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Nucleation and orientation of ^4He crystals

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Résumé. — Nous montrons qu'une surpression de 10^{-2} bars au-dessus de la pression de solidification est suffisante pour nucléer des cristaux d'hélium 4. Cette valeur, en désaccord avec les prévisions théoriques qui concernent la nucléation en volume, suggère qu'il s'agit d'une nucléation sur les parois, pour laquelle d'autres estimations théoriques seraient souhaitables. Sur une paroi de graphite, les cristaux peuvent croître continûment sans barrière de nucléation. On en déduit une méthode précieuse d'obtention de cristaux orientés.

Abstract. — It is shown that liquid ^4He can usually be overpressurized only 10^{-2} bars above the melting pressure. This value suggests that the nucleation takes place on the walls of the cell, not in the bulk liquid as calculated previously. Further theoretical effort on this problem is called for. In the presence of carefully degassed graphite we confirm that the barrier to the nucleation disappears, and a method of obtaining macroscopic oriented single crystals is found.

In an earlier work [1], our attention was drawn to the possibility of obtaining *overpressurized* liquid ^4He , i.e. liquid ^4He at a pressure P greater than the melting pressure P_m . The experiments reported here concern the nucleation of solid ^4He from the liquid near the phase transition curve, in the range 20 mK to 2 K. We found that there is generally an energy barrier to the nucleation : it needs the creation by thermal or quantum fluctuations of a seed whose energy is finite. This barrier leads to a finite degree of possible *overpressurization* $\Delta P = P - P_m$, above which solid ^4He nucleates with a reasonable probability per unit time. The experimental value of ΔP is two or three orders of magnitude less than the theoretical estimates for bulk nucleation [2, 3] and we interpret it as evidence for a nucleation on the walls of the cell. These new results are thus presented as a call for further theoretical effort on this subject.

Under certain circumstances, the energy barrier is suppressed : this is the case when carefully degassed grafoil is settled in the cell. According to previous measurements [5, 6], a macroscopic h.c.p. solid phase can grow continuously on grafoil from the liquid as the pressure is raised up to P_m . We confirm this result and show that this provides a very useful method of getting oriented single crystals of h.c.p. ^4He .

1. Nucleation of ^4He crystals. — Experiments have been performed in various cells attached to a pure

^3He or to a ^3He - ^4He dilution refrigerator. These cells are connected to an external high pressure He gas cylinder *via* a fill line, whose main flow impedance consists typically in a one meter long, 0.35 mm inner diameter stainless steel tube. This impedance probably limits the residual pressure of air in the cell to 10^{-2} torr after the pumping procedure which precedes the cooling. The various metals and insulators which constitute the cell are thus probably covered at least by a monolayer of adsorbed air. On the other hand, this impedance makes it possible to look at the overpressurization of liquid He in a very simple way as follows : starting from an equilibrium situation with liquid in the cell at, say, $P_m - 0.5$ bars, the regulator on the cylinder is fixed at $P_m + 0.1$ bars and the pressure rises slowly (typically 3×10^{-3} bars s^{-1}) in the cell as a function of time. The temperature is regulated with an accuracy of 10^{-5} in order to eliminate pressure variations due to temperature variations when the solidification starts. The pressure in the cell is measured with a Straty and Adams type gauge and a conventional AC capacitance bridge (General Radio 1615 A) which can, in our case, display variations of P of the order of 2×10^{-4} bars. As shown by the figure (upper part, curve A) the fill line does not block, even below 0.78 K when the slope of the melting curve is slightly negative and the pressure usually rises above P_m . It then drops abruptly down to a plateau which is assumed to be P_m . This

Fig. 1. — *Upper part* : Two examples of the nucleation of solid ^4He in a cell where the difference ΔP between the pressure P and the melting pressure P_m is measured as a function of time during a pressurization process. Curve A : overpressurization is observed. Curve B : the presence of clean grafoil makes it impossible to obtain liquid He at $P > P_m$.

Lower part : The degree of possible overpressurization ΔP as a function of temperature. Black circles : without grafoil ; open circles : with clean grafoil ; triangles : with re-polluted grafoil. The two circles labelled A and B correspond respectively to the curves A and B.

sudden drop is attributed to the nucleation of solid He and its height is a measure of how far the liquid has been pressurized into the region of stability of the solid, that is the quantity ΔP already mentioned. On the diagram (lower part of the figure) several such measurements of ΔP have been plotted as a function of temperature (black circles ; we do not consider yet the open circles and triangles which concern the nucleation on grafoil, they will be examined later in the text). These values were obtained in various cells. The higher values were systematically obtained with a faster pressurization rate than for the lower ones. At a constant pressurization rate, the measurement of ΔP was very reproducible. The nucleation cannot be triggered by mechanical disturbances. We did not observe any evidence of a seed remaining below P_m from a previous solidification. The diagram leads to a few further remarks :

1) The value of ΔP is nearly constant in temperature and lies in the range of 10^{-2} bars. The values above 1.46 K, where the crystal is b.c.c., are smaller than those for the h.c.p. crystal. This could be due either to a smaller energy barrier for the nucleation of the b.c.c. crystal, or to a quantum nucleation process which becomes thermally activated above 1 K.

