An experimental investigation of roughening phase transitions in 4He crystals


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The equilibrium shape of 4He crystals was studied in the vicinity of roughening phase transitions on the basal (0001) plane ($T_{x_{0}} = 1.2$ K) and on a family of (1010) (or (1120)) planes ($T_{x_{0}} = 0.9$ K). For $T > T_{x_{0}}$ the surface rigidity $\delta(\varphi)$ shows an appreciable angular dependence for $\varphi < 0.08$ rad and depends weakly on temperature in the range $T - T_{x_{0}} < 0.07$ K. It was found that there is no edge in the equilibrium shape of the crystal. The experimental results are compared with the predictions of contemporary theories of two-dimensional phase transitions.

1. INTRODUCTION

The concept of a roughening phase transition, i.e., the transition from an atomically rough to an atomically smooth state of a crystal surface at some temperature $T_{x}$, was introduced by Barton and Cabrera and was developed by Barton, Cabrera, and Frank. From the macroscopic point of view, these two states differ in the nature of the dependence of the free energy per unit area of a surface, $a$, on its orientation $\varphi$ relative to the crystallographic directions. In the case of a smooth surface with $\varphi = \varphi_{c}$, the function $a(\varphi)$ is not analytical, viz., its first derivative $a_{\varphi}$ undergoes a finite discontinuity $\Delta a_{\varphi}$ for $\varphi = \varphi_{c}$, while for a rough surface $a(\varphi)$ does not have any singularities at $\varphi_{c}$. As was first shown in the equilibrium shape of the surface by Landau, the existence of a discontinuity $\Delta a_{\varphi}$ produces a plane section with linear dimensions proportional to the magnitude of the discontinuity. Roughening phase transitions are thus characterized by the appearance (disappearance) of faceting in the equilibrium crystal shape.

The theory of roughening transitions has recently undergone intense development (see, for example, the review of Weeks and Gilmer). Analysis of different microscopic models of a surface $^{10}$ leads to the conclusion that this transition can be ascribed to the Kosterlitz-Thouless class of phase transitions $^{11}$ with a critical exponential behavior of the discontinuity of the derivative:

$$\Delta a_{\varphi}(\varphi) = \exp(-b/(1-t)^{\gamma}),$$

where $t = T/T_{x}$ and $b = 1$. A theory of roughening transitions in the mean-field approximation was developed by Andreev, $^{11}$ analogous to the Landau theory of second-order phase transitions. In this case the critical behavior is entirely different:

$$\Delta a_{\varphi}(\varphi) = (1-t)^{\beta}.$$  

Measurements of the crystal surface that is in thermodynamic equilibrium permit, in principle, direct observation of the critical behavior in the vicinity of the phase transition. The temperature dependence of the magnitude of $\Delta a_{\varphi}$ can be obtained from measurements of the linear dimensions of the plane section for $T > T_{x}$, while the angular and temperature dependences of the surface rigidity $\delta = \delta(\varphi) + \delta(\alpha)/\partial \varphi^{2}$ can be determined by measurements of the curvature of the rounded sections of the surface. Different theories give contradictory predictions for the behavior of $\alpha$ in the vicinity of the roughening transitions. Renormalization group transformations $^{12}$ and also some of the microscopic models $^{13,14}$ predict that for $T > T_{x}$, $\alpha$ stays finite but has a singularity of the form

$$\alpha(T) = \frac{n}{2} \frac{\partial^{2} a}{\partial \varphi^{2}} \left[ 1 - \frac{(T_{x} - T)^{\gamma}}{2b} \right],$$

where $b$ is the same constant as in Eq. (1), and $d$ is the height of an elementary step on the surface. It also follows from Eq. (3) that the curvature of the surface at the point $\varphi = \varphi_{c}$ decreases discontinuously to zero at $T = T_{x}$. According to Refs. 14, 17 and 18, $\delta(\varphi)$ goes to infinity as $T \rightarrow T_{x}$ as

$$\delta(T, \varphi) = \frac{\text{const}}{\varphi^{2}} \sqrt{\varphi - \varphi_{c}}.$$  

