The First Roughening Transition of ^{3}He Crystals.

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Abstract. – We have observed the appearance of (110) facets on b.c.c. ^{3}He crystals at 0.08 K. This roughening temperature is consistent with an estimate of the surface stiffness and the universal relation from the critical theory of roughening. We also present a qualitative description of the various instabilities which occur in our experimental conditions (dendrites, needle and tip oscillating crystals, cellular instabilities) and discuss the effect of the roughening transition on these instabilities.

WOLF *et al.* [1] recently presented strong experimental support for the critical theory of roughening. By analysing the curvature and growth kinetics of h.c.p. ^{4}He crystals near their roughening transitions, these authors showed that the appearance or vanishing of facets on the surface of crystals is very likely the infinite-order phase transition described in this theory [1, 2]. Among many predictions about roughening, one of the most interesting is certainly the existence of a universal relation [3, 4] between the transition temperature T_R and the surface stiffness $\tilde{\alpha}(T_R)$ at the transition:

$$k_B T_R = 2 d^2 \tilde{\alpha}(T_R)/\pi . \tag{1}$$

The quantity $\tilde{\alpha} = \alpha + \partial^2\alpha/\partial\varphi^2$ is the sum of the surface energy α and its second derivative with respect to the orientation of the surface; d is the crystalline periodicity along the normal to the considered surface. This relation was verified by WOLF *et al.* [1]. Since (1) comes from a classical theory, the agreement further shows that quantum roughness [5] does not exist, at least for low Miller index orientations. As explained by FISHER and WEEKS [4], FRADKIN [6], IORDANSKI and KORSHUNOV [7], quantum fluctuations cannot delocalize a macroscopic surface. Clearly, eq. (1) predicts whether, in a given direction and at a given temperature, a crystal is rough or smooth (rounded or facetted). It is the new roughening criterion. However, many physicists are still using Jackson's empirical criterion [8] to predict roughening temperatures. The validity of this older criterion comes from the sort of proportionality which often exists between latent heats and surface

energies. The main interest of using latent heats is that they are much easier to measure than surface stiffnesses. However, one should be careful with Jackson's criterion which is proved wrong by ^{4}He, where it would lead to absurd predictions since the latent heat changes sign at low temperature. Thus it appeared interesting to see if eq. (1) also applies to ^{3}He, where the zero-point quantum energy is even higher than in ^{4}He. The result is the first observation of facets in ^{3}He: b.c.c. crystals form (110) facets as the temperature is reduced below 0.08 K (fig. 1 and 2). This temperature is close to the lowest of recent predictions by BALIBAR and CASTAING [9], in further support for the universality of eq. (1). Moreover, since the growth of our ^{3}He crystals is often dendritic, we also report preliminary and qualitative results on growth instabilities in ^{3}He. This includes observations of the modification of the instabilities by the roughening transition.

In order to observe the growth and quasi-equilibrium shapes of ^{3}He crystals, we immersed a deformable ^{3}He cell in a superfluid ^{4}He bath at variable pressure, which also acts as a thermostat. We used ordinary ^{3}He containing 200 p.p.m. ^{4}He. The ^{4}He bath is contained in one of the cells used by Wolf et al. [1]: it is attached to the mixing chamber of a dilution refrigerator inside an optical cryostat. The ^{3}He crystals can be observed visually down to 60 mK through two sets of seven windows. A pair of infra-red filters was added in the 4 K helium bath to further reduce the heat radiation into the cell. However, except at 0.32 K, where the melting pressure is minimal and the latent heat is zero [10], the equilibrium shape is generally perturbed by the existence of a small radial temperature gradient in the ^{3}He cell. This gradient is less than 10 μK/mm, as estimated from the shape of

