

How to Prepare an Ideal Helium 4 Crystal

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Abstract Given the running controversies on the interpretation of supersolidity, it appears important to measure more accurately what are the properties of helium 4 crystals in the absence of disorder. We recall how to prepare single crystals with no or very few dislocations. We then show that these crystals are extremely fragile and how to avoid the formation of defects. The main purpose of this article is to show how one can eliminate all helium 3 impurities from the solid: if the crystals are in equilibrium with liquid helium 4 below 50 mK, all helium 3 impurities are bound to the liquid phase with a large binding energy which we have calculated from the description of helium mixtures by Edwards and Balibar (Phys. Rev. B 39:4083, 1989).

Keywords Helium crystals · Supersolidity · Helium mixtures · Crystalline defects

1 Introduction

It is certainly difficult, if not simply impossible, to demonstrate experimentally that an effect does not exist. This statement applies to the question of supersolidity in ideal crystals, that is in crystals with no structural disorder nor any impurities. Numerical simulations by Ceperley et al. [1] and by Prokof'ev et al. [2, 3] lead to the

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conclusion that supersolidity is impossible in ideal crystals because they contain no free vacancies in the $T = 0$ limit. However, according to Anderson [4], there could be a concentration of vacancies of order 2 to 3×10^{-4} in ideal crystals so that these ideal crystals could be supersolid below about 50 to 70 mK. Whatever the arguments are in this *theoretical* controversy, it is an important *experimental* challenge to search for supersolidity in ideal helium 4 crystals. Among other authors, Rittner and Reppy [5, 6] have shown that supersolidity is highly sensitive to crystal quality and Kim et al. [7] have shown that it is also very sensitive to ^3He impurity concentration. For a review and more references, see Ref. [8]. But a fundamental question is not yet settled: is disorder *necessary* for supersolidity or is it only modifying supersolidity which already exists in the absence of disorder?

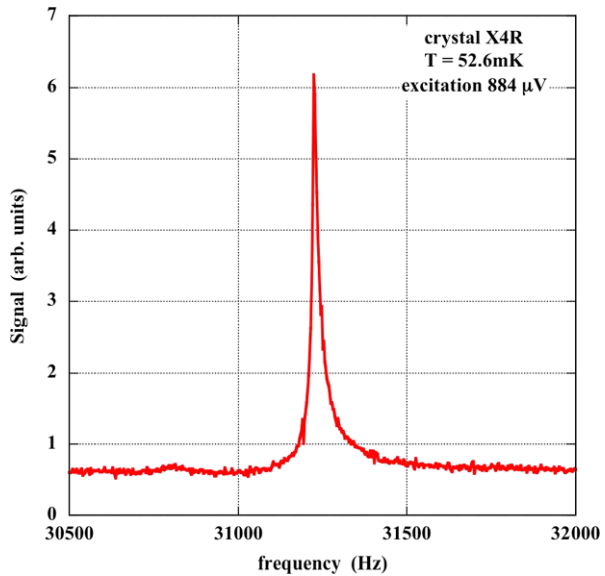
For an experimental investigation of this fundamental issue, one needs to measure various properties in crystals having the highest possible quality and purity. It has been already shown [9] that it is possible to prepare extremely high quality single crystals of helium 4, but our experiments confirm that hcp helium 4 crystals are extremely fragile and we explain here how to avoid the formation of defects after growth. As for eliminating all helium 3 impurities, we have realized that there is a simple method to do it: one simply needs to keep the crystal in equilibrium with liquid helium 4 at low temperature, typically below 50 mK. This is because helium 3 atoms go into this liquid phase where they are bound with a large binding energy ΔE_3 . We have calculated ΔE_3 which governs the ratio of concentrations X_3^h and X_3^L respectively in the hcp solid h and in the liquid L , thanks to the theory of helium mixtures by Edwards and Balibar [11]. As we shall see, we have found $\Delta E_3 = 1.359$ K, so that the concentration ratio is extremely small at low T : 10^{-12} at 40 mK.