Such a critical behavior is a characteristic of Pokrovskii-Talapov type phase transitions $^{6}$. On the other hand, according to mean-field theory, $^{15}$ $\delta(\varphi)$ goes to infinity as $T \rightarrow T_{x}$ as

$$\delta(T, \varphi) = \frac{\text{const}}{\varphi^{2}} \left| \varphi - \varphi_{c} \right|^{1/\beta},$$

while at the critical point itself

$$\delta(T_{c}, \varphi) = \frac{\text{const}}{\varphi^{2}} \left| \varphi - \varphi_{c} \right|^{-\beta/\gamma},$$

where $\beta, \gamma - 1$, i.e., the curvature of the surface for $T \rightarrow T_{x}$ goes steadily to zero.

The change in shape of the surface for a first-order roughening transition can also be described by a phenomenological approach. $^{16}$ In this case two stable states exist near $T_{x}$ with different surface energies $\alpha_{1}(\varphi, T)$ and $\alpha_{2}(\varphi, T)$, with $\alpha_{1}$ an analytical function of angle (i.e., it corresponds to a rounded surface), while the derivative of $\alpha_{2}$ has a finite discontinuity at $\varphi = \varphi_{c}$ (i.e., it describes a surface with an equilibrium roughness). Then $\alpha_{1} < \alpha_{2}$ for all $\varphi$ for $T > T_{x}$ and $\alpha_{1} > \alpha_{2}$ over some range of angles near $\varphi_{c}$ for $T < T_{x}$. This means that for $T > T_{x}$, a plane section arises in the equilibrium shape of the surface; the dimensions of these sections are in no way related to the magnitude of $\Delta a_{\varphi}$. The plane and rounded sections meet in this case at the finite angle $\delta$ (i.e., an edge arises in the equilibrium shape), with

$$\delta = (1-t)^{\gamma}.$$ 

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At the first-order phase transition the shape of the surface thus changes continuously and not discontinuously as a number of authors suggest.\(^{30-32}\) It must be noted, however, that the possibility of a first-order phase transition is considerably limited by the occurrence of strictional instability of the surface.\(^{23,24}\)

The question of the role of quantum effects in roughening transitions has recently produced a lively discussion.\(^{14,23,24}\) The existing models of the surface of a quantum crystal\(^{14,23,24}\) do not yet allow for the possibility of a sufficiently full experimental check. From the experimental point of view, the predictions\(^{23,24}\) of the existence of a narrowing of the region of critical behavior in the case when quantum effects are sufficiently strong, is most interesting. Under these conditions the magnitude of \(\Delta x\) can also be much less than its "inherent" value, even for \(T \approx T_a\).\(^{23,24}\)

An extremely long time for establishing equilibrium is a characteristic of the surface of a classical crystal, and for this reason the equilibrium shape can only be observed on specimens of sufficiently small dimensions, however, in this case the critical behavior characterizing the transition is complicated by size effects.\(^{34,35}\) Crystalline \(^3\)He, bounded by the superfluid liquid phase, is the most suitable system for an experimental study of the roughening transitions in view of the very short times for establishing the equilibrium surface shape, brought about by quantum effects.\(^{34,35}\) The equilibrium shape of \(^3\)He crystals has in fact been observed in different laboratories.\(^{30-33}\)

At present three roughening transitions in \(^3\)He have been recorded experimentally\(^{23,26-31}\) on a surface oriented parallel to the basal (0001) plane, 2) on a family of planes parallel to the c axis (10\(\bar{1}\)0) or (11\(\bar{2}\)0), 3) on the (10\(\bar{1}\)1) family (or, correspondingly, [112\(\bar{1}\)]). The critical temperatures \(T_s\), \(T_a\), and \(T_a\) are respectively 1.2, 0.9, and 0.36 K. Helium crystals have at \(T > T_a\) a fully rounded surface, and on lowering the temperature down to 0.07 K no other transitions are found.\(^{34}\)

