experimentally, the maximum NCRI observed so far is 16% [Rittner 2008] and the typical dislocation density in solid $^4$He is from $10^5$ to $10^9$ by ultrasound experiments [Iwasa 1979] [Iwasa 1980] [Tsuruoka 1979].
The atoms inside the dislocation network with a density of $\sim 10^{13}$ cm$^{-2}$ yield $\sim 1\%$ NCRIF. Although such a dislocation density is larger than that has been measured, it is not impossible in bad quality samples. There are other possibilities. One is that not only atoms inside the dislocation lines but also those outside are involved in NCRI because of the stain field of the dislocation network. Another possibility is that the atoms undergo transition might be less than those participate in the flow. For example, superfluidity is associated with BEC transition, but superfluidity density is 100$\%$ while only around 10$\%$ of atoms are condensed to ground state at zero temperature [Balibar 2003]. Because NCRI was also observed in Vycor and porous gold, an important question to be answer in the future is that how the dislocation network looks like in the porous materials.

1.2.1.3 Grain boundaries

Grain boundaries have been also studied in detail [Burovski 2005] [Sasaki 2006] [Pollet 2007]. It has been proposed that liquid $^4$He exists between crystalline grains and results in the superflow observed in solid. Onset of superfluidity in helium films has been theoretically understood with Kosterlitz-Thouless theory [Kosterlitz 1973] and experimentally studied [Chester 1973] [Bishop 1978] [Agnolet 1989]. At 200 mK, the effective thickness of the superfluid film is about 1/5 of a monolayer. The total superfluid density scales with the total area of the grain boundaries.

The same order of magnitude of NCRIF has been observed in samples grown by constant pressure/temperature method, blocked capillary method and grown in porous
materials [Clark 2007] [Kim 2004b] [Kim 2004]. The surface area between different quality samples varies by $10^5$ times. The 1% NCRIF, typical value for blocked capillary growth samples, requires an average crystallite size with linear dimension of 20 nm, which is 5000 times smaller than the measured value [Schuch 1962] [Armstrong 1979].

Balibar et al. suggested that grain boundaries connect larger number of micro-sized pockets of liquid [Balibar 2007]. However, no liquid regions have been detected so far. Furthermore, the maximum coexistence pressure of liquid and solid on the melting curve below 1 K is only 25 bar, while NCRI has been detected at pressures as high as 137 bar [Kim 2006].

Dash and Wettlaufer treated the role of the liquid differently [Dash 2005]. They proposed slippage of the solid due to grain boundary premelting between the solid and the container wall as an alternative explanation for NCRI. It is difficult to explain the fact that the same order of magnitude of NCRIF has been observed in bulk samples and in porous materials. It can not explain the critical velocity effect in [Kim 2004] [Kim 2004b] either.

In summary, grain boundaries can’t explain the fact of similar NCRIF in different quality samples.

1.2.1.4 Glasses and vortex liquid

Other than traditional crystalline defects, it has been suggested that the observed NCRI is the consequence of solid helium forming a glassy state or the inclusion of glassy
regions in the sample [Boninsegni 2006b] [Prokof'ev 2007] [Nussinov 2007] [Grigor'ev 2007] [Balatsky 2007]. A specific heat that is linear in temperature is characteristic of glasses [Phillips 1972] [Anderson 1972] and would therefore provide evidence for the existence of a helium glassy phase. No such linear term has been clearly detected with direct calorimetry methods. Still, the existence of a linear specific heat has been under debate prior to the work of this dissertation. We clearly show that there is no linear term similar to what was reported in solid $^4$He in previous heat capacity measurements. Further discussion will be deferred to 1.3.2 and 3.2.1. In [Balatsky 2007], Balatsky et al. mistreated the excess heat capacity due to $^3$He-$^4$He phase separation that was observed by Clark and Chan [Clark 2005]. Balatsky et al. analyzed the phase separation entropy as that of solid $^4$He, which is inappropriate.

Anderson conjectured that solid helium is an incommensurate three-dimensional density wave rather than a solid [Anderson 2007]. He described NCRI as the rotational susceptibility of a vortex liquid phase. The true transition for the vortex state is believed to be much smaller than the onset temperature of NCRI. Vortices move in response to the superfluid so as to counteract or reduce the circulating superflow. The high temperature tail of NCRI reflects the finite response time of vortices to the oscillating flow fields generated by the TO. The coupling of $^3$He atoms to the cores of such vortices will further slow their response, because they must be dragged through the lattice. The consequence of this interaction is to extend the apparent onset to higher temperature, as observed. In addition, it was found that for isotopically pure solid $^4$He the NCRIF data of eight different samples collapse onto a single curve with a distinctly sharper onset temperature
[Clark 2007]. A frequency effect consistent with this theoretical model has also been observed [Aoki 2007], described in 1.2.2.1.

1.2.1.5 Summary

In summary, among hundreds of theoretical and numerical works carried out on the subject of supersolidity, (most of them after 2004), disorder is generally believed to be of essential importance. Although which types of disorder and how they facilitate NCRI are still unclear, a dislocation network is currently the best candidate. However, the primary mechanism behind the behavior of solid $^4$He below ~200 mK is still far from understood.

1.2.2 Experimental searches

1.2.2.1 Torsional oscillator experiments

There were a lot of experimental efforts to look for the superfluid-like property in solid $^4$He after the fundamental theoretical work in 1970s. In spite of many attempts the first convincing evidence, obtained with a TO, supporting a supersolid phase of $^4$He was not put forth until 2004 [Kim 2004] [Kim 2004b]. This observation has been replicated
in various laboratories by the same technique [Rittner 2006] [Aoki 2007] [Kondo 2007] [Penzev 2007] [Rittner 2007].

In the TO used by Kim, the sample cell containing an annulus of solid $^4$He was suspended by a Be-Cu rod and oscillated at resonance. The resonant period of an ideal torsional oscillator is $2\pi\sqrt{\frac{I}{K}}$, where $I$ is the moment of inertia and $K$ is the spring constant of the Be-Cu rod. Therefore, a decrease in the moment of inertia reduces the resonant period of the oscillator. If the temperature dependence of the spring constant is known, the moment of inertia of the sample container with or without the solid helium inside can be calculated by measuring the resonant period. When part of the solid helium acquires superfluid-like properties and thus stops contributing to the moment of the inertia, an unexpected drop in the moment of inertia is observed. This disappearance of a portion of the mass is called non-classical rotational inertia. The ratio of missing atoms to the total number of atoms is defined as the NCRIF. Kim observed a period drop below 200 mK and interpreted it as NCRI, thus claiming evidence in support of a supersolid state. A typical trace of the resonant period is shown in Figure 1-1. The temperature dependence of the apparent NCRI is characterized by the saturation in the low temperature limit and a gradual decay to zero at high temperature.
The most important control experiment in previous TO studies was the blocked annulus experiment. If the period drop is due to solid helium in the annulus entering the supersolid phase, then a barrier in the annulus should hinder the superflow and reduce the period change. The effect was observed by Kim and Chan [Kim 2004b], and later

**Figure 1-1**: Typical temperature dependence of the resonant period. The dashed line is the expected classical helium moment of inertia as the function of temperature.
confirmed by Rittner and Reppy [Rittner 2008b]. In the recent experiment by Rittner and Reppy, 16% NCRIF was observed in a 73 μm annulus, and the period drop vanished after the annulus was blocked in the same cell. The blocked annulus experiment supported the picture that NCRI resulted from the superflow along the annulus.

The temperature where we can distinguish NCRI from the noise is called the onset temperature $T_O$. $T_O$ is found to vary between 100 to 300 mK in studies with commercially ultra high purity (UHP) $^4$He (about 0.3 ppm $^3$He impurity). Such a variation occurs not only from cells to cells but also between samples grown within the same TO. Recent measurements on the same sample at two different frequencies, with a double frequency oscillator, found that the onset temperature is also a function of the resonant frequency [Aoki 2007]. The conventional torsional oscillator made of one solid $^4$He container attached to a single torsion rod has one resonant frequency. Aoki et al. used an oscillator containing two masses, and only one of them was the $^4$He container. When two masses moved in phase $^4$He was rotating at 496 Hz while when they moved out of phase, the resonant frequency was 1173 Hz. For the same sample onset temperature at 1173 Hz is found to be higher, consistent with the vortex liquid model proposed by Anderson [Anderson 2007].

The onset temperature can be modified by the addition of $^3$He impurities [Kim 2004] [Clark 2007] [Kim 2008]. It is found that $^3$He atoms broaden the transition and typically increase the onset temperature. A possible understanding of the $^3$He dependence is the condensation of the $^3$He atoms onto the dislocation lines [Kim 2008], as discussed in 1.2.1.2.
Variations in the saturated NCRIF at low temperature are also observed. NCRIF varies with different cell geometries and sample growth procedures. Samples in a thin 0.15 mm width annulus were found to have NCRIF values as high as 16% [Rittner 2008] while NCRIF values in thicker annular channels were on the order of 1%. Samples in open geometries were generally found to have smaller NCRIF than those confined to

**Figure 1-2**: Overview for a range of supersolid fractions as a function of surface to volume ratio from different researchers for bulk $^4$He. The red star for second Cornell is from the new result Rittner and Reppy presented in APS March meeting 2008 [Rittner 2008b].
annular channels. In most cases, larger surface to volume ratio samples result in larger NCRIF in bulk solid $^4$He, but samples confined in porous materials display NCRIF within couple percents. The surface to volume ratio dependence of NCRIF is plotted in Figure 1-2. There are a few notable exceptions. One recent experiment found that in an annular cell of width 1.3 mm the NCRIF was on the order of 0.01%, the smallest seen to date [West]. The sample quality effect of NCRI has also been studied within a single TO. Solid $^4$He crystals grown under constant pressure or constant temperature are of higher quality, and perhaps for this reason possess smaller NCRIF values [Clark 2007]. NCRIF in these high quality samples shows no observable dependence on annealing, while samples grown under the blocked capillary method typically exhibit a reduction in NCRIF following annealing [Rittner 2006] [Clark 2007]. It has also been observed that NCRIF increased after annealing. [Penzev 2007] [Clark 2007]. Other than geometry and sample quality effects, the dependence of NCRIF on pressure and $^3$He concentration have also been investigated [Kim 2006] [Kim 2008]. NCRIF extrapolates to zero near 170 bar. $^3$He impurities above 0.3 ppm tend to suppress the NCRIF. In short, NCRIF seems to be affected by many experimental parameters and among those parameters the annealing effect and pressure dependence can be associated with changes in the sample quality.

NCRIF is also influenced by the oscillation amplitude (or velocity) of the TO. NCRIF is only attenuated above some critical velocity. Typical values for the critical velocity are on the order of ~ 10 μm/s, but the precise value varies with sample quality and perhaps other parameters such as geometry of the container. Hysteresis of NCRIF following changes of velocity and temperature was also noticed by two groups [Aoki 2007] [Clark 2008b].
A TO study of solid para-H$_2$ has been carried out down to 20 mK to search for NCRI [Clark 2006]. A resonant period drop was observed below 180 mK but it was not a consequence of superflow for the following reasons: (1) the blocked annulus control experiment found a larger period decrease; (2) no critical velocity was observed; (3) extremely long relaxation times were observed. The period drop in solid H$_2$ was associated with the motion of residual ortho-H$_2$ molecules in the solid; details are in Clark’s dissertation [Clark 2007b].

1.2.2.2 Mass flow experiments

Prior to Kim & Chan’s TO study in 2004, there were several dc mass flow experiments that searched for supersolidity in bulk $^4$He. There was no observed mass flow in plastic flow measurements [Meisel 1992] [Andreev 1969b] [Suzuki 1973] [Tsymbalenko 1976] [Dyumin 1989] [Zuev 1998], which spanned pressures from the melting curve (25 bar) up to 150 bar. However, the minimum temperature in these experiments was only 0.5 K. Greywall looked for mass flow through small capillaries connecting two helium reservoirs with a pressure difference of 1 to 2 bar [Greywall 1977]. There was no mass flow observed between 25 and 50 bar down to 30 mK. Bonfait later extended the flow experiment down to 4 mK on the melting curve, and failed to observe any mass flow [Meisel 1992] [Bonfait 1989]. The $^3$He concentrations in these flow experiments usually were not specified.
There were four dc flow experiments after the NCRI was observed in bulk $^4$He. Day studied the flow in solid $^4$He by squeezing the solid through an array of glass capillaries of 25 $\mu$m in diameter [Day 2006]. There was no anomaly found between 35 mK and 1 K. Day also studied the pressure induced flow of solid $^4$He within Vycor glass and found no mass redistribution that could mimic supersolid decoupling [Day 2005].