Fig. 1. — ^{3}He crystals growing slowly at 70 mK ($T < T_R$, $r < 1$ μm/s). The facets of the polyhedrons are 110 facets.
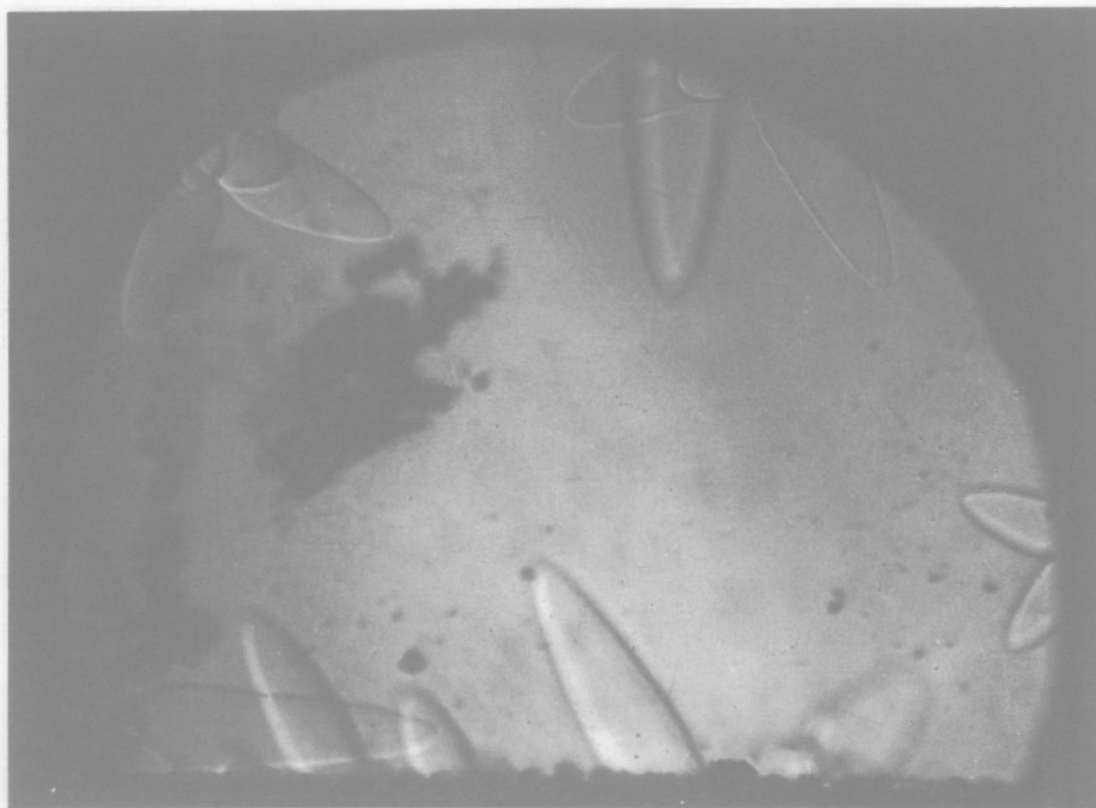
Fig. 2. – ^{3}He needle crystals growing at 100 mK ($T > T_R$): there are no visible facets.

large single crystals submitted to both the temperature gradient and gravity. It is one of the reasons why the results presented in this letter do not concern equilibrium properties, but crystals growing at various velocities (0.1 µm/s to 10 mm/s). In any case, although kinetic or static properties are not strictly equivalent [1, 2, 11] in determining a roughening temperature, looking at the existence of facets in slow growth is actually a more accurate method than looking at equilibrium facet sizes [1].

Growth was always obtained by changing the ^{3}He pressure at constant temperature. Above 0.32 K, it was possible to do this from the outside through the ^{3}He fill line, a 0.6 mm inner diameter capillary which remained unblocked if the cell was the coldest spot. When the temperature was lower than 0.32 K, solid He blocked the fill line and the crystals were grown by compressing the ^{3}He cell with the surrounding superfluid ^{4}He. Indeed, this cell has two parts: the lowest visible part is a copper·cylinder (diameter: 4 mm, length: 5 mm) closed at both ends by two indium-sealed sapphire windows. The cylinder is connected through a 2 mm little tube to a Be-Cu double membrane which allows a change in volume of about 5% by changing the outside ^{4}He pressure from 0 to 25 bars. Photographs or videorecordings were taken by illuminating the crystals with a sodium lamp. A 5 times magnified image was formed with a conventional enlarger lens outside of the cryostat. Finally, since the crystal refractive index (~ 1.032) is very close to that of the liquid (~ 1.030), we improved the image contrast by placing a mask near the focal point of the lens.