2 Zero Defects

As summarized in the review article by Balibar, Alles and Parshin [12], the quality of crystals depends on their growth conditions. In 1995, Rolley et al. [13] grew ^4He crystals at the liquid–solid equilibrium pressure and at low temperature by adding mass into their cell. Their fill line (typically 0.5 mm inner diameter) was thermally anchored at 1 K, on the still at 0.7 K of their dilution refrigerator and on the 50 mK plate below the continuous heat exchangers. This way, it was rarely blocked by the solid. In the region at 0.8 K where the melting pressure has a shallow minimum, the pressure was above the local melting pressure by less than 0.01 bar so that helium could stay in a metastable liquid state. They started the growth of their sample from a small crystalline seed (about 1 mm in size) around 100 mK and never exceeded a growth speed of 0.1 $\mu\text{m/s}$. By proceeding so, they obtained single crystals without visible stacking fault. They measured the typical difference in chemical potential $\Delta\mu$ across a facet during growth and found $\rho_c \Delta\mu = 2 \times 10^{-3}$ mbar (ρ_c is the crystal density and $\Delta\mu$ is taken per unit mass). This value was similar to what had been measured as a threshold for the spiral growth of their crystals by Wolf et al. in a previous experiment [14]. It corresponds to a dislocation density of 10^4 cm^{-2} .

In a more recent experiment, Ruutu et al. [9] obtained crystals with densities of screw dislocations in the range 0 to 100 cm^{-2} by growing them at 20 mK without

Fig. 1 (Color online) A typical acoustic resonance measured with 884 μV excitation voltage in a 1 cm^3 cell filled with a single crystal (X4R) of ^4He . In this particular case, the quality factor is 2800

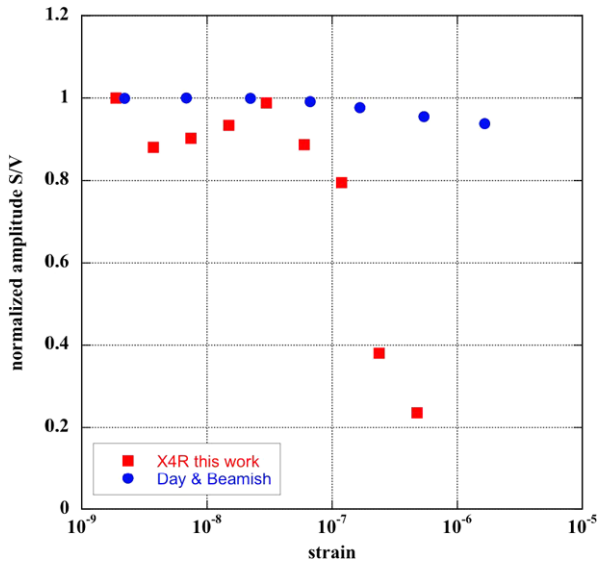


special care on the growth speed. The evidence for the absence of screw dislocations was obtained from the growth proceeding by terrace nucleation instead of spiral motion of steps attached to screw dislocations. It is likely that, if there were no screw dislocations there were no edge dislocations either. This is probably a consequence of the high mobility of steps in the $T = 0$ limit. It appears possible to grow single crystals of ^4He without structural defects by adding mass in a cell at constant pressure, at the lowest possible temperature, for example around 20 mK. It is likely that this method also works at slightly higher temperature if the growth is slow, 0.1 $\mu\text{m/s}$ for example.

If the crystal has to fill an experimental cell, one has to be careful with the cell shape. Indeed, it has been shown that the liquid-solid interface has a contact angle with solid walls of order 45 degrees [12, 15]. As a consequence, the cell fills like any volume by a non-wetting fluid. In order to be completely filled, it needs to have a convex shape with no sharp corners, otherwise liquid regions would be trapped in these corners. Of course, since gravity drives the crystal to the bottom part of the cell, the orifice of the fill line needs to be the highest point of the cell, otherwise it gets blocked before the cell is full of solid.