Another experiment investigated mass flow in liquid solid coexistence and observed a flow of liquid through the solid phase [Sasaki 2006]. This effect is explained as the superflow of liquid $^4$He through either grain boundaries or channels formed by grains and the sample cell walls [Caupin 2008]. A recent flow experiment found superfluid-like transport of mass through solid $^4$He off the melting line [Ray&Hallock unpublished]. In this experiment, a solid sample was created between two Vycor pieces. Helium in Vycor, which remained in the liquid state for the pressures studied, was connected to liquid reservoirs at high temperature. Atoms could then be fed into the solid via one piece of Vycor. The pressure change on the other piece of Vycor was explained as the flow through the solid. Because of the heat brought down by the liquid inside the Vycor, the minimum temperature of this experiment is only 400 mK. This flow behavior was only observed in samples grown from superfluid but not in samples grown with blocked capillary method.
1.2.2.3 Pressure measurement

The pressure at constant volume of the solid phase has been measured in order to detect the presence or absence of zero point vacancies, glassy subsystems, and/or a thermodynamic anomaly. The temperature dependence of pressure for a simple Debye crystal, like $^4$He, is dominated by thermal phonons and therefore goes as $T^4$. If the vacancies undergo BEC transition or there is another excitation besides phonons, the temperature dependence of the pressure is expected to show an anomaly. For example, if the vacancies are under Bose-Einstein condensation then the temperature dependence of pressure should be $T^{5/2}$ [Landau 1980]. Thus, one looks for deviations from Debye behavior using an ultra-sensitive pressure gauge such as that of the Straty-Adams type [Straty 1969], which can have a sensitivity on the order of microbar (corresponding to a few parts in $10^8$).

For Debye crystals the pressure can be related to the specific heat through the relation Eq. 1.4:

$$\left( \frac{\partial P}{\partial T} \right)_V = \frac{\gamma C_V}{V}$$  \hspace{1cm} (1.4)

where $\gamma$ is Grüneisen parameter and $V$ is the molar volume. The Grüneisen parameter is almost independent of temperature for $^4$He below 0.5 K. In a general case, the specific heat and pressure can be connected by Eq. 1.5:

$$\left( \frac{\partial P}{\partial T} \right)_V = \sum_i \frac{\gamma_i C_{Vi}}{V}$$  \hspace{1cm} (1.5)
where $\gamma_i$ and $C_i$ are the Grüneisen parameter and the heat capacity of the $i$th subsystem [Grigor'ev 2007].

No anomaly was detected in the pressure experiments down to 1.5 mK [van de Haar 1992] [Remeijer 1997] before the Kim’s experiments in 2004. In the most recent pressure measurements, carried out between 100 to 500 mK (the authors claimed the minimum temperature was 50 mK but the data shown was only down to 100 mK), an additional $T^2$ contribution, which became dominant at temperature less than 300 mK, was found aside from the usual phonon $T^4$ contribution [Grigor'ev 2007]. This additional $T^2$ term in pressure decreased by an order of magnitude after the sample was annealed. Given the scatter in the pressure data, the reduced value is almost indistinguishable from zero. A $T^2$ term in pressure indicates a linear specific heat, which was then interpreted as evidence for a glassy phase [Grigor'ev 2007]. More discussions about the linear specific heat will be presented later in 1.3.2 and 3.2.1.

1.2.2.4 Shear modulus, sound, neutron scattering, thermal conductivity, and melting curve pressure measurements

Day and Beamish measured the shear modulus of solid $^4$He down to 20 mK [Day 2007]. They found considerable enhancement of the shear modulus occurred below 200 mK, with similar $^3$He concentration and temperature dependencies as in TO experiments [see Figure 1-3]. The relationship between these two experiments is not yet well understood.
Goodkind and his coworkers [Ho 1997] reported an anomaly in ultrasound measurements. The sound velocity of solid $^4$He increased sharply below 200 mK for samples containing minute concentrations of $^3$He (less than 14 ppm). The anomaly was explained as a continuous phase transition from a Bose condensed state to a normal state. The new phase was associated with coherent waves carried by so called thermally activated excitations. Syshchenko and Beamish performed transverse ultrasound measurements in single crystal $^4$He [Syshchenko 2008]. In one out of eleven crystals they observed a very large increase in attenuation and a corresponding decrease in the

Figure 1-3: Shear modulus anomaly in solid $^4$He for a range of $^3$He impurity concentrations, figure adopted from [Day 2007].
velocity around $T = 95$ mK. The transition was associated with a very long time constant. The origin of the transition is unclear.

A fourth sound mode in supersolid helium was predicted by Saslow and Liu in the 1970s [Saslow 1977] [Liu 1978]. According to their theory the velocity of this mode for a 1% supersolid fraction should be about 50 m/s. Aoki et al. have looked for fourth sound propagation in solid $^4$He in the temperature and pressure ranges of 40 to 500 mK and 25 to 56 bar, respectively, but the search so far has turned out negative [Aoki 2007] [Aoki 2008]. The experiment was done by generating a heat pulse and detecting the thermal response at the opposite end of the sample with a superconducting-edge bolometer. It is unclear if the bolometer has sufficient sensitivity to detect the possible fourth sound mode. Moreover, it is possible that the critical velocity of the supersolid phase was exceeded during each heat pulse.

A recent sound measurement observed low frequency resonance modes that depend on the presence of defects in the solid $^4$He sample [Mukharsky 2007]. The experiment was performed using a low-frequency (500 Hz compared with MHz in ultrasound measurements), low-level mechanical excitation (1 Pa compared with 300 Pa in the mass flow measurements). Anomalous features were found below 0.8 K, which were absent in solid $^3$He. How it is related to NCRI observed in TO experiments is uncertain.

Several neutron scattering measurements on solid $^4$He have also been carried out [Wallacher 2005] [Adams 2007] [Diallo 2007]. However, indications of a supersolid phase have not been detected.
The thermal conductivity of solid $^4$He was measured down to 30 mK [Armstrong 1979], but no significant departure from the $T^3$ phonon conductivity was observed. The samples in this study were grown by blocked capillary method and believed to be polycrystalline.

The pressure of the solid-liquid coexistence has been measured as a function of temperature with high accuracy [Todoshchenko 2006] [Todoshchenko 2007] [Todoshchenko 2008]. The pressure along the melting curve is determined by the entropy and density differences between liquid and solid. The melting curve measurements observed no deviations from the phonon contributions. The scatter in the data after correcting for an instrumental effect (~4 μbar) is roughly ~2 μbar. The density of liquid $^4$He was measured carefully with a superconducting microwave cavity along the melting curve down to 0.1 K, from which the entropy of the solid $^4$He was calculated [Hanson 1976]. Assuming the liquid specific heat goes as $T^3$, only the phonon contribution was found in the solid along the melting curve.

1.3 Previous specific heat measurements on solid $^4$He

Although the observation of NCRI has been replicated in various laboratories, no thermodynamic signature of the possible supersolid transition has been seen before our work. However, previous experimental attempts imply that there is a new state in solid $^4$He that we do not completely understand, although the experimental work we have done does not provide us enough hints to describe the microscopic picture. If the NCRI stems
from a genuine transition between the normal solid and the supersolid phases of $^4\text{He}$, it is interesting to consider whether there is a heat capacity anomaly accompanying this phase change. That is the motivation behind our high resolution measurements of the specific heat of solid helium.

Although people looked for the supersolid phase before 2004 with many different techniques, there is no specific heat measurements designed for probing the supersolid phase. In fact, before the NCRI was observed in 2004, the last paper on the specific heat of solid $^4\text{He}$ was in 1980, and only extended to 0.1 K. Early heat capacity measurements all agreed with the existence of the Debye phonon term but disagreed with each other in details. For example, it was unclear whether the specific heat is $T^3$ only or $T^3$ plus other dependences at low temperature. There are three heat capacity studies extending below 200 mK. Castles and Adams [Castles 1975] observed an excess linear heat capacity in addition to the Debye term. However, Hébral et al. found only a $T^3$-dependence down to 100 mK [Hebral 1980]. Clark and Chan found that the specific heat follows a $T^3$ dependence with a hint of upward deviation below 100 mK [Clark 2005].

### 1.3.1 Debye term

In an ideal crystal the Debye phonon model describes specific heat as Eq. 1.6:

$$C_v = \frac{12\pi^4 R}{5} \left(\frac{T}{\theta}\right)^3$$

(1.6)
where R is the gas constant and θ is the Debye temperature, which depends on density and has been measured in experiments.

Many measurements of the heat capacity of solid 4He have been carried out since the 1960s [Heltemes 1962] [Edwards 1965] [Sample 1967] [Gardner 1973] [Castles 1975] [Hebral 1980] [Clark 2005], all reporting the $T^3$-dependence expected for a Debye solid at sufficiently low temperature. As mentioned above, θ depends on density and therefore does the crossover to “pure” Debye behavior. For instance, a 21cc/mol solid sample only exhibits a $T^3$-dependence below 0.5 K while a 15 cc/mol solid already possesses this trait below 1 K. The departure from $T^3$ at high temperature has been recently explained in terms of phonon dispersion within the solid [Maris 2007].

### 1.3.2 Linear specific heat

Heltemes and Swenson measured the specific heat of 4He down to 0.3 K [Heltemes 1962]. The $^3$He impurity concentrations in 4He samples were not described, as is the case for many other papers discussed in this section. They found that the specific heat could not be described by a Debye function, since an anomalous linear term was observed. There was a tendency of a higher linear term at higher molar volumes. A linear term was also observed by Franck from 0.4 to 2 K, but it was about 5 times smaller in magnitude [Franck 1964]. Franck found that the linear term became 3 times smaller after annealing. Although Sample and Swenson observed the linear specific heat in 1967, they did not find any effect due to annealing or cooling the sample down slowly [Sample
Castles and Adams found a linear specific heat in samples annealed for two hours [Castles 1975].

Heltemes, Sample and Castles measured the specific heat of $^3$He too. The linear term was observed in most of the solid $^3$He samples as well. However, Greywall reexamined the solid $^3$He specific heat in 1977 and concluded that there is no evidence of linear contribution below 0.5 K [Greywall 1977b].

Castles, Franck and Greywall suggested the linear specific heat might come from vibrating dislocation lines. According to the analysis of Granato [Granato 1958], the dislocation heat capacity is linear above a characteristic temperature (for dislocation density $10^9$ cm$^{-2}$ in solid helium, this characteristic temperature is in the order of 0.1 K). However, the theoretical estimate of this contribution is at the very least 1000 times smaller than the observed linear deviations from Debye phonons.

These four experiments discussed above all fabricated the calorimeter with Be-Cu, which is linear in heat capacity. The linear terms reported were about one-third to one-tenth of the calorimeter linear heat capacity, indicating the mistreatment of background could be responsible for the linear term. There are other possibilities for the origin of the linear anomaly. Systematic errors like temperature calibrations and improper estimation of addenda heat capacities (e.g., stainless steel capillary) are possible candidates.

Clark and Chan used aluminum as the construction material of their calorimeter [Clark 2005]. Aluminum is superconducting below 1.17 K so its heat capacity is non-linear. Their results indicate that a much smaller linear term may be present down to 80 mK. The ratio of linear term to Debye term increases with decreasing temperature. However, at the base temperature of this experiment, the linear term to Debye term ratio
is only 10%. Considering the several percents uncertainty in this experiment, the systematic error of temperature calibration, and improper estimation of addenda heat capacities, the linear term is questionable.

The linear specific terms of several samples from different experiments are listed in Table 1-2. With higher resolution heat capacity measurement in our work, we conclude that there is no linear term of the same order of magnitude as reported in references [Heltemes 1962] [Franck 1964] [Sample 1967] [Castles 1975] [Clark 2005] (see 3.2.1 for details).