We observed a rather large variety of growth morphologies. At and below 80 mK, when the crystals were growing slowly ($v < 2$ µm/s at 80 mK), the growth shapes were
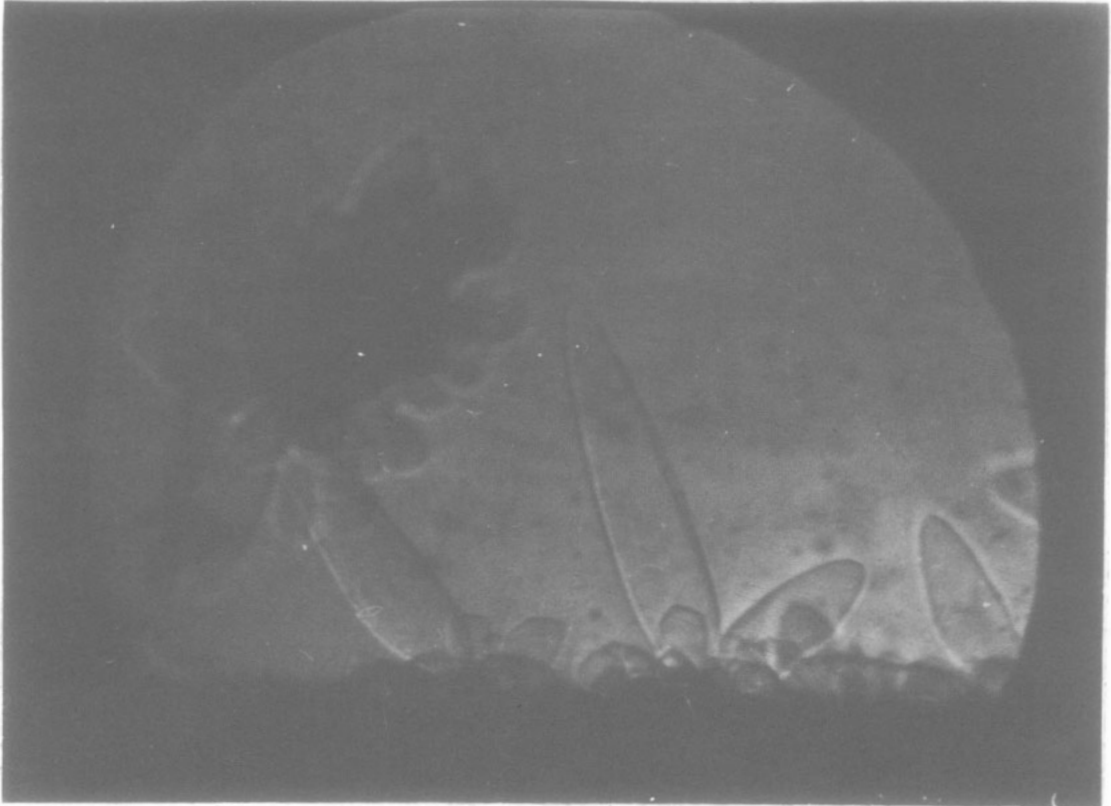
Fig. 3. – ^{3}He crystals growing at 80 mK although $T < T_R$, the velocity is too large to allow the development of facets on growth shapes ($v = 16$ μm/s).

rhombohedral dodecahedrons made of (110) facets (see fig. 1). Now, we also observed that the polyhedral shapes disappear if the applied overpressure or the resulting growth velocity is too high. The velocity required for this disappearance depends on the temperature T but, as an example, when $v > 2$ μm/s at $T = 80$ mK or $v < 10$ μm/s at 70 mK, we observed rounded crystals. These are often simultaneously of two types: needle crystals (fig. 3) or tip oscillating dendrites (fig. 4). We could not figure out what triggers the existence of one or the other type.