After the growth of an ideal crystal, it is necessary to preserve its high crystalline quality. This has to be done carefully because ^4He crystals are extremely fragile. Obviously, the crystals need to be kept at the liquid-solid equilibrium pressure P_{eq} . Even there, they need to be carefully protected against mechanical perturbations. This is because helium crystals are not like classical crystals where the plasticity threshold strain ϵ_p is of order 10^{-2} , also the threshold ϵ_{nl} for non-linear elastic behavior and the threshold strain ϵ_f for fracture. As shown by Day and Beamish [16], ϵ_{nl} is about 3×10^{-8} and ϵ_p about 10^{-6} in polycrystalline samples of ^4He . We have used a similar acoustic technique (Fig. 1) to measure these two quantities in poly- and in single crystals. Our results are similar. Note, however, that these thresholds have not

Fig. 2 (Color online) The threshold strain for non-linear elastic behavior. Our set of data (*squares*) is taken at 52.6 mK with the same single crystal (X4R) as on Fig. 1. We have found a dependence on strain of the signal/excitation S/V which is much stronger than found by Day and Beamish (*circles*) with a polycrystal at 18 mK. But the value of the threshold strain ($\epsilon \approx 3 \times 10^{-8}$) is the same



yet been measured in crystals free of defects, where they might be much larger, as is usually found in classical crystals.

Figure 2 shows some of our measurements compared with those by Day et al. [16]. In a nearly cubic cell with inner volume 1 cm^3 , we have used two piezoelectric transducers to generate and detect shear waves (for a preliminary report on these experiments, see Ref. [10]). As first observed by Day and Beamish, we have found that the resonance frequency shifts to a high value at low temperature, something which indicates that the supersolid transition is accompanied by a transition from a soft to a stiff state of solid ^4He . We have also measured the maximum signal S at resonance on one of the transducers as a function of the excitation voltage V on the other transducer. We found fundamental modes around 30 kHz with a quality factor in the range 500 to 3000 depending on temperature (see Fig. 1 where $Q = 2800$). For this, we used very small excitation amplitudes (about 1 mV). Our piezoelectric transducers are “shear bars” made with their “C5800” PZT material by Channel Industries (USA). Their piezoelectric coefficient d_{15} is $390 \cdot 10^{-12} \text{ m/V}$ at room temperature. As shown by Day et al. [17], this coefficient is smaller by a factor 5 at liquid helium temperatures, so that we estimate the displacement u_0 at the surface of our transducers as $0.8 \text{ \AA}/V$ ($0.8 \cdot 10^{-3} \text{ \AA}$ for 1 mV !). For a resonance with a quality factor Q , the maximum displacement u_{max} of the displacement is Q times the excitation amplitude u_0 . Finally, for a wavelength λ of order 1 cm as in our cell, the maximum strain is $\epsilon = Qu_0/\lambda$. For the graph on Fig. 1, which corresponds to the single crystal X4R and a 0.884 mV excitation, we have found $Q = 2800$. With this value, we have found a non-linearity threshold in agreement with Day and Beamish’s results ($\epsilon \approx 3 \times 10^{-8}$). Figure 2 shows a dependence on strain which is much stronger than found by Day and Beamish but our experimental conditions are slightly different from those in the experiment by Day and Beamish: our temperature is 52.6 mK which is near the high temperature end of the transition to the stiff state in our case [10], while Day and Beamish have measured it at their lowest temperature (18 mK) in the stiff state below

the transition temperature. Furthermore, they studied polycrystals while we studied single crystals. Obviously, this non linearity threshold needs more measurements in various types of solid samples and also a quantitative interpretation.

We define the plasticity threshold as the strain beyond which irreversible changes in the resonance frequency are observed, probably due to the creation of additional defects. We have found that it is of order 10^{-6} , that is larger by about 2 orders of magnitude than the non-linearity threshold, and once more in agreement with Day and Beamish.

A careful study of these two thresholds is in progress in our laboratory. We are particularly interested in measuring them with very high quality crystals where finding much higher values would be a strong indication of the absence of defects. In any case, it is already clear that helium crystals need to be carefully protected against damage by mechanical vibrations. Since the typical shear modulus of solid ^4He is 115 bar at the melting pressure [18], the threshold stress for irreversible changes in usual crystals is less than 1 mbar. Mechanical vibrations could produce stresses above the plasticity threshold. This is probably the reason why the elastic properties of our crystals often change after each transfer of liquid helium into our dewar: we observed random changes of the resonance frequency by about 100 Hz (0.3%). In summary, we recommend that single crystals are very carefully handled after growth.