<table>
<thead>
<tr>
<th>Year</th>
<th>Density [cc/mol]</th>
<th>Linear term [J/[mol.K^2]]</th>
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<tbody>
<tr>
<td>[Heltemes 1962]</td>
<td>1962</td>
<td>14.50</td>
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<td></td>
<td></td>
<td>16.74</td>
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<td>20.64</td>
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<td>21.04</td>
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<tr>
<td>[Franck 1964]</td>
<td>1964</td>
<td>14.88</td>
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<td></td>
<td></td>
<td>16.30</td>
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<tr>
<td>[Sample 1967]</td>
<td>1967</td>
<td>12.23</td>
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<tr>
<td>[Castles 1975]</td>
<td>1975</td>
<td>19.43</td>
</tr>
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<td></td>
<td></td>
<td>20.59</td>
</tr>
<tr>
<td>[Clark 2005]</td>
<td>2005</td>
<td>20.1</td>
</tr>
</tbody>
</table>

1.3.3 Summary of previous specific heat measurements

The Debye and linear terms are not the whole story of previous specific heat measurements. Gardner carried out the heat capacity measurement from 1.8 K to 0.35 K
and reported a Debye term plus a $T^7$ term [Gardner 1973]. Edwards measured the heat capacity of solid $^4$He from above 2 K to 0.3 K and observed no deviations from Debye theory [Edwards 1965]. Furthermore, Hebral’s experiment extended down to 0.1 K and confirmed Edwards’ result [Hebral 1980]. By analyzing the uncertainty of the data, Edwards concluded that if there was a linear term in their study, it was less than 5% of what Heltemes reported. Except for Franck, samples studied by other people we discussed before were all made by blocked capillary method. Four out of five samples by Franck were made with constant temperature method [Franck 1964]. The specific heat measurements extending below ~0.3 K are summarized in Table 1-3.

| Table 1-3: Summary of previous specific heat measurements. |
|---------------------------------|-----------------|-----------------|-----------------|
| Main material of calorimeter    | Volume (cc)     | Temperature range | Conclusion of specific heat |
| [Heltemes 1962] Be-Cu           | 0.78            | 0.2K to >2K      | $T^3+T$          |
| [Edwards 1965] Cu               | 0.28            | 0.3K to >2K      | $T^3$            |
| [Sample 1967] Be-Cu             | 1.2             | 0.2K to >2K      | $T^3+T$          |
| [Gardner 1973] Be-Cu            | 11.45           | 0.35K to 1.8K    | $T^3+T^7$        |
| [Castles 1975] Be-Cu            | 0.9             | 0.13K to 1.4K    | $T^3+T$          |
| [Hebral 1980] Epoxy+ CMN        | 6.25            | 0.1K to 1.6K     | $T^3$            |
| [Clark 2005] Al                 | 0.5             | 0.08K to 0.5K    | $T^3+T$          |
Except for Clark et al, the empty cell background severely limited the sensitivity in previous heat capacity studies. Calorimeters used in these experiments were typically constructed of metal, as listed in Table 1-3, such that the heat capacity contribution from the calorimeter at low temperatures was much larger than that of the $^4$He. For example, at 0.15 K, the ratio of background heat capacity to that of helium was 430% in reference [Castles 1975] and at 0.1 K such a ratio was 1500% in reference [Hebral 1980].

Figure 1-4 gives an example of how severe the background issue could affect the

![Debye temperature as a function of temperature and density.](image)

Figure 1-4: Debye temperature as a function of temperature and density. The two black lines indicate the Debye temperature (17.87 cc/mol sample) assuming a change ±1% of the background heat capacity, pointed out by the authors. The region where Debye temperature is constant depends on the density.
reliability of the heat capacity measurement. More discussions on the background heat capacity will be presented in 2.1.1.
Chapter 2
Experimental Details

2.1 AC Calorimetry

Ac calorimetry is also called ac-temperature calorimetry. The AC calorimetric technique periodically modulates the power that heats the sample and produces temperature oscillations around a mean temperature. The amplitude of the temperature oscillations depends on the modulating power and the heat capacity of the sample. Corbino first discovered this principle around 1910 and carried out the first modulation measurement of specific heat.

The term ac-temperature calorimetry was not used until the 1968 paper by Sullivan and Seidel [Sullivan 1968]. These authors considered a heater and a thermometer connected to a sample that was in contact with a thermal bath via a weak thermal link. Figure 2-1 shows a diagram of this model. $K_i$ and $C_i$ represent the thermal conductance and heat capacity of the $i$-th element respectively. The subscripts $b$, $h$, $s$, and $\theta$ denote the bath, heater, sample, and thermometer, respectively.

A sinusoidal heat is generated in the heater at the rate $\dot{Q} = \dot{Q}_0 \cos^2 \frac{1}{2} \omega t$ which results in temperature oscillations $T_{ac}$ in the sample around an average temperature $T_{dc}$. The thermal equations for this system are given by Eq. 2.1:
If the temperature oscillations are sufficiently small, the various heat capacities and thermal conductivities can be considered constant. The steady-state solution for $T_\theta$, the temperature of the thermometer, consists of a constant term $T_{dc}$ that depends upon the

\[ C_h \dot{T}_h = \dot{Q}_h = \dot{Q}_0 \cos^2 \frac{1}{2} \omega t - K_h (T_h - T_s) \]

\[ C_s \dot{T}_s = \dot{Q}_s = K_h (T_h - T_s) - K_b (T_s - T_b) - K_\theta (T_s - T_\theta) \]  \hspace{1cm} (2.1)

\[ C_\theta \dot{T}_\theta = \dot{Q}_\theta = K_\theta (T_s - T_\theta) \]
thermal weak link between the sample and the bath and an oscillatory term $T_{ac}$ that depends upon the heat capacity of the sample. $T_\theta$ is expressed in Eq. 2.2:

$$
T_\theta = T_b + \frac{\dot{Q}_0}{2K_b} + \frac{\dot{Q}_0}{2\omega C} \cdot (1 - \delta) \cos(\omega t - \alpha)
$$

(2.2)

$$
T_\theta = T_{dc} + T_{ac}
$$

where $(1 - \delta)$ is a complicated factor involving the heat capacities and thermal conductance in Eq. 2.1, $\alpha$ is a phase angle of little interest and $C = C_s + C_\theta + C_h$. If three criteria are met, we can simplify the $(1 - \delta)$ term. First, the heat capacities of the heater, thermometer and thermal weak link are much less than that of the sample. Second, the modulation frequency $f$ is much larger than the inverse of the sample to bath relaxation time. This time constant involved here is called the external thermal time constant $\tau_{ext}$, and $\tau_{ext} = C/K_b$. $C$ is the total heat capacity or the sample heat capacity based on the first criteria. Lastly, the whole system reaches thermal steady state much faster than the inverse of the driving frequency $\omega/2\pi$. This time constant involved here is called the internal thermal time constant $\tau_{int}$. If these three criteria are satisfied, then the factor $1 - \delta$ can be simplified to Eq. 2.3 with the first order of $\omega^2$ and $\omega^{-2}$.

$$
1 - \delta = \left[ 1 + \frac{1}{\omega^2 \tau_{ext}^2} + \omega^2 \tau_{int} \right]^{-1/2}
$$

(2.3)
If the finite thermal conductivity of the sample $K_s (K_s = Ak / L$, $A$ is sample cross section area, $L$ is sample thickness and $k$ is thermal conductivity coefficient) is taken into account, then the magnitude of $T_{ac}$ becomes Eq. 2.4:

$$T_{ac} (L, t) \approx \frac{1}{2\omega C_s} \left[ 1 + \frac{1}{\omega^2 \tau_{ext}^2} + \omega^2 \tau_{int}^2 + \frac{2K_b}{3K_s} \right]^{-1/2} \quad (2.4)$$

Eq. 2.4 is an exact expression for the total heat capacity of the sample. If we operate the calorimeter (1) at a frequency such that the frequency dependent terms do not dominate $T_{ac}$, which implies that $\omega$ should be $1/\tau_{ext} << \omega/2\pi << 1/\tau_{int}$ and (2) the conductivity of the thermal weak link is much less than that of the sample under investigation, then Eq. 2.4 can be further simplified to Eq. 2.5:

$$T_{ac} = \frac{\dot{Q}}{2\omega C} \quad (2.5)$$

The requirement of the conductivity of the thermal weak link can be satisfied by selecting the appropriate wire gauge, length and material. To experimentally check the requirements of $1/\tau_{ext} << \omega / 2\pi << 1/\tau_{int}$, frequency scans at different temperatures are necessary. Frequency scans can be accomplished by applying the same power and measuring the temperature oscillations over a range of frequencies. The calculated heat capacity as a function of frequency should typically show a plateau for a well designed calorimeter. The data acquisition should be performed in the frequency independent
region. Two other requirements are assumed to be fulfilled in the previous discussion. First, the internal time constant of thermometer should be shorter than the thermal relaxation time constant between the thermometer and the sample. Second, the thermal conductivity from the electric leads should be negligible compared to the thermal weak link.

In short, first of all, power at a known amplitude voltage is applied to the sample. Second, the frequency of the power should be within the plateau region. Third, the resulting temperature oscillations $T_{ac}$ in the sample is measured by monitoring the thermometer resistance. We can determine the heat capacity of the sample from the power, frequency and the temperature oscillation magnitude.

Compared with the traditional adiabatic calorimetry, ac calorimetry has some advantages. The sample can be thermally coupled to the bath, so calibration of the calorimeter thermometer can be done in situ. Changes in heat capacity with some experimentally variable parameter can be recorded directly. The last one and the most important one is that in ac calorimetry extremely small heat capacities may be measured with accuracy. A review of modulation calorimetry can be found in the reference [Kraftmakher 2002].

### 2.1.1 Calorimeters

One motivation of the $^4$He heat capacity measurement is to look for the thermodynamic signature of the possible supersolid transition. Hence the temperature
The region relevant to this study is below several hundred milli-Kelvin (mK), where continual operation of a $^3$He-$^4$He dilution refrigerator is a necessity. The low temperature environment was achieved by a MNK-126-TOF dilution refrigerator from Leiden Cryogenics Company. The base temperature of this dilution refrigerator is 15 mK.

![Graph: Heat capacity of the background as a function of temperature. The background is always less than the expected helium heat capacity and at least 10 times less than the measured heat capacity.](image)

**Figure 2-2:** Heat capacity of the background as a function of temperature. The background is always less than the expected helium heat capacity and at least 10 times less than the measured heat capacity.

Calorimeters used in previous experiments were typically constructed of copper, epoxy and sometimes included paramagnetic salts. Solid helium is a non-magnetic, crystalline insulator. The excitations in solid helium are phonons, arising from vibrations...
of the atoms. At low enough temperature, solid helium is believed to be a Debye solid and its specific heat changes with $T^3$. Normal metals have freely moving conduction electrons, which can be thermally excited and add a linear heat capacity in addition to the lattice vibrations. Epoxy is non-crystalline solid and at low temperature its specific heat roughly scales with temperature. Magnetic specific heat usually scales with $T^2$. The heat capacity of those materials involved in previous experiments contributes significantly to the total heat capacity at low temperatures. Clark and Chan used superconducting material, aluminum, to construct the sample cell in 2005 [Clark 2005]. They successfully cut down the background contribution, but due to the poor thermal conductivity of the aluminum they were not able to follow the deviation mentioned in section 1.3 below 85 mK.

Table 2-1: Summary of solid $^4$He specific heat measurements at low temperature.

<table>
<thead>
<tr>
<th>Year</th>
<th>Cell</th>
<th>Volume (cc)</th>
<th>Temperature limit</th>
<th>$C_{cell}/C_{He}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Swenson 1962,1967</td>
<td>Be-Cu</td>
<td>0.78,1,2</td>
<td>0.2K to &gt;2K</td>
<td>N/A</td>
</tr>
<tr>
<td>Edwards 1965</td>
<td>Cu</td>
<td>0.28</td>
<td>0.3K to &gt;2K</td>
<td>N/A</td>
</tr>
<tr>
<td>Gardner 1973</td>
<td>Be-Cu</td>
<td>11.45</td>
<td>0.35K to 1.8K</td>
<td>66% at 0.35K</td>
</tr>
<tr>
<td>Adams 1975</td>
<td>Be-Cu</td>
<td>0.9</td>
<td>0.13K to 1.4K</td>
<td>430% at 0.15K</td>
</tr>
<tr>
<td>Hebral 1980</td>
<td>Epoxy+ CMN</td>
<td>6.25</td>
<td>0.1K to 1.6K</td>
<td>1500% at 0.1K</td>
</tr>
<tr>
<td>Clark 2005</td>
<td>Al</td>
<td>0.5</td>
<td>0.08K to 0.5K</td>
<td>10% at 0.2K</td>
</tr>
<tr>
<td>This work 2006</td>
<td>Si</td>
<td>0.93</td>
<td>0.04K to 0.6K</td>
<td>5% at 0.1K</td>
</tr>
</tbody>
</table>

In order to reduce the background heat capacity, undoped silicon was used as the helium container. Pure silicon was chosen because its low heat capacity and good thermal
conductivity at the temperature region of interest. The silicon container were >99.999% purity from Lattice Materials LLC and were machined by the same company. With silicon as the main construction material, the background heat capacity was cut down to be less than 10% of the solid $^4$He over the entire temperature range of the data presented. Table 2-1 summarizes previous experiments that went down to 0.3 K [Heltemes 1962] [Edwards 1962] [Sample 1967] [Gardner 1973] [Castles 1975] [Hebral 1980] [Clark 2005] and the work of this dissertation. The background heat capacity of one sample cell is shown in Figure 2-2.