Above 85 mK, we never observed facets, the crystals are always rounded (fig. 2, 5 and 6). Thus the first roughening transition occurs in ^{3}He around this temperature. We observed various growth morphologies for these rough (or rounded) crystals: when the latent heat is not too large, we observed dendrites with a parabolic tip, sometimes with lateral branches (fig. 5). Above 0.5 K, where the latent heat presumably becomes large enough, the radial temperature gradient in the cell stabilizes the crystal near the cold copper cylinder but a cellular instability [12] seems to occur.

Let us now discuss these observations starting with the roughening transition. For simplicity we consider that its temperature is 0.08 K. According to the universal eq. (1), the first roughening transition is expected to occur for the largest value of the product $\tilde{\alpha} d^2$ ($\tilde{\alpha}$ is the surface stiffness, d is the crystal periodicity). If one supposes that $\tilde{\alpha}$ is nearly isotropic, the 110 facet should appear first as the temperature is decreased. This is observed, and the corresponding roughening temperature is coherent with eq. (1) if the surface stiffness is
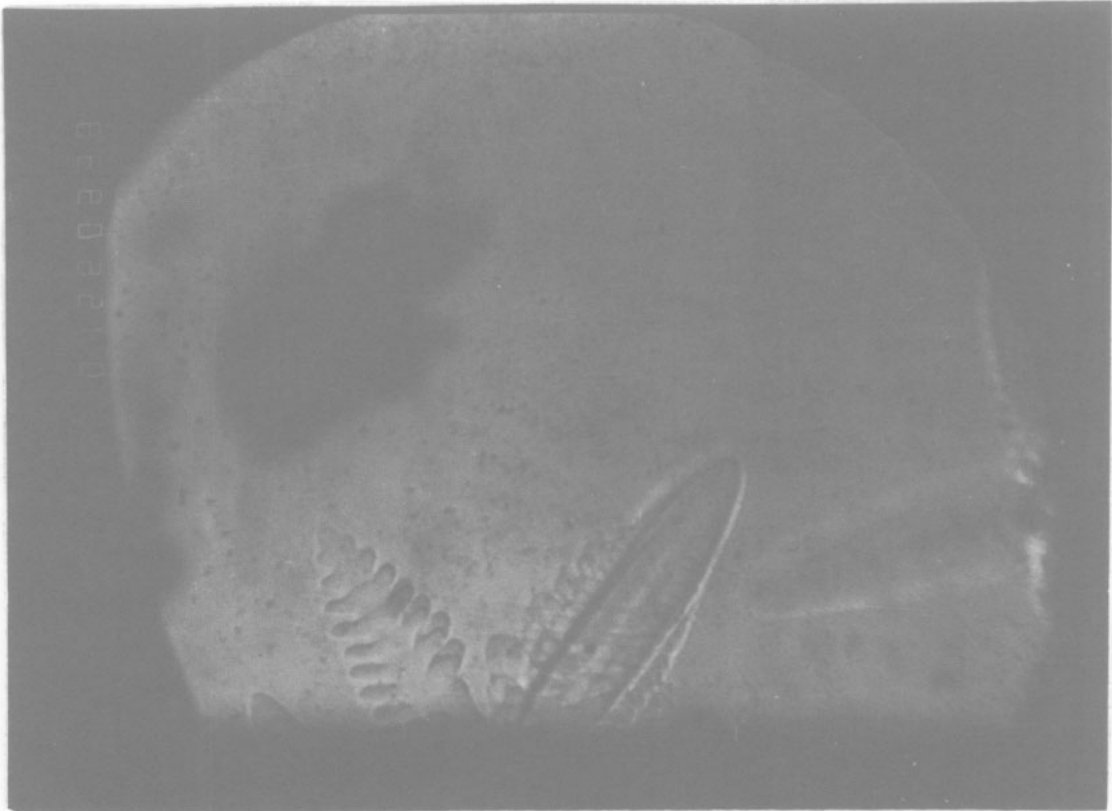
Fig. 4. – Two examples of various instabilities observed below T_R (here $T = 80$ mK): the left crystal presents a tip oscillating instability ($v = 19$ μm/s), the right one is tip stable, and presents side branching ($v = 17$ μm/s).