3 Zero Impurity: The Binding Energy to the Liquid

Edwards and Balibar [11] have given semi-empirical formulas for the chemical potentials μ_4 and μ_3 of ^4He and ^3He atoms in helium mixtures which can be liquid or solid. Here we only need the low helium 3 concentration and low temperature region of the phase diagram, where several useful approximations can be made, as we shall see. Our goal is to calculate the concentration ratio X_3^h/X_3^L of ^3He impurities respectively in the hcp solid h and in the liquid L . We assume that ^3He concentrations X_3 are smaller than 10^{-3} , consequently much less than 1, and we restrict our calculation to temperatures less than 200 mK. To go beyond this restricted domain, one has to use the full theory described in Ref. [11].

We need to calculate the chemical potential of ^3He atoms in the phases h and L which are nearly pure solid and liquid ^4He . At low concentrations $X_3^{h,L}$, equating the chemical potential of ^4He atoms in L and h forces the liquid–solid equilibrium pressure P to be very close to that of pure ^4He , $P_{\text{eq}} = 24.993 \text{ atm} = 25.324 \text{ bar}$ [20].

Let us calculate all energies in Kelvin per atom (K/at) and start with the chemical potential μ_3^h of ^3He atoms in hcp solid ^4He . Following equation (10) in Ref. [11], one has

$$\mu_3^h(X_3^h, P, T) = g_3^b(P, T) + A(P) + T \ln X_3^h + \Delta_3(P), \quad (1)$$

where we have neglected the concentration X_3^h with respect to 1. Equation (1) was derived in Ref. [11] from the regular solution model which was proven to fit experimental data very well [11].

For our present purpose, the pressure $P = P_{\text{eq}}$. The quantity $g_3^b(P, T)$ is the Gibbs free energy of pure bcc solid ^3He extrapolated to P_{eq} . This is a reference energy which is bound to disappear when writing $\mu_3^h = \mu_3^L$.

The quantity $A(P)$ is the main parameter in the “regular solution model”. It is equal to 0.76 K at 35.8 atm [11]. Since its pressure derivative is

$$dA/dP = B = -0.364 \text{ cm}^3/\text{mol} = -4.436 \times 10^{-3} \text{ K/atm.at,} \tag{2}$$

we find

$$A(P_{\text{eq}}) = 0.76 + 10.8 \times 4.436 \times 10^{-3} = 0.808 \text{ K/at.} \tag{3}$$

The energy difference $\Delta_3(P) = g_3^h(P, T) - g_3^b(P, T)$ originates in the change in volume per atom when going from the bcc to the hcp ^3He phase. Since the phonon entropy is negligible for our purpose, this difference is independent of T and we obtain it by extrapolating from the bcc-hcp equilibrium line of pure ^3He at $T = 0$. As explained in Ref. [11], one has

$$\Delta_3(P) = (P - P_3^0) \left[\delta v_3^0 + \frac{1}{2} \beta_3 (P - P_3^0) \right], \tag{4}$$

where $P_3^0 = 105 \text{ atm}$, $\delta v_3^0 = -0.09 \text{ cm}^3/\text{mol}$ and β_3 is such that

$$\delta v_3 = \delta v_3^0 + \beta_3 (P - P_3^0) = -0.176 \text{ cm}^3/\text{mol} \tag{5}$$

at $P = 35.8 \text{ atm}$. We find

$$\beta_3 = 1.243 \times 10^{-3} \text{ cm}^3/\text{mol.atm,} \tag{6}$$

so that

$$\delta v_3(P_{\text{eq}}) = -0.189 \text{ cm}^3/\text{mol.} \tag{7}$$

Finally,

$$\Delta_3(P_{\text{eq}}) = 0.137 \text{ K/at} \tag{8}$$

and

$$\mu_3^h = g_3^b + 0.945 + T \ln X_3^h \text{ K/at.} \tag{9}$$

Let us now calculate the chemical potential of ^3He atoms in the ^4He -rich liquid L . Here we simplify Edwards and Balibar’s calculation [11]. Since the concentration is less than 10^{-3} , interactions can be neglected. We further assume that the temperature is low (say, less than 200 mK) but high compared to the Fermi temperature T_F^* of the ^3He impurities, so that the gas of ^3He atoms can be approximated by a perfect classical gas of particles with an effective mass $m_3^* = 3.3m_3$ [11, 19]. One has