Two similar calorimeters (cell A and cell B) were used in this study. The general features are shown in Figure 2-3. The calorimeter consists of undoped silicon, a small aluminum cap, and a minimal amount of epoxy. Before the top and bottom pieces of silicon were glued together by epoxy, it was necessary to drill a small diameter hole through the 1 cm thick silicon, so that the capillary could be inserted. Two methods have been used in drilling the silicon. One could use either the flat end of a drill bit with 9 micron diamond paste as a grinding compound or a diamond core drill bit to drill the silicon in a water bath. The first method was used in cell A. It allows us to drill hole as small as 0.4 mm diameter but it generates holes of irregular cross section and it takes about 10 days to drill through 1 cm. The second method, with a diamond core drill bit, used in cell B, generates regular 1 cm deep holes within a day. The drawback of this method is that the smallest diamond core drill commercially available is about 0.7 mm. After the top piece of silicon was drilled though, the capillary and aluminum cap were connected to it with Stycast 2850 black epoxy. This epoxy with catalyst 11 was found to
have strong bond to silicon and was used on both calorimeters, we will simply refer to it as black epoxy from now on. The aluminum cap was necessary to create a reliable seal between the capillary and silicon, because of the expansion coefficient difference among different materials. The capillaries were 0.1 mm inside diameter glass in cell A and 0.2 mm inside diameter Cu-Ni in cell B. After the polyimide coating outside the glass tubing was removed, the glass capillary could be sealed to the aluminum cap by black epoxy. It was found that $^4$He could diffuse through the glass tubing at room temperature but it was leak tight to liquid $^4$He below 4 K. The cell was mechanically secured to the refrigerator with four nylon screws. The ends of nylon screws were sharpened to make it as little contact area as possible. The photo of the cell A is shown in Figure 2-4.

Figure 2-3: Diagram of the silicon cell.
In cell A, the calorimeter thermometer was commercially available RuO$_2$ 2200 (resistance of ~2200 at room temperature). For cell B, a germanium crystal thermometer was used. The germanium thermometer was much more sensitive than the RuO$_2$ 2200 as shown in Figure 2-5. However, the resistance of the germanium thermometer was only 30 $\Omega$ at 0.3 K thus lead resistances need to be considered carefully. At every cool down from room temperature the thermometers were calibrated based on the mixing chamber main thermometer, which is a carbon resistor thermometer provided by Leiden company. The mixing chamber thermometer was calibrated by $^3$He melting curve thermometry and confirmed by a CMN thermometer; details are discussed in the third section of this chapter. The heaters of the calorimeters were metallic thin films deposited on an undoped
silicon wafers. The films were 75 angstrom chromium plus 80 angstrom gold. The resistance of the heaters was about 3000 Ω and it had very small temperature dependence (within 0.5% between 1K and 20mK). Superconducting wires were used as heater leads in order to cut down the uncertainty of the power used in the measurement. The commercial superconducting wires used in this experiment were superconductor bundles inside copper wire. The copper coating was dissolved in acid to minimize the thermal conductivity of the wires.

Figure 2-5: Temperature dependence of RuO$_2$ 2200 and germanium thermometers.
The weak thermal links were copper wires of 5 cm in length and 0.08 mm in diameter connecting between the mixing chamber and the calorimeters. The thermal conductivity of the copper wire varies with the defects inside, depending on how the copper wires were bent or twisted at room temperature. The contacts between the copper wire and the calorimeter were also important. In cell A, copper wire was pressed down by a sharpened nylon screw on the top of the silicon. In cell B, the copper wire was first connected to a flat copper foil and then glued to the silicon by GE-vanish. It was found out that the thermal conductivity of two weak links differed by a factor of 5. The actual thermal conductivities of the copper wires can be determined via the frequency scans and the length of time to complete the solidification during sample growth. In the experiments with constant pressure growth, which will be discussed later this chapter, a 10 cm length and 0.25 mm diameter 99.999% aluminum wire connected the calorimeter to the mixing chamber thermal bath in parallel with the copper thermal weak link. Therefore, during the ⁴He crystal growth, the cooling power of the calorimeter was improved by the normal aluminum wire bypass. In the experimental temperature range, i.e. less than 0.5 K, the conductivity of superconducting aluminum contributed almost nothing compared with the copper wire.

2.1.2 Electronics

The magnitude of the thermal oscillation was synchronously recorded by monitoring the resistance of the calorimeter thermometer with a home-made ac-
Wheatstone bridge. The block diagram of the thermometer circuit in the heat capacity experiment is shown in Figure 2-6. As shown in the simplified circuit, the lock-in amplifier was synchronized to the bridge excitation signal. It detected a voltage depending on the ratio between the standard resistance and the calorimeter thermometer resistance. This voltage, calibrated against the mixing chamber carbon thermometer while the calorimeter was empty and no power was applied to the heater, became a measurement of the temperature of the calorimeter.

Figure 2-6: Block diagram of the thermometer circuits used in the solid helium specific heat studies.
The function generator Stanford DS345 produced a 700 Hz signal as the excitation for the circuit and also provided the reference for the Stanford SR810 lock-in amplifier. This signal went through the 1:1 ST-248 isolation transformer and then the signal was split into two parallel paths, one through the ac ratio standard, and the other one through the standard resistance and the thermometer. The ac ratio standard was always set to 0.5 and its output was connected to the ground. The high frequency lock-in amplifier measured the voltage potential of the point between the standard resistor and the thermometer relative to the ground. The Agilent 33401A voltmeter recorded 500 readings from the lock-in output with a trigger frequency set by another function generator (typically 10 Hz). If there was a low frequency temperature oscillation on the thermometer resulting from the sinusoidal power on the heater (usually less than 1 Hz), the magnitude of the 700 Hz signal detected by the lock-in would display the same oscillation. Therefore, the computer could analyze a data package with 500 continuous readings from the voltmeter and the Fourier transform of the data set should show a peak at the applied power frequency. From the magnitude of the peak in frequency space, we could then calculate the temperature oscillation. Figure 2-7 shows a Fourier transform from one of the measurements. The code for Fourier transform was written in LabView and the system was tested by feeding known sinusoidal functions from a function generator to the lock-in.

The trigger frequency was the sampling frequency of the digital voltmeter. The sampling frequency was chosen so that there were enough oscillations (usually ~20) in a data package and there were enough data points (usually ~20) in each oscillation. The
voltmeter always read 500 points in a row, so if the sampling frequency was set to 10 Hz, then voltmeter acquired 500 points from the lock-in amplifier output every 0.1 second. The optimum heater frequency we induced was about 0.4 Hz (depending on the thermal weak link) and the best sampling frequency was 10 Hz. The high frequency lock-in should operate with a short time constant to minimize the low frequency signal attenuation, and the attenuation also needed to be taken care of in the $T_{ac}$ calculation. Converting the signal to digital voltmeter and analyzing with the computer was an alternative to traditional double lock-in technique. We found that this alternative had the advantage of reducing noise and requiring less equipment.

Figure 2-7: The Fourier transform program. Temperature oscillations correspond to 0.3 mK with a power frequency of 0.8 Hz.
The reason for using the transformer, lock-in amplifier and ac ratio standard instead of providing a dc excitation for the thermometer is to reduce any influence of noise and interference. RG108A/U and TWINAX plugs were found to be better than regular coaxial cable and BNC connectors in cutting down the noise. Compared with coaxial cable, RG108A/U has an external copper ground shield to screen the inner conductor pairs. Shielding was continuous everywhere along each line. A filter box was fabricated to cut down the noise at room temperature. Another filter box was fabricated inside the fridge and mounted on the mixing chamber. The low temperature filter box is not shown in Figure 2-6. In these boxes low-pass RF filtering (LC filters with 4 μH and 20 nF at room temperature) was inserted into every measurement line. The filters at room temperature were mounted inside of a doubly shielded container. The filters at the mixing chamber stage were mounted inside a single shield container combined with a section of homemade thermocoax cable as the extra filtering for the highest frequency noise. The thermocoax cables were semi-rigid coaxial cables with stainless steel as outer conductor, NiCr as inner conductor and MgO powder as dielectric. All equipment and cables were grounded to the dilution fridge carefully. It was shown that the careful shielding and grounding was extremely important in this experiment. The bridge circuit signal to noise ratio was optimized by choosing the standard resistor according to the target resistance and adjusting the phase of the lock-in.

Metal film resistors were used as standards at room temperatures for measuring the RuO₂ 2200 thermometer. When the germanium was used as the thermometer, the measurement circuit was modified from Figure 2-6. The resistance of the germanium
thermometer was only 30 Ω at 0.3 K, so the variation of the lead resistance with the environment, such as the liquid helium level in the experimental helium Dewar, should be considered. Therefore, the standard resistor of the germanium thermometer was put inside the dilution fridge and thermally attached to the mixing chamber. The standard resistor for germanium was a 75 angstrom chromium plus 80 angstrom gold thin metallic film deposited on an undoped silicon wafer. The standard resistor was made with the same recipe of the heaters.

The circuit for the heater is not shown in Figure 2-6. The power was generated by the third function generator and fed into the heater after passing through the filter boxes. Because of the filters, attenuators, and lead resistance in the heater circuit, the voltage across the heater resistor was measured by a four lead method at low temperatures. During the measurement, voltage was applied to the sample heater at typically between 0.1 and 1 Hz.
2.1.3 Frequency scan

Figure 2-8: Frequency scan of cell A with the RuO$_2$ thermometer.

Figure 2-9: Frequency scan of cell B with a Ge thermometer.
Figure 2-8 shows the heat capacity data of solid $^4$He and cell A. They were measured by RuO$_2$ against heating frequency in log-log scale between 40 and 400 mK. The error bar at each temperature was determined by the standard deviation of five to ten successive measurements. The data acquisition in cell A was performed at 0.1 Hz. Figure 2-9 shows the frequency scan for the germanium thermometer of cell B between 30 and 300 mK. The data acquisition was performed at 0.4 Hz. Both frequency scans showed a plateau to satisfy the requirement of $1/\tau_{\text{ext}} \ll \omega/2\pi \ll 1/\tau_{\text{int}}$ over the entire temperature range. The operation frequency difference between two cells was due to the weak link thermal conductivity difference. The uncertainty of the measurement was improved considerably by using the germanium thermometer.

2.2 Growth of helium samples

2.2.1 Blocked capillary method

Three methods of growing solid helium crystals are blocked capillary, constant pressure, and constant temperature. The blocked capillary method could be more accurately described as the constant density method. In a blocked capillary growth, the fridge is first warmed up to an appropriate temperature, and then high-density liquid is introduced the sample cell. When the fridge is cooled down a block will be formed somewhere in the capillary. The density below the block is then fixed and the sample is
cooled along the melting curve into the solid phase, as shown in Figure 2-10. The initial liquid density needs to be more than that of the 25 bar solid at low temperatures. Samples grown by the blocked capillary were found to grow crystals with linear dimension larger than 1 mm [Schuch 1962] [Armstrong 1979] and with dislocation line density of $10^9$ cm$^{-2}$ [Tsuruoka 1979] (The authors claimed their samples were grown under constant pressure condition, but in their experimental details they mentioned they blocked the inlet tube after they observed the onset of the solidification.)

Figure 2-10: Illustration for constant pressure method and blocked capillary method.
The gas handling system of cell B is shown in Figure 2-11. The purpose of installing long capillaries and many stages of heat sink was to cut down the heat propagation to the calorimeter through the capillary. The capillary was weakly heat sunk at the 1K pot (1.8 K), still (0.7 K), and 50 mK plate, but directly heat sunk at the mixing chamber. Two heat exchangers at mixing chamber stage were filled with silver sinters and the third one is simply an open space. The other heat exchangers were made of 1 meter long Cu-Ni capillary wound around a copper tube of diameter 1 cm. Heat
exchangers at the 1K pot, still, and 50 mK plate had their own heaters and thermometers. During sample growth, heat was applied to the heat exchangers to make sure that the capillary was open at least 15 minutes after the mixing chamber cooled below the freezing point and a block near the mixing chamber was formed. Most of the capillary was 0.012 inch inside diameter Cu-Ni capillary with a 0.007 inch stainless steel wire or 0.007 inch inside diameter Cu-Ni capillary with a 0.0055 inch stainless steel wire. The total length of capillary below the 4 K plate was about 7 meters. Gas handling system for cell A was simpler with less heat exchangers and shorter length of capillaries.