about 0.02 erg/cm^2. (From the molar volume [10], d is 3.067 Å in the 110 direction.) As explained by BALIBAR and CASTAING [9], this value is very close to that estimated from the pore condensation experiment of Eckstein *et al.* [13]. In fact, ECKSTEIN *et al.* obtained values of $\tilde{\alpha}$ ranging from 0.2 to 0.44 erg cm^{-2} but there is a factor $\rho_L/(\rho_s - \rho_L)$ missing in their eq. (1) so that they should have found $0.01 < \alpha < 0.022$ erg cm^{-2}. Higher values of $\tilde{\alpha}$ were obtained from experiments in Vycor [14]. Although a direct measurement of $\tilde{\alpha}$ is still necessary (and presently in progress in the experiment described here), it seems likely that the universal relation (1) is also verified for b.c.c. ^{3}He crystals and that 0.02 erg cm^{-2} is a good average value of $\tilde{\alpha}$. Of course, the quantity $\tilde{\alpha}(T_R)$ entering our eq. (1) is not an average but the value in the precise (110) direction right at $T_R \simeq 0.08$ K. However, we first think that the anisotropy of $\tilde{\alpha}$ is small. Indeed, b.c.c. ^{4}He has a small anisotropy [15]. Furthermore, we could obtain small ^{3}He crystals in contact with the windows (fig. 6). Such quasi-equilibrium crystal shapes were obtained after a typical relaxation time of one hour and did not seem to further evolve. Whatever the physical origin of such a relaxation time (heat or mass diffusion), these quasi-circular shapes indicate that the anisotropy of $\tilde{\alpha}$ above T_R (here $T \simeq 0.2$ K) is less than 4%. As for the possible variation of $\tilde{\alpha}$ along the melting curve, it is hard to predict but the quantity $\rho_L/(\rho_s - \rho_L)$ only varies by 5% from 0.08 to 0.032 K; finally the critical variation of $\tilde{\alpha}_{110}$ near T_R presents a well-known square-root cusp [1, 3], but the cusp total amplitude should again not exceed a few percent, otherwise a
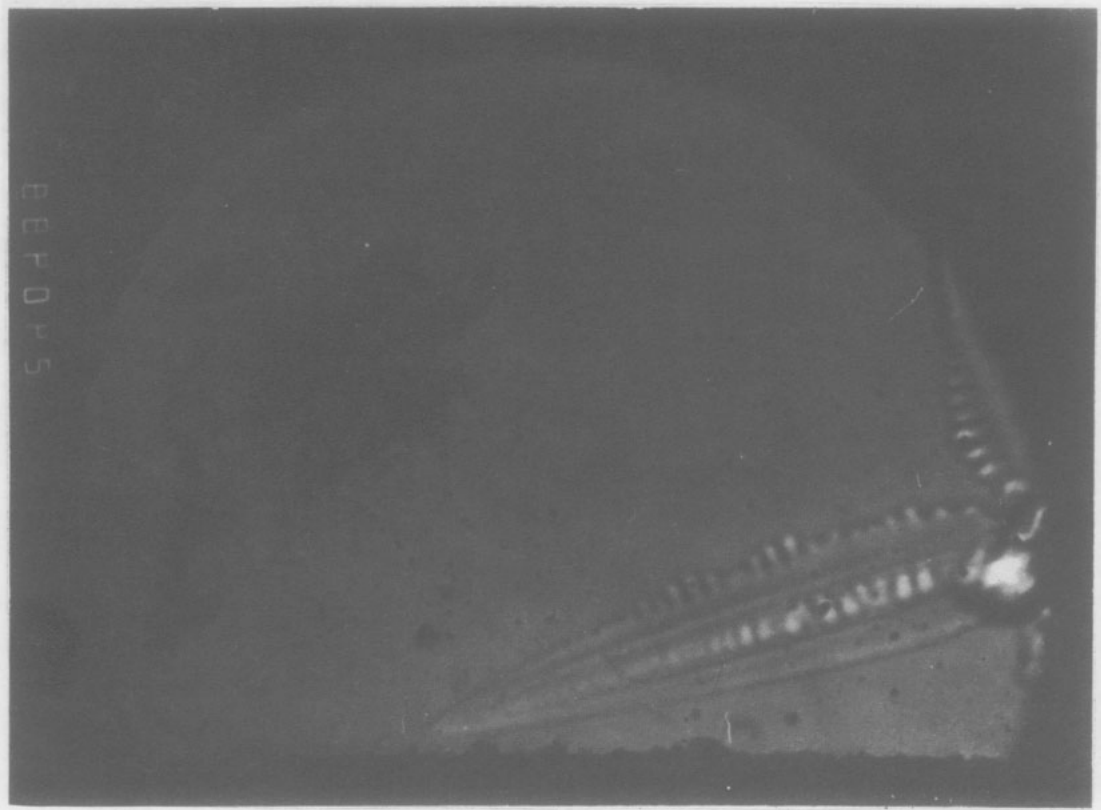
Fig. 5. – Dendrite above T_R (here $T = 85$ mK) presenting side branching ($v \simeq 30$ μm/s).