2. EXPERIMENTAL METHOD

A \(^4\)He optical cryostat\(^{13}\) was used in the experiments. The experimental chamber was a 25 mm long ferrochrome cylinder with inner diameter 15 mm; the axis of the cylinder was placed horizontally. Plane glass windows were stuck to the ends of the cylinder so that the whole inner volume remained open to observation. The horizontal copper base of the container (8 mm wide and 25 mm long) was connected to the \(^4\)He bath by a cold-finger. The temperature of the experimental space was maintained constant to an accuracy not worse than \(3 \times 10^{-4} \) K by an electronic stabilizer.\(^{36}\) or could vary according to some set pattern. The filling capillary entered through the upper part of the container.

The working part of the experimental cell could, when necessary, be cut off from the outside connections by a bellows valve, controlled by helium pressure in an independent high pressure line, which was situated immediately before the entry of the capillary to the container and was in good thermal contact with the \(^4\)He bath.

When measuring the equilibrium shape of a crystal near some determined crystallographic orientation and in the gravitational field, it is essential to arrange for the face studied to be horizontal. As before,\(^{30}\) we used a wire-electrode electrical capacitor (diameter 2.5 mm and length 15 mm), placed in the upper part of the experimental container. For an appropriate choice of temperature in the experimental space (0.9-1.0 K) and magnitude of the electric field, crystallization starts on the surface of the capacitor, the nucleus of solid phase then has a volume \(\approx 1 \) mm.\(^3\) The crystallite then grew to a size of 2 mm or more, after which it fell to the plane bottom of the container on the (0001) face. A motion picture of the fall of one of the crystallites is shown in Fig. 1. In practice, crystals could be "stacked" by this method so that the departure of the basal (0001) plane from the horizontal was not more than \((2-3) \times 10^{-3} \) rad. In addition, by varying the temperature and the regime of growing the nucleus, it is often possible to set one of the faces parallel to the c axis horizontal (certainly, with somewhat lower accuracy), and also to obtain crystals with the basal plane with a desired small \((\approx 0.1 \) rad) inclination to the horizontal. In equilibrium, a crystal occupies the lower part of the chamber and its surface forms a convex meniscus, corresponding to poor wetting of the solids walls,\(^{30-32}\) as shown in Fig. 2. The length of the specimens was 25 mm (\(X\) axis), width 10-14 mm (\(Y\) axis), and height 2-4 mm (\(Z\) axis). In such a geometry, the curvature of the surface in the longitudinal direction is appreciably less than the transverse. Under these conditions, the shape of the interphase boundary for \(x^\prime\) can be found with sufficient accuracy from solving the one-dimensional equilibrium equation (see, for example, Ref. 19).

\[
\sigma_x^{(0)} - \rho_x x^\prime = 0, \tag{8}
\]

where \(\rho_x\) is the difference in density between the solid and liquid phases, while \(g\) is the acceleration due to gravity. The accuracy in measuring the angles of inclination of a particular face relative to the horizontal \(x^\prime\) was not more than \(1 \times 10^{-2} \) rad. The angle \(\phi_{10}\) was not more than \(2.5 \times 10^{-3} \) rad for specimens with a horizontal basal plane (in the case of transition 1), while the angle \(\phi_{01}\) was chosen within the limits from 0 to \(3.3 \times 10^{-2} \) rad. In all the results presented...
below, the angle of inclination of a surface was reckoned from the particular face (0001), i.e., $\varphi = \varphi_0 - \omega$.