### 2.2.2 Constant pressure method

Constant pressure method has been shown to grow better quality samples than those grown with the blocked capillary method. Constant pressure growth is achieved by slowly cooling the cell while maintaining a specific freezing pressure. This requires that the $^4\text{He}$ filling line remain open during the solidification process and the sample cell should be kept to be the coldest point in contact with the liquid (or solid) $^4\text{He}$. It is believed that this results in a crystal with much less internal strain. The difference between constant pressure grown and blocked capillary grown is illustrated in Figure 2-10. The first extensive investigation demonstrating that large single crystals were reliably grown at constant pressure method was in situ x-ray diffraction studies with sound velocity measurements [Greywall 1971]. Ultrasound measurements showed that samples
grown by the constant pressure method typically had a dislocation line density of $10^5$ to $10^6$ cm$^{-2}$ [Iwasa 1979] [Iwasa 1980].

The heat exchangers inside the fridge were modified from Figure 2-11 to achieve this growth method. In order to make sure the entire fill line was free from the nucleation of solid, every heat exchanger was weakly thermally attached to the fridge and had its own heaters and thermometers to control the temperature. An aluminum wire between the bottom of the calorimeter and the mixing chamber was added to improve the conductivity at about 2 K, the temperature where we grew the solid sample (see details in 2.1.1). This extra thermal link was needed to handle the additional heat brought down by the liquid helium in the capillary. The pressure was maintained constant by the gas handle system at room temperature.

2.2.3 Accuracy and uncertainty in the $^3$He concentration

The $^4$He used in our experiments consisted of a commercially ultra high purity (UHP) $^4$He gas cylinder and an isotopically pure $^4$He. For the UHP $^4$He, we have used $x_3=0.3$ ppm as the $^3$He concentrations. This is a typical $^3$He concentration number found in the literature [Paalanen 1981]. The precise concentration varies with the source, but nominal values are always less than 1 ppm. For example, the Bureau of Mines has reported that $x_3 = 0.205$ ppm from Texas oil mines [Cornelius] and $0.384$ ppm $< x_3 < 0.52$ ppm from the North Sea oilfields [Ballentine 1996]. Additional numbers and references can be found in [Brown 1998]. The original source of the 1 ppb helium
sample was the U.S. Bureau of Mines (now known as the Bureau of Land Management) and was kindly given to us by John Lipa of Stanford University. According to publications from the Bureau of Mines and the Helium Field Operations, 1 ppb should be considered as the upper limit of the \( ^3 \text{He} \) concentration. For example, see reports in references [Tully 1975]. For the commercially UHP (0.3 ppm) and the isotopically pure (1 ppb) samples, we have taken every precaution, such as using new capillaries, valves and heat exchangers to avoid contamination from impurities (\( ^3 \text{He} \), as well as air, etc.).

To study \( ^3 \text{He} \) concentration above 0.3 ppm, the cell was first warmed to higher than 5 K and emptied. A measured quantity of \( ^3 \text{He} \) was then condensed into the cell before the introduction of commercially UHP \( ^4 \text{He} \). The \( ^3 \text{He} \) concentration we dosed was actually the upper limit. Details of the \( ^3 \text{He} \) concentration in the cell will be discussed in 4.2.

2.3 Thermometry

2.3.1 \( ^3 \text{He} \) melting curve

The internationally accepted temperature scale is defined by ITS-90. ITS-90 extends upwards from 0.65 K to the highest temperature measurable using an optical pyrometer. The temperature scale is based on a set of well defined fixed points and specified methods of interpolating between them. However, the temperature range of interest for our experiment is below 0.65K. In this low temperature regime, practical but
no officially accepted low-temperature fixed points and scales are applied. For example, a
cryogenic temperature scale CTS-2 was developed in 1994 which spans the range from 6
to 750 mK. The new provisional temperature scale from 0.9 mK to 1 K is PLTS-2000
[Rusby 2002] with an uncertainty of 0.3% (up to a maximum of 0.5 mK). The
temperature scale used in this work was calibrated by the $^3$He melting curve thermometry
described in PLTS-2000.

Figure 2-12: Melting curve of $^3$He, adopted from [Pobell 1996].

The behavior of the melting curve of $^3$He below 1 K is shown in Figure 2-12. The
shape of the melting in PLTS-2000 can be expressed by Eq. 2.6:

$$p / MPa = \sum_{i=-3}^{9} a_i (T_{2000} / K)^i$$  (2.6)
where \( p \) is the pressure of the solid-liquid coexistence in million Pascal and \( T_{2000} \) is the PLTS-2000 temperature scale in Kelvin. The coefficients \( a_i \) were listed in the reference [Rusby 2002]. There are four fixed points in the melting curve and the only one in our temperature range is the minimum point where the pressure is 2.93113 MPa and the temperature is 315.24 mK. By measuring the pressure of the melting curve, one can determine the temperature to calibrate the other thermometers. In this work, the carbon thermometer in the mixing chamber was calibrated and used as the standard to cross calibrate the calorimeter thermometers later.

For the measurement of the \(^3\)He melting curve, the \(^3\)He sample in liquid-solid coexistence was confined with an in-situ Straty-Adams type capacitive pressure gauge [Straty 1969]. The pressure gauge was thermally anchored to the mixing chamber stage and its capacitance was measured directly by an Andeen-Hagerling (2500A 1K Hz ultra-precision) capacitance bridge. The calibration of the capacitive pressure gauge was done at 4 K with a Paroscientific 9000-2K-101 (0.01% uncertainty above 200 psi) at room temperature by pressurizing the cell with high pressure liquid or gas.

The \(^3\)He used in this study was 99.995% pure, the highest purity that was commercially available. The \(^3\)He gas handling system was similar to that of the \(^4\)He gas handling system shown in Figure 2-11. When liquid-solid coexistence samples were grown, the initial density was controlled within the region shown in Figure 2-13. In this study the pressure gauge was filled with the appropriate density of liquid at high temperature and then a block was formed at the still stage.
2.3.2 CMN thermometer

The CMN (cerium magnesium nitrate) thermometer is another conventional method to measure temperatures below 1 K. It is based on the $1/T$ dependence of the paramagnetic susceptibility. CMN can be nearly perfect paramagnet down to 10 mK. A CMN thermometer described in reference [Greywall 1988] was used to cross check the temperature scale established by the $^3$He melting curve.

Figure 2-13: Density of liquid and solid $^3$He along the melting curve, adopted from [Greywall 1982].
The CMN thermometer was mounted on the mixing chamber stage with a reference inductor. A four-lead circuit similar to the one used in reference [Greywall 1988] was used to improve the sensitivity. The circuit was driven at frequency of 700 Hz. The temperature scale from the $^3$He melting curve thermometer was confirmed by the CMN thermometer below 0.1 K, shown in Figure 2-14.

**Figure 2-14:** Quantity proportional to the magnetic susceptibility of the CMN sample plotted as the inverse of the temperature.
Chapter 3

Specific heat of solid $^4$He

The purpose of this study was to search for the thermodynamic signature of the possible supersolid transition. Results of commercially ultra high purity $^4$He (0.3 ppm $^3$He impurities) and isotopically pure (1 ppb $^3$He impurities) $^4$He samples grown under different conditions are presented in this chapter. Heat capacity peaks were observed in the temperature range where NCRI was detected. In this chapter, the discussion is divided to four sections. The first section presents the heat capacity of liquid $^4$He as a control experiment. The second and third sections focus on the behavior of the specific heat of solid $^4$He. The last section relates the specific heat result to other experiments especially TO.

3.1 Specific heat of liquid $^4$He

Previous experiments on liquid $^4$He at low temperatures have shown that there is only a phonon $T^3$ term in the heat capacity [Greywall 1978]. For example, zero bar liquid has been found to be $T^3$ between 140 and 460 mK; 25 bar liquid has been found to be $T^3$ between 220 and 340 mK. In the work of this dissertation, the specific heat of liquid $^4$He was measured in both cells as the control experiment (See Figure 3-1). The red and green lines are the $T^3$ fit for those two sets of data. The phonon term was observed between 100
and 400 mK. The heat brought down by the liquid prevented the measurement from cooling to lower temperature. In comparison, the solid helium samples made with the blocked capillary technique exhibited the deviation from $T^3$ at 140 mK in cell A and 200 mK in cell B (presented in next section). The coefficients of the phonon term are consistent with previous experiments, as shown in Figure 3-2. The heat capacity of liquid $^4$He was measured to ensure that there is no systematic problem in our experiment.

---

Figure 3-1: Liquid $^4$He heat capacity as a function of temperature. The black star is an 11 bar sample (0.3 ppm) in cell A and the purple square is a 25 bar sample (1 ppb) in cell B.
Samples grown by blocked capillary method from cell A and cell B were studied. It is found that the 0.3 ppm $^3$He impurity does not affect the specific heat result therefore commercially UHP $^4$He and isotopically pure $^4$He samples are discussed together. For
each concentration in each cell, the specific heat results presented in this section were reproduced at least twice. All samples were intentionally grown with a finishing solid pressure of about 33 bar at low temperature. The background heat capacities due to sample cell were always at least 10 times smaller than the total measured heat capacity over the entire temperature range. All the solid $^4$He heat capacity results shown in this chapter have had the background subtracted.

### 3.2.1 Cell A

The specific heat of solid $^4$He with 0.3 ppm $^3$He impurities under a pressure of 33 bar in cell A is shown in Figure 3-3. The sample was grown with blocked capillary technique and it took about 20 hours to finish the solidification. Since there was no in situ pressure gauge inside the cell, the pressure of the sample was calculated from the density deduced from the pressure and temperature of the high density liquid, just before the capillary was blocked. The error bar shown in Figure 3-3 was converted from the standard deviation of 10 successive measurements, typically about 2-3% of the measured heat capacity for the RuO$_2$ thermometer. The minimum temperature we could take data for this cell was 40 mK. The results from cell A have been published [Lin 2007].
The heat capacity of solid helium was found to obey Debye-$T^3$ law between 150 and 450 mK. For the sample in Figure 3-3, the Debye temperature deduced from the $T^3$ region is 27.6 K, while the expected Debye temperature from a previous study [Edwards 1965] is 28 K (with melting point around 1.8K). The departure from a $T^3$ dependence above 500 mK has been observed in a number of previous experiments [Heltemes 1962] [Edwards 1965] [Sample 1967] [Gardner 1973] [Castles 1975] [Hebral 1980]. It has

Figure 3-3: Specific heat of 33 bar 0.3 ppm solid as a function of temperature in a log-log plot.
recently been pointed out [Maris 2007] that phonon dispersion within the solid can possibly account for this behavior. The most striking finding of this study is the excess heat capacity in addition to the Debye term at low temperature. The excess specific heat can also be observed in a linear scale plot (Figure 3-4). In order to find out if this excess heat capacity was related to 0.3 ppm $^3$He impurities, the entire gas handling system was rebuilt and samples of isotopically pure $^4$He were studied. The result of 1 ppb specific heat.
heat is shown together with the 0.3 ppm result in Figure 3-5. It is clear that specific heat from 1 ppb sample is nearly identical to that of the 0.3 ppm sample except that the density of that 1 ppb sample is slightly higher.

![Figure 3-5: Specific heat of 0.3 ppm and 1 ppb solid samples as a function of temperature.](image)

In most cases, an annealing effect was observed in the NCRI studies [Rittner 2006] [Clark 2007] [Penzev 2007]. The solid helium samples shown here were annealed
at 0.1 K below the melting point for 3 hours. There was no observable change in heat capacity. In 3.2.2 more annealing effects will be discussed. It was pointed out the crystal quality can be improved more easily by thermal cycling than by annealing [Remeijer 1997]. Samples in this study were rapidly warmed up to above 1.5 K and cooled down to 1 K within 30 minutes three times. There was no observable heat capacity change after the attempts to change the sample quality.

It has also been suggested that the observed NCRI is the consequence of solid helium forming a glassy state or the inclusion of glassy regions in the sample [Rittner 2007] [Prokof'ev 2007] [Nussinov 2007] [Grigor'ev 2007]. A specific heat that is linear in temperature is a characteristic of glasses [Phillips 1972] [Anderson 1972]. In an attempt to extract such a linear term from Figure 3-5, we plot the specific heat divided by temperature versus $T^2$ (Figure 3-6). If, in addition to the $T^3$ term, there were a component that scales linearly with temperature, the data would lie on a straight line with a non-zero y-axis intercept. The data for 0.3 ppm and 1 ppb samples do yield straight lines between 140 and 430 mK. However, both lines extrapolate exactly through the origin, indicating that the specific heat above 140 mK is purely $T^3$. The inset of Figure 3-6 demonstrates that there is no such a linear heat capacity over the entire temperature range. Figure 3-6 also demonstrates that the deviation from $T^3$ observed in Figure 3-5 exists only below 140 mK. Hysteretic behavior and long time constants are characteristics of a glassy system. We tried to search for, but failed to find any hysteresis. The heat capacity of 0.3 ppm and 1 ppb samples were measured upon warming and cooling to look for signs of hysteresis. We also failed to find any time-dependent effects longer than the time.
associated with taking the measurements. For instance, the 0.3 ppm sample was set at 100 mK and heat capacity was measured for 10 hours. There was no observed time dependence.