larger anisotropy would appear in fig. 6. From all these arguments we think that it is possible to use eq. (1) to estimate the surface stiffness of ³He crystals at low temperature from the observed value of T_r, and that it is about 0.02 erg cm⁻². This is one fifth of the surface stiffness of b.c.c. ⁴He crystals. It may not be surprising, since surface energies may vary as the square of $(\varrho_s - \varrho_L)/\varrho_L$ which is about twice as much in ⁴He than in ³He.

However, as reasonably suggested by one of our referees, these results have perhaps to be taken only as lower bounds for both T_r and $\tilde{\alpha}$. Indeed, the temperature is measured in the ⁴He bath, not in the ³He. The heat which is radiated into the ⁴He cell from the 300 K outer environment was estimated as 50 μW in an earlier experiment [1]. Despite the addition of infra-red filters, this heat flux may remain of order 10 μW. Now, even if the amount which is effectively adsorbed by the ³He cell is of the order of a few percent of these 10 μW, as was the case in another experiment [16], it is not impossible that the ³He cell absorbs 1 μW. Due to the large Kapitza resistance between the cell and the ⁴He bath, such a heat flux could warm the ³He up to 150 mK when ⁴He is at 100 mK. Recalling that our temperature is measured in the ⁴He, our value $T_r = 0.08$ K may be too small by a factor two. We thus only consider 0.08 K and 0.02 erg cm⁻² as lower bounds for the roughening temperature and surface stiffness of ³He crystals.