A He-Ne laser was used for measurements of the surface profile $z(x)$, operating in the single mode regime with a Gaussian intensity distribution in the beam. The narrow laser beam fell at a small glancing angle (3-5°) on the surface being studied. The angular inclination of the beam $\theta$ in the $(X,Y)$ plane as a function of $x$ (Fig. 2) was fixed so that the $z(x)$ dependence was measured directly, taken along the cross-section of the surface corresponding to the condition $z_x = 0$. The width of the beam ($\sim 0.3$ mm) was chosen so that the angular broadening of the reflected beam due to the curvature of the surface and due to diffraction effects should be optimized. In addition, when a plane section occurred in the equilibrium shape of the crystal surface, we could measure its longitudinal dimension (i.e., in the $Y$ direction) by a diffraction method, as before.\(^{1324}\)

3. RESULTS AND DISCUSSION

Typical experimental curves are shown in Fig. 3a. Curve 1 corresponds to $T > T_A$, when the surface is completely rounded; curve 2 is for $T < T_A$ and in this case a plane section appears in the equilibrium shape (the region where $\varphi = 0$ in Fig. 3a) the dimensions of which decrease continuously to zero if $T \to T_A$. In equilibrium, the angle $\varphi$ at the boundary between the plane and rounded sections changes continuously. In other words, the equilibrium shape of the surface does not contain an edge, which indicates uniquely that the two transitions studied (namely transitions 1 and 2) are not of first order. The solid curve shown for comparison in Fig. 3 is calculated for a first-order phase transition according to Keshishev et al.\(^{1324}\) with the linear dimension of the plane section taken as the same as in curve 2.

In the absence of an edge, the behavior of the curvature of the rounded section of the surface near its junction with a plane face is uniquely related to the asymptotic behavior of the quantity $\tilde{a}(\varphi)$ for $\varphi \to 0$ [Eq. (8)]. In particular, if $\tilde{a} = \varphi$ (Refs. 9, 10, 14) then $z^{\*} = x^{-1/2}$ should hold. On the other hand, mean field theory predicts that $\tilde{a} \to \text{const}$ for $\varphi \to 0$ and, correspondingly, $z^{\*} \to \text{const}$. As can be seen from Fig. 3b, our experimental results agree well with this latter prediction. We also carried out measurements of the shape of the surface on three inclined specimens ($\varphi_0 \approx 0.1$ rad) at temperatures appreciably below $T < T_A$ (down to 0.6 K). In all cases the magnitude of $z^{\*}$ at the meeting point stayed constant, i.e., the $z^{\*} \propto x^{-1/2}$ relation was not observed in the angular region studied ($5 \times 10^{-2}$--0.1 rad).

An attempt to measure directly the temperature dependence of the plane dimensions $1(T)$ was not successful. As in our earlier experiments,\(^{1324}\) in which we studied the critical behavior of the size of a plane section near transition 1, we observed fairly considerable hysteresis phenomena and also a poor reproducibility not only from specimen to specimen, but even in the course of one experiment. The most probable reason for such non-reproducibility must be considered the difference in the growth kinetics of atomically smooth and atomically rough surfaces.\(^{1324}\) In face, the short time for establishing the thermodynamically equilibrium shape is only characteristic of rough surfaces,\(^{1324}\) while the mobility of an atomically smooth surface remains extremely low, as in ordinary classical crystals.
By the absence of a noticeable temperature dependence of the Wolf \( z(x) \).

If, however, the angular range of \( \varphi \) corresponding to such a "transition" region, under our experimental conditions was sufficiently small (not more than \( 5 \times 10^{-2} \) rad) and had no effect on the results of the measurements.