Figure 3-6: Plot of $C/T$ against $T^2$ for 0.3 ppm and 1 ppb samples.

Figure 3-6 shows that above 140 mK there is only a purely $T^3$ Debye contribution. The $T^3$ phonon term originates from lattice vibrations and it should exist for both the
temperature range above and below 140 mK. When the $T^3$ phonon contribution is subtracted, a broad peak in the specific heat (centered near 75 mK) is seen for the 1 ppb and 0.3 ppm samples. The peaks are shown in Figure 3-7. The data at high temperature (T>150 mK) exhibit a larger scatter because the uncertainty scales with the total measured heat capacity. The peak height in both samples shown in Figure 3-7 is about 20 μJ mol$^{-1}$ K$^{-1}$ ($\sim$2.5*10$^{-6}$ k$_B$ per $^4$He atom). If we assume the specific heat extrapolates
linearly to zero at T=0 K, the additional entropy associated with the peak increases from zero to about 28 μJ mol⁻¹ K⁻¹ (3.5*10⁻⁶ k_B per ⁴He atom) as the temperature increases from 0 K to 140 mK.

### 3.2.2 Cell B

![Figure 3-8](image)

**Figure 3-8:** Specific heat of 33 bar 1 ppb and 0.3 ppm solids in cell B as a function of temperature in log-log plot.
The specific heat of 1 ppb and 0.3 ppm $^4$He under a pressure of 33 bar in cell B is shown in Figure 3-8. In cell B, a higher sensitivity thermometer was mounted to the calorimeter. Details of thermometer are presented in 2.1.1. The new thermometer was about 15 times more sensitive than that used with cell A. The thermal conductivity of the weak link was also increased to achieve lower base temperature. Samples were grown with blocked capillary technique and only needed about 4 hours to finish the solidification compared with 20 hours in cell A. The reason for different amount of time needed in solidification was also because of the copper weak link thermal conductivity difference. Due to the new thermometer with higher resolution, higher weak link conductivity and better heat sinking of the heat exchangers, the minimum temperature of data acquisition was improved from 40 to 25 mK. Since the external time increases with the weak link conductivity (also discussed in 2.1.1) the experiment needs to be performed at a higher frequency to satisfy the frequency independent criteria in 2.1.3. The resolution of ac calorimetry scales with inverse frequency. Therefore, we have gained resolution from the new thermometer and sacrificed some to lower the minimum experimental temperature by changing the weak link. The overall result is that the resolution of the measurement in cell B was improved about 4 times as compared with cell A.
Similar to the result in cell A, there is a Debye $T^3$ region for the high temperature data and below about 0.2 K, the deviation from $T^3$ is observed. There is no linear term found for the entire temperature if the data are plotted as $C/T$ vs $T^2$. The specific heat peaks are confirmed by subtracting the $T^3$ term, shown in Figure 3-9. The improvement of the resolution by using the new germanium thermometer is obvious in this plot. The data at higher temperature have larger scatter because of the same reason we discussed.
before. The peak centers around 110 mK. The peak height in both samples in cell B shown in Figure 3-9 is about 45 μJ mol⁻¹ K⁻¹ (~5.4*10⁻⁶ k_B per ^4He atom). If we assume the specific heat extrapolates linearly to zero at T=0 K, the additional entropy associated with the peak increases from zero to about 86 μJ mol⁻¹ K⁻¹ (1.0*10⁻⁵ k_B per ^4He atom) as the temperature is raised from 0 K to 200 mK. Consistent with the previous data, no hysteretic behavior or long time constants were found in the 0.3 ppm and 1 ppb samples in cell B.

Figure 3-10: Annealing effect of specific heat peak. The peak magnitude was 5% smaller after annealing. The annealing was done 50 mK below the melting temperature for 4 hours.
In Figure 3-9 it is clear that the temperature of the maximum excess specific heat is higher and the peak magnitude is larger in the new cell. A reasonable speculation to the specific heat difference in two cells is that the peak is related to the sample quality. It took about 4 hours to finish the solidification in cell B while it took about 20 hours in cell A. It is reasonable to assume that solid sample grown in 20 hours is of higher quality than that grown in 4 hours, because the pressure change during sample growth can be released in a longer period of time. In one of the 1 ppb samples, a tiny annealing effect was observed, as shown in Figure 3-10. That particular sample was annealed 50 mK below the melting point for four hours and cooled down slowly over a period of two hours to 1 K. More annealing of the same sample did not reduce the specific heat peak any further. Such a small annealing effect might not be observed in cell A because of the lower sensitivity. However, a thermal cycling effect was not observed in either cell.

3.3 Specific heat of solid $^4$He grown under constant pressure

The results from blocked capillary growth samples indicate the heat capacity peak is related to sample quality. Solid helium under constant pressure growth is proven to have larger crystalline size and smaller dislocation density. The specific heat of constant pressure samples is shown in Figure 3-11. To achieve constant pressure growth requires a more complicated gas handling system, discussed in 2.2.2. Therefore, the measurement temperature range was narrowed because of the heat brought down from the capillary.
The $T^3$ coefficient of the constant pressure sample was smaller because its density was higher [Edwards 1965]. Details of the sample growth are shown in Figure 3-12. The maximum pressure fluctuation during the growth of this constant pressure was 3 psi. With an aluminum wire bypass, the constant pressure sample finished the solidification within 1.5 hours.

---

**Figure 3-11**: Log-log plot of the specific heat of a constant pressure grown solid and a blocked capillary sample in cell B. The constant pressure sample was 38 bar and the constant volume sample was 33 bar. Both samples were made of isotopically pure $^4$He.
The specific heat peak of the constant pressure sample is shown in Figure 3-13. Results from two blocked capillary samples are also shown. The size of the specific heat peak of the constant pressure sample is smaller and the peak position is at lower temperature. The peak height for the constant pressure sample is about 5 μJ mol⁻¹ K⁻¹ (≈6×10⁻⁷ k_B per ³He atom), eight times small than that of blocked capillary sample in the
same cell. The sample grown under constant pressure has the best quality and the sample grown with blocked capillary in 20 hours has better quality than that grown in 4 hours, as discussed before. The different peak temperatures, different peak magnitudes and the annealing effect in the blocked capillary sample imply that sample quality is the cause of the variation in the specific heat peaks. There is no linear term found for the entire temperature if the data are plotted as $C/T$ vs $T^2$.

Figure 3-13: Specific heat peak as a function of temperature for three 1 ppb samples. From top to bottom are (1) Brown, blocked capillary in cell B, growth time was 4 hours (2) red, blocked capillary in cell A, growth time was 20 hours and (3) orange, constant pressure in cell B, respectively.
3.4 Comparison with other measurements

3.4.1 Torsional oscillator experiments

Figure 3-14: NCRIF of samples grown with blocked capillary method and constant pressure method in the same cell [Clark 2007]. Heat capacity results from samples with blocked capillary and constant pressure growth are plotted together.
There is a wide variation in the onset temperature of NCRI in bulk samples (varied from 100 to 300 mK) [Clark 2007] [Kim 2004b]. It is found that blocked capillary samples possessed a larger high temperature tail of NCRI compared to the constant pressure samples. One set of TO results of samples grown with blocked capillary method and constant pressure method in the same cell [Clark 2007] are plotted together with the heat capacity results in cell B, as shown in Figure 3-14. The observed specific heat peaks are near the NCRI onset temperature for both the constant pressure and blocked capillary samples. This coincidence makes it probable that we have observed the thermodynamic signature related to NCRI.

A dislocation network is believed to be strongly related to the NCRI observed in TO. Dislocation lines in solid $^4$He intersect with each other and form a 3-dimensional network. If the dislocations possess a superfluid, superfluid is confined in a multiply connected geometry. Superfluidity density, which is NCRIF in this picture, is limited by the dislocation density. Constant pressure growth technique generates samples with smaller dislocation density than that from blocked capillary samples, as discussed in chapter 1. Therefore, samples grown under constant pressure method show a smaller NCRIF.

Heat capacity peaks have been found in $^4$He film confined in multiply connected geometry, such as porous gold and porous glasses [Yoon 1997] [Finotello 1988] [Zassenhaus 1999]. The temperature dependence of NCRI in 1 ppb samples may be consistent with a transition that falls into the same universality class as the $\lambda$ transition in liquid $^4$He [Clark 2007]. If this is indeed the case then NCRIF can be calculated by means of Josephson relation [Josephson 1966] and the two-scale-factor universality
hypothesis [Stauffer 1972] [Hohenberg 1976], where the superfluidity density can be calculated from the heat capacity singularity. This prediction has been tested and found satisfactory for the superfluid transition of liquid $^4$He under pressure [Singsaas 1984] and for liquid helium confined in porous media [Yoon 1997] [Finotello 1988] [Zassenhaus 1999]. An expression between heat capacity and the superfluidity density could be written down as Eq. 3.1:

$$\frac{A_L}{A_s} = \left( \frac{\rho L T_{CS}}{\rho_s T_{CL}} \right)^3$$

(3.1)

where $T_{CS}$ and $T_{CL}$ are the transition temperatures in solid and liquid, $\rho$ is the superfluidity density and $A$ is the singular specific heat. If we use the peak height as the amplitude of the singular specific heat then, when compared with the superfluid transition, the NCRIF is 0.04% for constant pressure samples in cell B, 0.06% for blocked capillary samples in cell A and 0.075% for blocked capillary samples in cell B. Those numbers are consistent with the TO results shown in Figure 3-14.

The total length of the dislocation lines per mole can be calculated by multiplying the dislocation density and the mole volume. If we assume the neighbor atoms along the dislocation lines are separated by the average lattice distance, the total number of atoms inside the dislocation network can be estimated. Helium atoms in a dislocation network of $5 \times 10^{11}$ cm$^{-2}$ are about 0.05% of the total. Such a dislocation density is larger than the typical dislocation density measured by ultrasound, which ranges from $10^5$ to $10^9$. The ultrasound measurement calculated the dislocation density based on the interaction between the sound and the vibration of dislocations. The average length of dislocation
lines between two pinning nodes is measured to be around 5 μm. Because the wavelength of ultrasound is around 10 μm, the dislocation density could be underestimated in ultrasound experiments because dislocation segments shorter than micron might not change the ultrasound velocity or attenuate the sound magnitude. The heat capacity contribution from dislocation lines is predicted to be linear in temperature [Granato 1958]. Because there is no observable linear heat capacity in our measurement, the upper dislocation density limit in our samples is $10^{15}$ cm$^{-2}$ based on Granato’s theory.

The onset temperature of NCRI has been found to be a function of $^3$He. However, the peak position in temperature is independent of $^3$He impurities between 1 ppb and 0.3 ppm samples. There is evidence that the higher $T_o$ values found in higher $^3$He concentration samples are due to finite vortex response time [Aoki 2007] [Anderson 2007], and that the true onset temperature in the zero frequency limit may also be lower than that observed in TO, independent of $^3$He concentration. If $^3$He impurities only affect the dynamic measurements, study in NCRIF of different $^3$He concentrations with a double frequency oscillator should be important in the future. For the same sample, the NCRI onset temperature difference between two resonant frequencies might be larger at higher $^3$He concentrations.

NCRIF has been found to be larger than 10% in solid $^4$He confined in annulus of around 0.15 mm. If the specific heat peak is associated with NCRI, then the solid $^4$He confined in similar geometry should exhibit larger peak. A heat capacity experiment of solid $^4$He confined between layers of thin wafers should be interesting to test this hypothesis in the future.
As discussed above, the specific heat peak is probably the thermal dynamic signature of the supersolid transition. However, even it is not related to NCRI, the unexpected specific heat peak itself is very interesting.

3.4.2 Pressure measurement

Pressure measurements in solid $^4$He have been performed from 100 to 500 mK [Grigor'ev 2007]. Aside from the usual phonon contribution $T^4$ term, there was an additional $T^2$ contribution observed in a sample that was cooled down as quickly as possible after the solidification. This $T^2$ term decreased by an order of magnitude after the solid sample was annealed. The sample studied in this measurement had no more than 10 ppm of $^3$He impurities.