2) When solid helium has nucleated in the cell at a temperature $T_0 < 0.78$ K (i.e. below the minimum of the melting curve [16]) there is a length of the fill line where the pressure is higher than the local melting pressure. The value 10^{-2} bars is just big enough to avoid the nucleation of solid on this length, since the depth $P(0)-P(0.78)$ of the melting curve minimum is 8×10^{-3} bars and the local pressure goes down by 1.7×10^{-3} bars every 10 cm, when one goes up in the fill line because of the hydrostatic correction. When the liquid in the cell is overpressurized (i.e. just before the nucleation in our experiment) solid helium nucleates sometimes in the fill line, but very rarely if the liquid flow is fast enough. We have not yet found a convincing explanation for this phenomenon.

3) The value 10^{-2} bars is two or three orders of magnitude less than the theoretical estimates for bulk nucleation [2, 3]. This must be the sign of a different process and we think that the nucleation takes place on the wall of the cell.

4) The value 10^{-2} is fairly reproducible from one cell to another, regardless of the pieces inside. On the other hand, the angle of contact of the liquid-solid interface with a solid wall, as measured by Balibar *et al.* [1] with a copper wall, and by J. Landau *et al.* [8] with a glass wall, are very similar. We think therefore that the quantities measured in both cases are related to the free energies of the interfaces between solid air already adsorbed on the walls and liquid or solid ^4He . The value 10^{-2} bars probably characterizes the nucleation of solid ^4He on a wall made out of solid air. A calculation of such a process, instead of bulk nucleation, would be very interesting. Let us add at this stage that the probability of nucleation of one seed per second and per unit volume is a function which varies extremely fast with the degree of overpressurization of the liquid. Moreover, very fast growth velocities ($> 1 \text{ cm s}^{-1}$) have been observed in the case of ^4He crystals [8, 15]. We believe therefore that the quantity ΔP measured here is the one for which the probability of getting one seed per second in 150 cm^3 (the volume of our cell) is of order unity. We think also that ΔP is a function which varies very slowly with time, number of seeds and volume, so that our measurement is very general.

5) In the classification of adsorption made by Dash [9] and Peierls [10] solid ^4He has been found to be class II on a copper substrate [1]. We confirm in this experiment that it is class II on all the various metals and insulators which constitute our experimental cell, but which are covered with a monolayer of air as already mentioned. Let us further note that this does not imply that the nucleation of the solid has to take place in the bulk liquid instead of on the wall, under the pretext that it does not *wet them perfectly*. It just implies that there is an energy barrier for the nucleation, consequently a finite ΔP , as measured in this experiment.

2. Orientation of He crystals. — As some previous experiments [5, 6] reported that h.c.p. ^4He is class I on grafoil, we looked at ΔP in the presence of some grafoil. ΔP had to be zero : a bulk solid phase can grow continuously from the surface of grafoil as the pressure in the cell reaches the melting pressure. We first used some grafoil which had been degased under vacuum (10^{-6} torr) at 1 000 °C (red hot), but which had *seen* the air during its transfer into the experimental cell. Despite the usual two days pumping procedure of the refrigerator, the ΔP obtained was similar to the previous one. We then degased some grafoil directly inside the cell in order to avoid any pollution of its surface by air. The cell is maintained around 4 K so that the vacuum inside is fairly good, due to cryopumping. A 1.5 A, 2.5 V DC current is then passed through a $0.2 \times 2 \times 50 \text{ mm}^3$ thin rectangle of grafoil, for 20 s, with the aid of superconducting leads. This is the time necessary to warm the leads up to their transition to the normal state. It would be enough to warm the grafoil above 500 °C. As shown by curve B (upper part of the figure), the plateau at $P = P_m$ is reached without any overshoot, without any measurable ΔP . This is attributed to the continuous growth of solid ^4He on grafoil already mentioned by Landau *et al.* [5]. A recent neutron scattering experiment [6] showed that h.c.p. He crystals grow on grafoil with a c -axis perpendicular to the planes of the graphite hexagones. Our cell was equipped with a few heaters and detectors for heat pulse propagation experiments. We could then measure the orientation of our crystals using the anisotropy of the velocity of sound [11, 12]. Without grafoil we obtained successive crystals with c -axis pointing in arbitrary directions (0 to 90° from the vertical). With clean grafoil set horizontally at the bottom of the cell, all the crystals had a c -axis oriented within 20° from

the vertical, half of them being within 5°, the accuracy of the experimental determination. During all the experiments, it has always seemed difficult not to grow a single crystal, as mentioned also by B. A. Fraass [13]. We conclude therefore that several sites for the nucleation on the surface of grafoil can generate macroscopic single crystals which then invade the whole cell (the c -axis of the various graphite planes are oriented within 20° from the normal to the grafoil piece). This provides a very useful method for getting oriented single crystals of h.c.p. ^4He , which we have already used for the study of several of their anisotropic properties [12].

Let us note, finally, that we have tried to pollute again the clean grafoil by warming up the refrigerator, letting air in, pumping again without efficient degasing and cooling down. The possibility to overpressurize liquid He reappeared as shown by the triangles on the diagram.

It would be very interesting to know whether or not the continuous growth of solid ^4He on grafoil is a kind of epitaxy. The obtention of oriented crystals could be simply due to the presence of large clean graphite faces which very strongly attract the helium atoms, favour the formation of a first compact layer and then the growth of successive layers with the same 6-fold symmetry, that is a c -axis normal to the graphite original plane. In this case, a cleaved metal could eventually be used in place of grafoil. It has been reported [14] that solid ^3He wets perfectly MgO powder. b.c.c. ^3He crystals might eventually be oriented if nucleated on a cleaved MgO facet.

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