We obtained the fullest experimental results for transition \( 1 \) at \( T < T_{c1} \). The equation for equilibrium (8) was used directly to establish the angular dependence of the surface rigidity \( \dot{\alpha}(\varphi) \) at fixed temperature. Solution of such a problem comes down to seeking the \( z(\varphi) \) dependence and also the second derivative \( z''(\varphi) \) from the known function \( z'(\varphi) \). In the case of weakly inclined specimens (i.e., \( 0 < \varphi < 1 \)) the numerical value of the undetermined constant of integration for establishing \( z(\varphi) \) can be obtained from the symmetry condition, i.e., \( \dot{\alpha}(-\varphi) = \dot{\alpha}(\varphi) \). An example of a numerical treatment for one of the typical experimental curves with the corresponding uncertainty range is shown in Fig. 4a.

The results of analyzing measurements made on 7 specimens of different dimensions with different values of \( \varphi_{0,0} \) and of angles between the \( X \) and \( Z \) axes are shown in full in Fig. 4b. The maximum value of the angle \( \varphi_{0,0} \) was \( 3.3 \times 10^{-2} \) rad.

We did not find any regular temperature dependence of \( \dot{\alpha}(T) \), outside the limits of experimental error, over the temperature of the investigation, \( T - T_{c1} < 0.007 \) K and angles \( |\varphi| < 8 \times 10^{-3} \) rad. This is in agreement with the results of Wolf et al.\(^{16} \) and of Balibar et al.\(^{24} \) which are distinguished by the absence of a noticeable temperature dependence of the surface rigidity over a wider interval, \( T - T_{c1} < 0.2 \) K, and contradicts the temperature dependence \( \dot{\alpha}(T) \) predicted by microscopic theories [Eq. (3)] for the case of \( \beta > 1 \).

The existence of a noticeable angular dependence \( \dot{\alpha}(\varphi) \) for \( \varphi \leq 1 \) and, at the same time, the absence of a temperature variation of \( \dot{\alpha} \) in the assumptions of mean-field theory\(^{15} \) means that the temperature range of our measurements is appreciably narrower than the characteristic temperature region of critical behavior, i.e., \( T \approx T_{c1} \). In this case, the \( \dot{\alpha}(\varphi) \) dependence should be described by Eq. (6); the best curve of this form, with the adjustable parameter \( \alpha(0) \approx 3 \times 10^{-2} \) erg \( \cdot \) cm\(^{-2} \), is shown in Fig. 4b by the dashed line. Assuming that \( \alpha(0) \approx 0.1 \) erg \( \cdot \) cm\(^{-2} \), we obtain \( T \approx 0.3 \) K.

In recent French work\(^{14,24} \) using another method of optical measurements on smaller specimens (\( \approx 1 \) mm), an angular dependence \( \dot{\alpha}(\varphi) \) also emerges for transition \( 1 \) such that \( (1/\dot{\alpha})(\partial^2 \dot{\alpha}/\partial \varphi^2) = -26 \pm 5 \) (the full curve in Fig. 4b), with \( \dot{\alpha}(T = T_{c1}, \varphi = 0) = 0.246 \pm 0.015 \) erg \( \cdot \) cm\(^{-2} \). The results were obtained from measurements of the profile of an equilibrium surface \( z(x) \) over an appreciably wider angular range \( |\varphi| < 0.4 \) rad, which on analysis by the numerical method used could lead to considerable errors due to "averaging" of the singularity for \( \varphi = 0 \).

At temperature 0.02–0.03 K below critical, when the dimensions of the plane section are still not too large, only the mean value of \( \dot{\alpha} \) in the angular range \( 5 \times 10^{-3} \) rad \( < |\varphi| < 2.5 \times 10^{-2} \) rad can be determined with sufficient accuracy. The corresponding values for four specimens as a function of temperature are given in Fig. 5. No regular temperature dependence or difference of the results obtained from the mean value in the angular interval shown, \( \dot{\alpha}_{\text{mean}}(T < T_{c1}) \) (the dashed line in fig. 5) was found. A similar result was found in the experiments of Wolf et al.\(^{14} \) and of Balibar et al.\(^{24} \).