$$k_B T_F^* = \hbar^2 (3\pi^2 n_3)^{2/3} / 2m_3^*. \tag{10}$$

In the above equation, n_3 is the number density of ^3He atoms in the ^4He -rich liquid. It is equal to $X_3^L N_A / V_4^L$ where N_A is Avogadro’s number and the molar volume V_4^L is 23.146 cm^3 . One finds

$$T_F^* = 1.85 (X_3^L)^{2/3} \text{ K,} \tag{11}$$

which is 18.5 mK for $X_3^L = 10^{-3}$.

The chemical potential of a classical gas of ^3He atoms in liquid ^4He is

$$\mu = -k_B T \ln \left[\frac{2V_4^L}{X_3^L N_A} \left(\frac{2\pi m_3^* k_B T}{h^2} \right)^{3/2} \right] \tag{12}$$

$$= k_B T \ln \left[X_3^L \left(\frac{T}{1.7} \right)^{-3/2} \right]. \tag{13}$$

Now we express the chemical potential μ_3^L in K/at as

$$\mu_3^L(P, T) = g_3^L(P, 0) + E_3(P) + T \ln \left[X_3^L \left(\frac{T}{1.7} \right)^{-3/2} \right], \tag{14}$$

where the quantity $E_3(P)$ is the difference in free energy for one ^3He atom in liquid ^4He compared to liquid ^3He at $T = 0$. According to Ref. [11] its value is -0.273 K at 25.289 atm and it’s pressure dependence is small enough that its value at P_{eq} is the same.

The reference energy $g_3^b(P, T)$ reappears because

$$g_3^L(P, 0) = g_3^b(P, T) + T \ln 2 + (1/k_B) \int_{P_3^m(0)}^P [v_3^L(P', 0) - v_3^b(P', 0)] dP', \tag{15}$$

where $P_3^m(0) = 33.95$ atm is the melting pressure of pure ^3He at $T = 0$ and $k_B \ln 2$ is the nuclear spin entropy of solid ^3He at low temperature. Following again Ref. [11], one has

$$v_3^L(P, 0) - v_3^b(P, 0) = (1.241 \text{ cm}^3/\text{mol}) \left[1 - \frac{P - P_{\text{min}}}{157.4 \text{ atm}} + \frac{T_{\text{min}}}{5.26 \text{ K}} \right],$$

where $T_{\text{min}} = 0.319$ K and $P_{\text{min}} = 28.932$ atm [21], so that the integral in (15) is -0.141 K/at at $P = 24.993$ atm.

Finally, one obtains

$$\mu_3^L(P, T) = -0.141 + T \ln X_3^L - 0.273 + T \ln (1.70/T)^{3/2} + T \ln 2. \tag{16}$$

Equating the two chemical potentials leads to

$$0.945 + T \ln X_3^h = -0.414 + T [\ln X_3^L + \ln (1.7/T)^{3/2} + \ln 2] \tag{17}$$

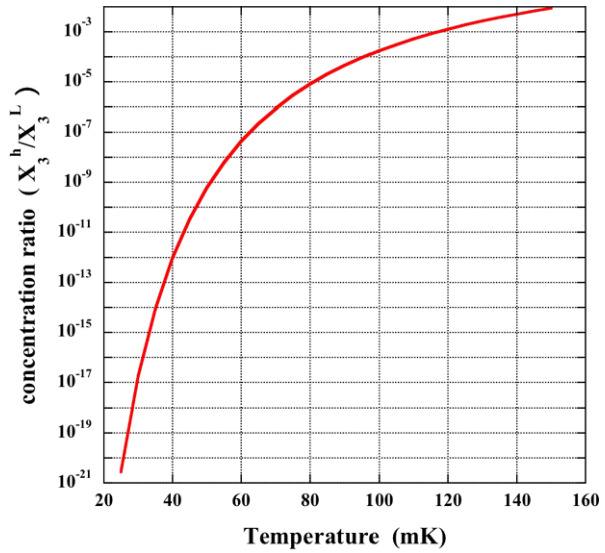
and to our final result:

$$\frac{X_3^h}{X_3^L} = 4.43 T^{-3/2} \exp \left(-\frac{1.359}{T} \right) \tag{18}$$

with T in K.