The relationship between the pressure and the specific heat of the solid is Eq. 1.4. The Grüneisen constant for Debye solid $^4$He has been measured in [Gardner 1973] down to 0.35 K, and molar volume of helium can be deduced from the solid pressure. By applying Eq. 1.4, and assuming the Grüneisen constant does not change with temperature, the pressure as a function of temperature can be calculated from the specific heat result, as plotted in Figure 3-15. The green and red lines are from the pressure measurement. The red and green double sided arrows indicate the uncertainty of the pressure measurement. The blue triangle is calculated from the specific heat of 0.3 ppm sample (cell A) after being modified to compensate the density difference. The excess pressure calculated from heat capacity is indistinguishable from zero given the scatter in the pressure data. If the freshly grown sample $T^2$ term is converted to heat capacity, it
generates a linear heat capacity term, with coefficient of $\sim 3 \text{ mJ mol}^{-1} \text{ K}^{-2}$. There is no such dramatic annealing effect observed in the heat capacity measurement, which may be due to fact that the sample growth rate in our work is slower than the pressure experiment because of the conductivity limitation of the thermal weak link.

**Figure 3-15**: Calculated pressure as a function of $T^2$ from the specific heat measurement. The slope of a line is the $T^4$ coefficient in pressure and intercept is $T^2$ coefficient.
3.4.3 Melting curve of $^4$He

The liquid-solid coexistence boundary or the melting curve pressure of $^4$He (0.3 ppb of $^3$He impurities) was measured from 10 to 400 mK with the accuracy of about 0.5 to 2 μbar [Todoshchenko 2006]. After a systematic error from the pressure gauge was corrected, the authors concluded that the melting pressure of $^4$He follows the $T^4$ law due

Figure 3-16: Calculated pressure deviation as a function of $T^4$. 
to phonons over the temperature range from 10 to 320 mK [Todoshchenko 2007] [Todoshchenko 2008]. This implies a $T^3$ specific heat for both the solid and liquid phases. The relationship between the melting curve and the specific heat at the melting curve is known as the Clausius-Clapeyron equation (Eq. 3.2):

\[ \frac{dP}{dT} = \frac{S_{liq} - S_{sol}}{V_{liq} - V_{sol}} = \frac{S_{liq} - \int \frac{C}{T} dT}{V_{liq} - V_{sol}} \]  

(3.2)

The specific heat of a 25 bar liquid was shown to scale with $T^3$ from 220 to 350 mK [Greywall 1978]. If we also assume that solid in coexistence with liquid is thermodynamically identical to a solid near 33 bar, then any additional contribution to the pressure due to an anomaly in heat capacity can cause the pressure change, resulting in a deviation from a $T^4$ dependence. (Figure 3-16). The red square is the melting curve pressure from [Todoshchenko 2007]. We do not understand this apparent discrepancy between these two experiments. Although better quality samples in the same cell have smaller NCRIF, NCRI was still observed in single crystal [Clark 2007]. Solid in coexistence with liquid is of better quality because there is no stress inside. If the excess heat capacity is smaller in better quality samples, the deviation pressure from excess heat capacity of solid coexisting with liquid could be less than the sensitivity of this melting curve experiment.
3.4.4 Shear modulus anomaly

A recent experiment found an increase in the shear modulus that shares the same temperature and $^3$He concentration dependence as that of NCRI [Day 2007]. The shear modulus behavior is explained in terms of a dislocation network that is pinned by $^3$He at the lowest temperatures but becomes mobile above 100 mK. The relationship between

\[ C_n \text{[mJ mol}^{-1}\text{K}^{-1}] \]

\[ T \text{[K]} \]

Figure 3-17: Expected heat capacity changed due to the shear modulus anomaly. The red dashed line is the calculated heat capacity from a 20% increase of the shear modulus.
the shear modulus anomaly and the NCRI is not clear and the shear modulus anomaly can
not explain the excess heat capacity directly. Since the sound velocity increases in a
stiffer solid, an increase in the shear modulus implies a larger Debye term or a smaller
heat capacity. The expected maximum heat capacity change from a 20% shear modulus
anomaly is plotted in Figure 3-17. After the shear modulus anomaly is saturated at low
temperature end, the expected heat capacity is Debye temperature dependence with a
smaller $T^3$ coefficient.

In summary, specific heat peaks presented in this chapter are related to the sample
quality. It has found that the peak magnitude and position are different among samples
grown under constant pressure method, blocked capillary method in 20 hours and
blocked capillary method in 4 hours. Peak temperature and magnitude in better quality
samples are smaller. The specific heat peaks show no difference between samples made
of isotopically pure $^4$He and commercially UHP $^4$He.
Chapter 4

Specific heat of dilute $^3$He-$^4$He solid mixtures

Specific heat of solid $^4$He diluted with small amounts of $^3$He is discussed in this chapter. The heat capacity study on solid helium mixtures with less than 760 ppm $^3$He concentration has not been carried out before. We found that the 110 mK specific heat peak of isotopically pure solid $^4$He in cell B was also observed in mixtures with higher $^3$He impurities. Hysteresis and long time constant associate with phase separation (PS) were studied. An apparent constant heat capacity term due to PS in the solid mixture was found in most of the solid mixture samples.

This chapter is divided to three sections. The first section discusses the result of the 110 mK specific heat peak in cell B, which has been displayed in the previous chapter; the second section presents the results of PS and the last one concentrates on the apparent constant term resulting from the PS.

4.1 Specific heat peak independent of $^3$He impurity

The 110 mK specific heat peaks seen in isotopically pure and commercially UHP samples were observed in $^3$He-$^4$He mixtures and carefully studied in cell B. The 110 mK peaks in mixtures were almost identical to those in isotopically pure solid $^4$He, on top of signal from $^3$He impurities at low temperature, such as phase separation. The 110 mK specific heat peaks were found to be completely independent from to PS.
Seven samples under a pressure of 33 bar with noticeable phase separation effect were studied in cell B, labeled by the samples’ maximum $^3$He concentrations. Samples in the $^3$He impurity study were all grown with blocked capillary method. After measurement on each sample was completed, the calorimeter was first emptied above 4 K and cooled back down to base temperature. Traced amounts of $^3$He at room temperature were then dosed to the cell. The nominal $^3$He concentration was the maximum number, meaning that we calculate the concentration as if all the $^3$He went into the cell.

**Figure 4-1:** Specific heat without the $T^3$ contribution of sample 5ppm. The inset is specific heat in a log-log plot.
Specific heat of sample 5ppm is shown in Figure 4-1. The 110 mK peak seen in 1 ppb and 0.3 ppm samples was also observed in sample 5ppm, but there is an additional contribution from phase separation near 45 mK. We will discuss why this anomaly is due to phase separation in the next section.

Figure 4-2: Specific heat peak in the cooling scan of sample 10ppm_a.
In sample 10ppm_a, the heat capacity due to $^3\text{He}$ was larger than the 110 mK peak below 60 mK. However, the 110 mK peak could still be observed before PS happened, as shown in Figure 4-2. In the cooling scan of sample 10ppm_a, the 110 mK specific heat peak was observed all the way down to 63 mK. The 110 mK peaks between two samples (0.3ppm and 10ppm_a) are almost identical in term of magnitude and peak temperature. The slight differences might come from the sample quality differences.

In summary, 110 mK specific heat peak observed in isotopically pure $^4\text{He}$ or part of the peak has been observed in solid $^3\text{He}$-$^4\text{He}$ mixtures before the indication of PS. The magnitude and 110 mK peak position are similar to those in isotopically pure $^4\text{He}$ and commercially UHP $^4\text{He}$. We confirm the result that the peak we observed in chapter 3 does not originate from $^3\text{He}$ atoms in solid $^4\text{He}$.

4.2 Phase separation

We attributed the $^3\text{He}$ anomaly of samples 5ppm and 10ppm_a in the low temperature region to phase separation. Solid $^3\text{He}$-$^4\text{He}$ mixture splits into two nearly pure phases near 0 K. The simplified phase diagram is plotted in Figure 4-3. The first observation of $^3\text{He}$-$^4\text{He}$ solid mixture phase separation was obtained in 1962 with a heat capacity measurement [Edwards 1962]. Edwards and his coworkers measured the specific heat of solid $^3\text{He}$ with from 0.03% to 80% of $^4\text{He}$ impurities and found anomalies corresponding to the appearance of the mixing entropy, which suggested that the solid separated into two phases. The phase separation temperature was determined from the
anomaly in the temperature dependence of the specific heat during a rapid first cooling of the samples. It is found that from 0.97% to 20% of $^3$He, the phase separation temperature can be explained by the model of regular solutions [Edwards 1962].

![Figure 4-3: Phase separation temperature as a function of $^3$He concentration in a linear scale, adopted from [Edwards 1962].](image)

However, the regular solution model neglects the lattice different between solid $^3$He (bcc) and solid $^4$He (hcp) at low temperature. The calculation of the $^3$He-$^4$He phase diagram has been modified in order to include the hcp-bcc transformation [Edwards 1989]. The new model is in good agreement with the separation phase diagram constructed by the pressure measurement of solid $^3$He-$^4$He samples [Gan'shin 2000]. In this experiment the pressure of a sample with $^3$He impurity $> 2\%$ (20,000 ppm) in a
constant volume was measured as the sample cell was cooled or heated in steps. With certain assumptions, the $^3$He level of the phase separated dilute phase was deduced from the pressure changed. The authors concluded that their experimental data were in agreement with the theory of Edwards and Balibar, reporting a phase separation temperature of 81 mK (which is also the minimum temperature of the experiment) for 10 ppm $^3$He impurity. However, an ultrasound experiment [**Goodkind 2006**] found a phase separation temperature of 80 mK for a 220 ppm sample, with no signature of phase separation down to 50 mK for samples with 27 ppm and 14 ppm. Lastly, there have been many experiments employing a variety of techniques to study 0.3 ppm commercially UHP solid $^4$He down to at least 20 mK (predicted phase separation temperature is 60 mK for a 33 bar solid from the theory of Edwards and Balibar). There has been no report of phase separation in these experiments [**Armstrong 1979**] [**Paalanen 1981**] [**Kim 2004**] [**Kim 2004b**] [**Rittner 2006**] [**Aoki 2007**] [**Clark 2007**] [**Kondo 2007**] [**Penzev 2007**] [**Rittner 2007**]. The theory of Edwards and Balibar might need to be amended for very low $^3$He concentrations. For a review on the properties of solid $^3$He-$^4$He mixture at low temperatures see [**Edwards 1992**].

Measurements of the latent heat of mixing were carried out by [**Hebral 1981**] [**Schrenk 1991**] [**Clark 2005**] at lower $^3$He concentrations. Hysteresis and long time constants throughout the phase separation process were reported. The phase separation temperature as a function of $^3$He concentration (less than 5%) in a log-log scale is plotted in Figure 4-4.
In this section, we present details of the PS study. PS was observed only in cell B at the low temperature end. It could have happened in cell A but we did not have enough sensitivity to detect it. For instance, PS was observed in the sample 5ppm, as shown in Figure 4-4: The phase separation temperature as a function of $^3$He concentration in the $^4$He rich phase. Solid line and dash line are theoretical predictions for 33 bar solid $^4$He based on [Edwards 1962] and [Edwards 1989], respectively. Triangle is for a 27 bar solid (1000 ppm $^3$He) [Hebral 1981]; stars are for solids from 27 to 33 bar, the higher the pressure, the lower the transition temperature (4500 ppm and 9000 ppm $^3$He) [Schrenk 1991]; pentagon is for a 38 bar solid (760 ppm) [Clark 2005].
Figure 4-1. The heat capacity signal from phase separation is only several times larger than the best sensitivity of our experiment.

The nominal concentration was the largest possible concentration for the $^3$He impurities. There are two main effects that may modify the actual $^3$He concentration of the solid inside the calorimeter. Heat flush effect was known from previous experiences [Owers-Bradley 1988] [Ho 1997]. It was found that $^3$He atoms could be driven away from the sample container by temperature gradients. When a heat pulse was applied, a fraction of $^3$He was flushed out of the cell in the studies of low $^3$He concentration liquid mixtures. Thus the history of how the samples were prepared was extremely important because the gas handling system involved not only the calorimeter but also the heat exchangers at low temperature. Surface effect was the other one that may modify the $^3$He concentration in the calorimeter [Carmi 1989] [Carmi 1995]. It was found that $^3$He preferentially adsorbs on the liquid-solid interface. Again, the history of how the samples were prepared effects the $^3$He distribution.