On considering possible sources of errors in the measurements in the vicinity of \( T_{c1} \), it should be remarked that apart from the sources of errors mentioned earlier (vibrations of the apparatus, temperature instabilities, etc.),\(^{14} \) we observed equilibrium-surface distortions produced by heat flows from the external helium bath to the experimental space along the filling capillary (\( < 5 \times 10^{-4} \) W). Such an effect on the equilibrium shape of a crystal would lead to practically complete "smearing out" of its features produced by the critical behavior near \( T_{c1} \), which most probably explains the difference between the results given and those published earlier.\(^{24} \) In our most recent experiments, the use

FIG. 4. a) An example of the establishment of the \( \dot{\alpha}(\varphi) \) dependence, \( T < T_{c1} \); the error range is indicated by the dashed curve. b) The \( \dot{\alpha}(\varphi) \) dependence for seven specimens for \( T = T_{c1} < 0.07 \) K. The curves corresponding to different specimens and temperatures are indicated by different symbols. The arrow shows the universal value \( \alpha(0) \approx 0.295 \) erg \( \cdot \) cm\(^{-2} \) for transition

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FIG. 5. The temperature dependence of the mean value \( a_{\text{mean}} \) \( (5 \times 10^{-4} \, \text{rad/cell}) \) at \( T \approx T_k \) for four specimens.

of an additional valve having the He-bath temperature appropriately reduced the heat flux to the experimental cell. In a control experiment with the valve closed, no distortion of the shape of the crystal surface was noticed even when additional power \((\approx 10^{-4} \, \text{W})\) was dissipated in a heater placed on the capillary before it entered the valve, and also when the pressure in the external connections oscillated in a range \( \pm 1 \, \text{atm} \).

Transition 2 [on the \((10\bar{1}0)\) (or \((11\bar{2}0)\)] plane] has so far been studied in less detail. In this case, the symmetry of the particular face is lower than in the case of the basal plane; the value of \( \alpha \) can thus depend appreciably on the angle between the \( X \) axis and the \( C_6 \) crystal axis. This angle was within the limits of 70–85° in some of the specimens we studied.

Experimental results of measuring the profile of a surface in the case of transition 2 were obtained for three small \((\approx 7 \, \text{mm in diameter})\) specimens. The average value of \( \alpha \) in the angular range \( \pm 0.1 \, \text{rad} \) and for temperatures in the range \( 0 < T - T_k < 0.05 \, \text{K} \) was determined to be \( \alpha_{\text{mean}} \approx 0.25 \pm 0.05 \, \text{deg/cm} \) (Ref. 40). It is significant that, as in the case of transition 1, a plane section arises in the equilibrium shape of a surface without an intermediate "cylindrical" stage, the existence of which is predicted by mean field theories.15

As can be seen, the experimental results can not be fully explained by the present theories of surface phase transitions; to obtain a self-consistent picture of the phenomenon, further experimental and also theoretical results are thus essential.

From the experimental point of view there still remains unexplained the question of the behavior of the surface rigidity \( \alpha \) for \( T \to T_k \) and \( \alpha - \alpha_0 \). Extrapolation of the \( \alpha(\rho) \) dependence obtained to \( \alpha = 0 \) (Fig. 4b) gives values \( \approx 20\% \) above the universal value \( [\text{Eq. (8)}] \) predicted by a number of authors; however, in virtue of the finite resolving power of the method [on average \( \approx 5 \times 10^{-3} \, \text{rad} \) (Fig. 4a)] produced both by errors in the measurements and by the accuracy of the numerical analysis, a unique answer cannot be given to the question of whether \( \alpha(\rho = 0) \) remains finite for \( T \to T_k \) or becomes infinite. An experimental method with appreciably higher resolving power must be used to remove this indefiniteness. As before, an experiment for a temperature below \( T_k \) to elucidate the temperature dependence of the discontinuity in the derivative \( \Delta \alpha(\rho) \) [Eqs. (1) and (2)] is extremely urgent.

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