We now understand that the binding energy for ^3He atoms in liquid ^4He compared to solid ^4He is 1.359 K. As shown on Fig. 3, the concentration in the hcp solid is

Fig. 3 (Color online) The ^3He concentration ratio X_3^h/X_3^L as a function of temperature in the region where (18) is a good approximation



smaller than in the liquid by many orders of magnitude. It means that, if there is some liquid in equilibrium with the hcp solid, the solid is free of impurities, especially if one crystallizes helium which is already purified down to the ppb level (Some decades ago, purified helium 4 was commercially available from the US Bureau of Mines, today it can be purchased from P. McClintock at the University of Lancaster). One may ask if the diffusion coefficient D of ^3He impurities is sufficiently large for the equilibrium to be reached in a reasonable time. According to Schratte and Allen [22], D is inversely proportional to the concentration X_3^h , given by

$$DX_3^h = 2.6 \times 10^{-11} \text{ cm}^2/\text{s}, \tag{19}$$

so that the diffusion time on a 1 cm distance is in the range from a few seconds to one hour, depending on concentration. The experiments by Schratte et al. were done in crystals grown at constant volume, which are likely to be polycrystalline according to our observations [15]. If one had a classical crystal with ordinary diffusion, one might expect the diffusion to be enhanced by the presence of grain boundaries. But the $1/X_3$ dependence of this diffusion in the case of ^4He indicates that ^3He atoms are ballistic quasiparticles and that their diffusion is limited by their mutual collisions. In our opinion, it is likely that the diffusion in high quality single crystals is actually larger than measured by Schratte et al., except perhaps at very low temperature where ^3He atoms may bind to dislocations.

Of course, the much larger solubility of ^3He in liquid ^4He than in solid ^4He reminds us the “zone melting” method that is used for the purification of metals. In 1987, P.C. Hendry and P.V.E. McClintock [23] had optimized a purification method which used a heat flush in liquid helium. It might be possible to obtain even better purification by zone melting ^4He crystals.

Finally, one could include in the above calculation the presence of intermediate energy levels corresponding to ^3He atoms bound to dislocations. If thermodynamic

equilibrium is reached, dislocations make negligible corrections to the above calculation. According to Iwasa et al. [24, 25], the energy level on dislocations is $E_b \approx 0.3$ K below the energy in the bulk solid but according to Paalanen [26] $E_b \approx 0.7$ K. It means respectively 1.06 and 0.66 K above the energy level in the liquid. Let l be the average distance between two ^3He atoms on a dislocation. The ^3He density X_3^d on dislocations is

$$X_3^d = a/l = X_3^L (4.43 T^{-3/2}) \exp[(-1.359 + E_b)/T]. \quad (20)$$

In the worst case where $E_b = 0.7$ K and the liquid volume is only 0.1% of the cell volume so that, starting with ultrapure ^4He where $X_3 = 10^{-9}$, one has $X_3^L = 10^{-6}$ at low temperature, one obtains a maximum concentration on dislocations $X_3^d = 7.5 \times 10^{-10}$ at 50 mK. It means that, since the lattice spacing a is about 0.3 nm, the average distance l is 40 cm, much larger than the cell size, and even more at lower temperature. Below 50 mK, nearly all ^3He impurities should flow into the liquid, but it might take a long time if they don't flow along the dislocations themselves.

4 Conclusion

In summary, we believe that it is possible to prepare a ^4He single crystal with zero defects and zero impurities. It should be very interesting to measure its properties and see if they show rotation and acoustic anomalies corresponding to supersolidity. This measurement is in progress in our laboratory. It should be noted that, in the experiment by Sasaki et al. [27], no dc-mass superflow was found in single crystals of ^4He at 50 mK but, given the purity of crystals in equilibrium with liquid ^4He , these experiments should be repeated with improved accuracy below 40 mK where an elastic anomaly was recently found by Rojas et al. [10].

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