Due to the heat flush effect and surface effects, and the difficulty of simultaneous measurement of $^3$He concentration in the calorimeter, we could not identify the $^3$He concentration precisely. However, as shown in Figure 4-4, samples with larger $^3$He concentration should have higher phase separation temperature.
4.2.1 Hysteresis

Hysteresis was reported in previous solid mixture specific heat measurements. The results from sample 10ppm_a show the hysteresis clearly (See Figure 4-5). Specific heat from the cooling scans is always less than that in warming scan in all the samples showing hysteresis. The deviation temperature from UHP solid $^4$He is also at lower temperature in the cooling scan. In the cooling scan of sample 10ppm_a, the 110 mK

Figure 4-5: Hysteresis effect of sample 10ppm_a.
specific heat peak and the phase separation signal without the phonon contribution is shown together in Figure 4-2.

### 4.2.2 Long time constant

![Figure 4-6: Specific heat of sample 10ppm_b as a function of temperature on different scans. The history of the sample is indicated in the figure by the numbers and arrows.](image)
The long time constant effect was studied together with the hysteresis in sample 10ppm\_b, as shown in Figure 4-6. The sample was first kept at base temperature overnight and data was taken while warming up to 320 mK (scan 1, a->b). Then it was cooled down to base temperature and hysteresis was observed (scan 2, b->c). The third scan warmed up the sample to 320 mK again (scan 3, c->d), measuring specific heat smaller than the first scan but larger than the second scan. The last scan cooled down

Figure 4-7: Specific heat of sample 10ppm\_b for the entire temperature range. The inset is specific heat of scan 1 and 2 without the $T^3$ contribution. In the inset, other than the hysteresis from phase separation, part of the specific heat peak can be seen.
from 320 mK (scan 4, d->e) and waited at 50 mK for 10 hours (scan 4, e->f). Specific heat was found to continuously change with time. Typically the calorimeter reached thermal steady state after 1 to 2 hours in the region without the phase separation. After that the sample was cooled to base temperature (scan 4, f->g), warmed back up (scan 4, g->h), and found its specific heat following the first scan. Specific heat for the entire temperature range of the first set warming and cooling data with $T^3$ term subtracted is shown in Figure 4-7.

### 4.2.3 Phase separation temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{ps}$ [mK]</th>
<th>$X_3$ [ppm] based on Figure 4-4</th>
<th>Dosed $X_3$ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5ppm</td>
<td>N/A</td>
<td>N/A</td>
<td>5</td>
</tr>
<tr>
<td>10ppm_a</td>
<td>63 ± 5</td>
<td>0.8</td>
<td>10</td>
</tr>
<tr>
<td>10ppm_b</td>
<td>74 ± 6</td>
<td>7.5</td>
<td>10</td>
</tr>
<tr>
<td>30ppm</td>
<td>76 ± 5</td>
<td>9</td>
<td>30</td>
</tr>
<tr>
<td>100ppm_a</td>
<td>66 ± 4</td>
<td>1.5</td>
<td>100</td>
</tr>
<tr>
<td>100ppm_b</td>
<td>86 ± 4</td>
<td>36</td>
<td>100</td>
</tr>
<tr>
<td>500ppm</td>
<td>109 ± 5</td>
<td>290</td>
<td>500</td>
</tr>
</tbody>
</table>

Table 4-1: $^3$He concentration deduced from PS temperature. The sample 5ppm had insufficient sensitivity to tell the onset of PS.
PS temperature ($T_{ps}$) in our study was determined from the anomaly in the temperature dependence during a cooling scan, similar to previous studies. The $^3$He concentration dependence of $T_{ps}$ for a 33 bar solid has been plotted in Figure 4-4. By measuring the $T_{ps}$, we could estimate the actual $^3$He impurities in the mixture. Results are summarized in Table 4-1. However, the result is not satisfactory. The reason is probably that $T_{ps}$ is not sensitive to $^3$He concentration at low temperature range (from 1 to 100 ppm the transition temperature only changes from 64 to 96 mK according to the theory of [Edwards 1989]) while the reliability of $T_{ps}$ from the specific heat measurement was limited by the density of data points (usually in this temperature range we took measurement every 5 to 10 mK).

4.2.4 The heat capacity magnitude of phase separation

The heat capacity signals due to phase separation in samples 10ppm_b and 500ppm are plotted in Figure 4-8. The phonon contribution and the specific heat peak from a 0.3 ppm sample have been subtracted. The magnitude of the heat capacity in the warming scan is higher and the PS signal in warming scan also appears at higher temperature. The phase separation signal is very similar to the study in reference [Clark 2005]. As shown in Figure 4-8, the warming scans have larger heat capacity and higher onset temperature in both measurements.
The heat capacity magnitudes of the warming scan are summarized in Table 4-2. The more reasonable value to be compared with should be the entropy of PS. Because at our base temperature the PS is not completed, we could not estimate the mixing entropy. The heat capacity magnitude of the warming scan is used as the indicator of PS. It should be noted that the magnitude of the warming scan depends on the history of the sample. It was found that for the same sample, the magnitude of the warming scan became larger if

Figure 4-8: Comparison of phase separation in sample 10ppm_b, sample 500ppm and previous measurements of a 760 ppm sample [Clark 2005].
the sample stayed in the base temperature longer. The uncertainty of the phase separation temperature is about 5 to 10 mK.

Table 4-2: Summary of the phase separation heat capacity magnitude in our study, together with previous heat capacity measurement on $^3$He-$^4$He phase separation. The dosed $^3$He concentration is only the nominal number, indicating the maximum possible concentration. The real $^3$He concentration should refer to the phase separation temperature qualitatively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tps [mK]</th>
<th>Heat capacity magnitude [$\mu$J mol$^{-1}$ K$^{-1}$]</th>
<th>Dosed X$_3$ [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 ppm</td>
<td>N/A</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>10 ppm</td>
<td>63 ± 5</td>
<td>37</td>
<td>10</td>
</tr>
<tr>
<td>10 ppm</td>
<td>74 ± 6</td>
<td>59</td>
<td>10</td>
</tr>
<tr>
<td>30 ppm</td>
<td>76 ± 5</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>100 ppm</td>
<td>66 ± 4</td>
<td>34</td>
<td>100</td>
</tr>
<tr>
<td>100 ppm</td>
<td>86 ± 4</td>
<td>160</td>
<td>100</td>
</tr>
<tr>
<td>500 ppm</td>
<td>109 ± 5</td>
<td>450</td>
<td>500</td>
</tr>
<tr>
<td>[Clark 2005]</td>
<td>130</td>
<td>640</td>
<td>760</td>
</tr>
<tr>
<td>[Hebral 1981]</td>
<td>150</td>
<td>3*10$^3$</td>
<td>1000</td>
</tr>
<tr>
<td>[Schrenk 1991]</td>
<td>170-190</td>
<td>7*10$^3$</td>
<td>9000</td>
</tr>
</tbody>
</table>

4.3 Apparent constant heat capacity from PS

We reported a constant term in solid $^3$He-$^4$He mixtures in our previous publication [Lin 2007] below 400 mK. The apparent constant term was also observed later in cell B. In the more careful study with cell B, the apparent constant term in heat capacity is understood as a misinterpretation of PS.
The heat capacity of four samples in cell A containing different amounts of $^3$He impurities are plotted together in Figure 4-9 with isotopically pure $^4$He and commercially UHP $^4$He. The 10 ppm and 30 ppm are nominal concentrations. We have discussed the difficulty of knowing the $^3$He concentration precisely in cell B. Cell B had
more complicated capillary path and more heat exchangers than cell A. The actual $^3\text{He}$ concentrations in cell A were probably closer to the prepared amount in the room temperature density.

**Figure 4-10**: Plot of specific heat against $T^3$. Data for 0.3 ppm, 10 ppm and 30 ppm samples have been shifted upward by 1, 2, and 3 mJ mol$^{-1}$ K$^{-1}$. Inset, fits without data points to demonstrate the zero intercepts for 1 ppb and 0.3 ppm, and the non-zero values for 10 ppm and 30 ppm. The slope of the 0.3 ppm sample is different than the others is only because a slight density difference.
The scatter of the 30 ppm sample is larger because the signal is inversely proportional to the measured heat capacity. The low temperature behavior of the 30 ppm sample suggests a constant term in the specific heat. To test this hypothesis, we plot specific heat against $T^3$ in Figure 4-10. The linear fit was applied between 140 and 430 mK because below 140 mK the excess specific heat peak showed up.

Figure 4-11: Specific heat of the sample 100ppm_a with the phonon term subtracted.
The data for 1 ppb and 0.3 ppm samples fall on straight lines passing through the origin. The y-axis intercepts for the 1 ppb and 0.3 ppm samples are in distinguishable from zero; that is, they are within ±5 μJ mol⁻¹ K⁻¹. The data for the 10 ppm and 30 ppm samples also fall on straight lines with non-zero intercepts in this plot. The apparent constant terms from the fit for 10 ppm and 30 ppm samples are 59±10 and 430±40 μJ mol⁻¹ K⁻¹. A possible source of the apparent constant term is the presence of the ³He impurities in the solid. We suggested that it could be related to the high mobility of ³He in [Lin 2007].

<table>
<thead>
<tr>
<th>Scan</th>
<th>Constant term [μJ mol⁻¹ K⁻¹]</th>
<th>Time between base T and 200 mK [h]</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Warming 1</td>
<td>113±46</td>
<td>18</td>
<td>One data point every ~10 mK below 200 mK. Each point ~1 h.</td>
</tr>
<tr>
<td>Cooling 1</td>
<td>N/A</td>
<td>N/A</td>
<td>No enough data in this scan.</td>
</tr>
<tr>
<td>Warming 2</td>
<td>101±47</td>
<td>25</td>
<td>Similar to Warming 1, but the sample was left for 5 hours at 200 mK before taking higher temperature data.</td>
</tr>
<tr>
<td>Cooling 2</td>
<td>40±30</td>
<td>N/A</td>
<td>Cool down from Warming 2.</td>
</tr>
<tr>
<td>Warming 3</td>
<td>130±30</td>
<td>3</td>
<td>The sample was warmed up from base temperature to 200 mK directly, before taking higher temperature data.</td>
</tr>
<tr>
<td>Cooling 3</td>
<td>29±17</td>
<td>N/A</td>
<td>Cool down from Warming 3. The sample stayed at 320 mK for 2 extra hours.</td>
</tr>
</tbody>
</table>

The constant term of 10 ppm sample in cell A was believed to extend all the way to the base temperature (around 50 mK) in our previous publication [Lin 2007]. However,
in cell B, which was optimized for temperature below 200 mK, phase separation in this
temperature range was detected. With poor sensitivity in cell A, a broad peak signal from
PS was misinterpreted as a constant term, as shown in Figure 4-11.

The systematic study of the relationship between the apparent constant term and
PS was carried out in the sample 500ppm. In that sample, the magnitude of the constant
term was found to be related to the history of sample. The sample 500ppm was warmed
up and cooled down within different amount of time. The magnitude of the constant term
was observed to vary. The more separated $^3$He atoms are above 200 mK, the larger the
constant term from the fit. The result is summarized in Table 4-3. The results clearly
show that PS causes the apparent constant heat capacity term.

In summary, the study of the $^3$He-$^4$He mixtures showed that the specific heat peak
is independent of $^3$He concentration. Due to the improved sensitivity, phase separation
has been observed in cell B but it was not seen earlier in cell A. In light of this new
information, we determine that the constant term reported previously results from the
misinterpretation of PS.
Chapter 5

Conclusion

High resolution heat capacity measurements on solid $^4$He were carried out down to 25 mK. On top of the Debye $T^3$ term, a broad peak in specific heat was observed in the temperature range where NCRI has been observed. It has found that the peak magnitude and position are different among samples grown under constant pressure method, blocked capillary method in 20 hours and blocked capillary method in 4 hours. Peak temperature and magnitude in better quality samples are smaller, as is the case for the NCRI measured in TO experiments. The magnitude of the peak is on the order of $10^{-5}$ J mol$^{-1}$ K$^{-1}$ and the center of the peak varies between 60 and 110 mK. This peak could be the thermodynamic signature of the supersolid phase. We searched for but did not find any linear heat capacity for the entire temperature range.

In the heat capacity study of $^3$He-$^4$He solid mixtures, the specific heat peak was also observed and found to be independent of the $^3$He concentration. Why $^3$He dependence is observed in TO experiments but not in the specific heat result is still a puzzle. With sufficient amounts of $^3$He impurities, phase separation was observed together with the specific heat peak.
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