A more elaborate discussion of the various growth instabilities in ³He will be presented in another paper. Here, we restrict ourselves to general comments. The first one concerns the origin of our instabilities [17]. We think it is mainly due to the slow diffusion of ⁴He impurities in liquid ³He, not to the diffusion of heat. When using the usual terminology [17],
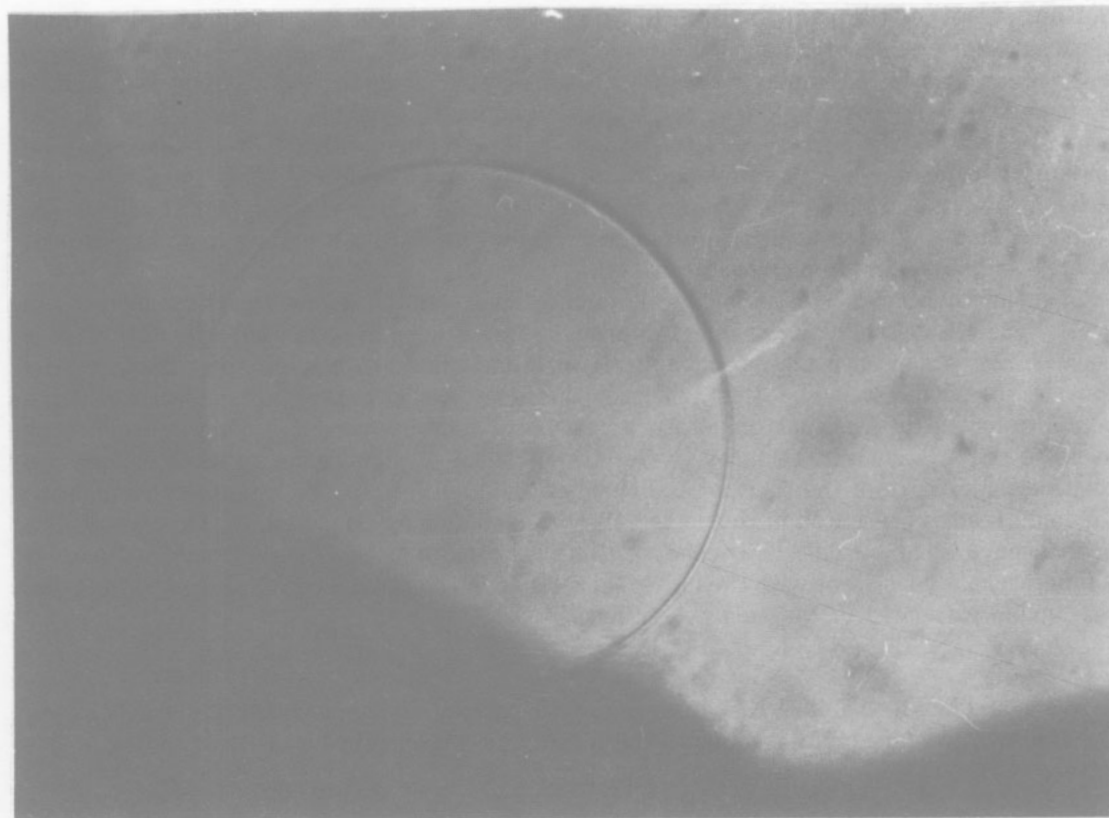
Fig. 6. – Crystal at quasi-equilibrium at 0.2 K (the diameter is about 0.5 mm): the anisotropy of the profile is less than 4%.

one would say that the instability origin is chemical, not thermal. Indeed our ^{3}He is very pure but not isotopically. As was explained above, it contains 200 p.p.m. ^{4}He and there is no fine filter with large adsorbing area which could purify it. Furthermore, above 0.5 K, the geometry is such that the heat diffusion stabilizes the interface. Therefore, the observed cellular instability must have a chemical origin. On the other hand, near the minimum of the melting curve (0.32 K) where the latent heat is small, the interface is no longer stabilized by the thermal gradient. We then observe dendrites with qualitatively the same shape whatever the exact value of the latent heat (positive, negative or zero). Although some heat has to go through the interface [18] even at 32 K, it seems likely that the instability mainly has a chemical origin.

Our second comment is on «how does the roughening transition affect the growth instabilities»? We think that it is mainly via a drastic change in the anisotropy of the growth rate. Facetted polyhedrons are obtained because, below T_R, the facet velocity at a given chemical potential difference $\Delta\mu$ is lower than that of adjacent rough surfaces by several orders of magnitude [1]. The existence of quasi-stationary facetted growth shapes needs $\Delta\mu$ across facets to be much larger than across the rounded edges which connect them together. This simply results from the large curvature of the rounded parts between the facets which thus nearly occupy the whole crystal surface. Below T_R, when the growth anisotropy is very large, it imposes a polyhedral shape with rather sharp edges. However, as again shown by WOLF *et al.* [1], the growth of facets is nonlinear: their mobility depends on $\Delta\mu$, and so does

the anisotropy of the growth rate. In other words, at small $\Delta\mu$, one gets polyhedrons because the growth rate is very anisotropic, but at higher $\Delta\mu$, the anisotropy is not so large and one may get growth shapes (needle crystals or various dendrites) which look similar to what is obtained above T_R. There is a transition between a regime with polyhedral shapes controlled by a large surface anisotropy and another regime with dendritic shapes whose instability originates in bulk diffusion processes. We actually observed that the further one is below T_R the larger is the growth velocity range for which the polyhedral shapes are stable. A similar kind of transition was observed by BEN JACOB et al. [19] in an experiment which simulates anisotropic crystal growth.

It seems that b.c.c. ^{3}He is a good system in which to study the effect of the anisotropy in crystal growth instabilities: a subject of growing importance in recent theories [20]. This is because the occurrence of a roughening transition allows to change the anisotropy by considerable amounts. For this purpose, one may work at various departures from equilibrium and at various temperatures around T_R. Moreover, it is easy to reduce or increase the ^{4}He concentration by two or three orders of magnitude, so as to change the relative importance of the thermal and chemical instabilities. In conclusion, we summarize the main results presented in this letter: the first roughening transition of ^{3}He crystals has been discovered above 0.08 K. It concerns the twelve (110) facets of the b.c.c. structure. Its temperature is consistent with the universal relation of the critical theory of roughening and reasonable estimates of the surface stiffness.

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REFERENCES

[1] WOLF P. E., GALLET F., BALIBAR S., ROLLEY E. and NOZIÈRES P., J. Phys. (Paris), 46 (1985) 1987.
[2] For review articles on this subject, see WEEKS J. D. and GILMER G. H., Adv. in Chem. Phys., edited by I. PRIGOGINE and S. A. RICE, Vol. 40 (Wiley, New York, N. Y.) 1976, p. 157; ref. [9], or BALIBAR S. and SAAM W. F., to appear in Rev. Mod. Phys. The long introduction in ref. [1] also summarizes the present understanding of the roughening transition.
[3] JAYAPRAKASH C., SAAM W. F. and TEITEL S., Phys. Rev. Lett., 50 (1983) 2017; see also JAYAPRAKASH C. and SAAM W. F., Phys. Rev. B, 30 (1984) 3916.
[4] FISHER D. S. and WEEKS J. D., Phys. Rev. Lett., 50 (1983) 1077.
[5] ANDREEV A. F. and PARSHIN A. YA., Ž. Éksp. Teor. Fiz., 75 (1978) 1511 (English translation: Sov. Phys. JETP, 48 (1978) 763).
[6] FRADKIN E., Phys. Rev. B, 28 (1983), 5338.
[7] IORDANSKI S. and KORSHUNOV S. E., Ž. Éksp. Teor. Fiz., 87 (1984) 927 (English translation: Sov. Phys. JETP, 60 (1984) 528).
[8] JACKSON K. A. and MILLER C. E., J. Crystal Growth, 40 (1977) 169.
[9] BALIBAR S. and CASTAING B., Surf. Sci. Rep., 5 (1985) 87.
[10] GRILLY E. R., J. Low Temp. Phys., 4 (1971) 615.
[11] GALLET F., NOZIÈRES P. , BALIBAR S. and ROLLEY E., to be published.
[12] MULLINS W. W. and SEKERKA R. D., J. Appl. Phys., 35 (1964) 444; R. F. SEKERKA, in Crystal Growth, an Introduction, edited by P. HARTMAN (North Holland, Amsterdam) 1973.
[13] ECKSTEIN Y., LANDAU J., LIPSON S. G. and OLAMI Z., Phys. Rev. Lett., 45 (1980) 1805.

[14] SHIMODA M., MIZUSAKI T., SUZUKI T., HIRAI A. and EGUCHI K., *Phys. Lett. A*, **102** (1984) 426; HAYNES S. R., Ph.D. Thesis, Sussex University (1986).
[15] GALLET F., WOLF P. E. and BALIBAR S., *Phys. Rev. Lett.*, **52** (1984) 2253.
[16] WOLF P. E., EDWARDS D. O. and BALIBAR S., *J. Low Temp. Phys.*, **51** (1983) 489.
[17] LANGER J. S., *Rev. Mod. Phys.*, **52** (1980) 1.
[18] CASTAING B. and NOZIÈRES P., *J. Phys. (Paris)*, **41** (1980) 701.
[19] BEN JACOB E., GODBEY R., GOLDENFELD N. D., KOPLIK J., LEVINE H., MUELLER T. and SANDER L. S., *Phys. Rev. Lett.*, **55** (1985) 1315.
[20] BEN JACOB E., GOLDENFELD N., LANGER J. S. and SCHÖN G., *Phys. Rev. A*, **29** (1984) 330; KESSLER D. A., KOPLIK J. and LEVINE H.: *Phys. Rev. A*, **30** (1984) p. 3161.