Faceting phase transitions of crystals

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A thermodynamic theory of the phase transitions associated with the appearance of crystal facets is developed. The equilibrium crystal shape and the angular dependence of the surface energy in the vicinity of a second-order faceting phase transition are determined. It is shown that the phase transitions associated with the appearance of edges and conical points on crystal surfaces cannot be second-order transitions.

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The equilibrium shape of crystals at low temperatures is characterized by the presence of facets, i.e., plane sections, each of which corresponds to the emergence to the surface of a crystal face with definite Miller indices. This nonanalyticity of the shape is a manifestation of the distinctive dependence of the surface energy of the crystal on the angles determining the orientation of the faces. Specifically, the surface energy is a continuous function of the angles, but this function has discontinuous derivatives everywhere. The linear dimensions of the planar parts for the various faces are proportional to the corresponding jumps of the angle derivatives of the surface energy, which in turn are proportional to the step energy for the face in question. All these quantities have their greatest values in the case of the most closely packed faces, and rapidly decrease with increasing Miller indices (see Landau's paper[1] and Chernov's[2] and Jackson's[3] review articles).

The thermal motion washes out the planar parts of fairly small dimensions; therefore, at any finite temperature only facets with not too large indices occur on a surface. A rise in temperature usually leads to the disappearance of the planar parts for the increasingly close-packed faces and, finally, to the total disappearance of the facet. It is clear from the foregoing that each crystal is characterized by a set of critical faceting-transition temperatures. The highest of them is the temperature below which the crystal first assumes its nonanalytic equilibrium shape. The rest are connected with the appearance of planar parts of the various types of faces. It may also be said that the discontinuities of the angle derivatives of the surface energy or the finite step-energy values first appear at the critical points of the faceting transition. The concept of faceting phase transitions was introduced by Burton and Cabrera[4,5] and since then such transitions have been qualitatively observed in many cases. Recently there has been an upsurge in interest in them both in connection with the general problem of surface phase transitions[6,7] and, especially, in connection with the experimental observation of facets of helium crystals.[8-10] The probability for the quantum processes of particle tunneling is extremely high in these crystals. This leads to anomalously low values for the characteristic equilibrium-shape establishment time, and therefore provides a unique opportunity for a quantitative investigation of the crystal shape near the critical points of the faceting transition. Let us also note that

only a few, most closely packed faces can exist in helium crystals at arbitrarily low temperatures. All the other planar parts are washed out by the quantum motion of the particles even at zero temperature (see Refs. 11 and 12).

In the present paper we carry out a thermodynamic analysis of the crystal shape and the angular dependence of the surface energy in the vicinity of the faceting phase-transition points. It turns out that in many cases these transitions can be second-order phase transitions, i.e., they can be accompanied by a continuous change in the crystal shape. The formulas describing these phase transitions are similar to the formulas of the Landau theory for ordinary phase transitions, the role of the order parameter being played by the jumps in the angle derivatives of the surface energy. In essence, however, there is an important difference. The critical face does not undergo any symmetry change below the transition point, and no order parameter characterizing it as such arises. As to the appearance at the transition point of discontinuities in the angle derivatives, it leads, in contrast to ordinary transitions, to the abatement of the fluctuations. Indeed, the energy deviation (from the equilibrium value) associated with a fluctuation-induced deflection of the normal to the surface is proportional to the square of the angles of deflection in the absence of discontinuities in the derivatives and to the first power of the moduli of the angles in the presence of discontinuities. The fluctuation energy is significantly higher (i.e., the fluctuations are significantly less intense) in the second case than in the first.

Besides the planar parts, the crystal surface may contain singular lines and points at low temperatures (see Ref. 12). The first of them are the so-called edges, along which finite jumps occur in the orientation of the normal to the surface; the second are conical (or angular) points, near which the crystal surface has the shape of a cone. The appearance of these anomalies as the temperature is lowered also determines a set of critical temperatures characteristic of the given crystal. The corresponding phase transitions cannot, as will be shown below, be second-order phase transitions.

1. GENERAL RELATIONS

The equilibrium shape of a crystal is determined by

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the condition that the surface energy, or, more exactly (see Ref. 13), the thermodynamic potential for the given crystal volume, be a minimum. If we write the equation of the crystal surface in the form $z = z(x_\mu)$, where $\mu = 1, 2$; $x_1 = x$, $x_2 = y$, x, y, and z being Cartesian coordinates, then we are talking about the minimality of the expression

$$\int f(h_\mu)\, d^2x, \tag{1}$$

where $f = \alpha(1 + h_\mu^2)^{1/2}$ and α is the surface energy; α and f can be regarded as functions of the angle variables $h_\mu \equiv \partial z/\partial x_\mu$. The additional condition that the volume be constant reduces to the condition for the constancy of the integral

$$\int z\, d^2x. \tag{2}$$

The formulated variational problem has, as is well known,[13] the following first integral:

$$f = \lambda \zeta, \tag{3}$$

where λ is a Lagrange multiplier and $\zeta = z - x_\mu h_\mu$.

Since $dz = h_\mu dx_\mu$, the differential of the variable ζ is equal to $d\zeta = -x_\mu dh_\mu$, so that $x_\mu = -\partial\zeta/\partial h_\mu$. Let us introduce the quantity $\eta_\mu \equiv \partial f/\partial h_\mu$. On account of the formula (3), we have

$$\eta_\mu = \lambda\partial\zeta/\partial h_\mu = -\lambda x_\mu, \tag{4}$$

i.e., in the equilibrium state the quantities η_μ differ from the coordinates x_μ only by a constant factor. Let us also introduce the new thermodynamic potential $\tilde{f}$ $= f - h_\mu\eta_\mu$. Since $df = \eta_\mu dh_\mu$, the differential of the potential $\tilde{f}$ is equal to $d\tilde{f} = -h_\mu d\eta_\mu$, so that $h_\mu = -\partial\tilde{f}/\partial\eta_\mu$.

Using the relations (4), we can rewrite the equilibrium condition (3) in the following equivalent form:

$$\tilde{f} = \lambda z. \tag{5}$$

The thermodynamic potential $\tilde{f}$, as a function of the variables η_μ, is thus connected directly with the crystal shape in the equilibrium state:

$$z(x_\mu) = \frac{1}{\lambda}\tilde{f}(\eta_\mu) = \frac{1}{\lambda}\tilde{f}(-\lambda x_\mu). \tag{6}$$

The critical points of the faceting transitions are determined by the appearance on the crystal surface of areas of zero curvature. Such areas can naturally arise through first-order phase transitions, i.e., through an abrupt change in the shape with the immediate appearance of finite-sized planar sections at the critical temperature. It would, however, be interesting to investigate the possibility of continuous faceting transitions. In these cases, as the critical temperature is approached from above, some point $x_\mu = x_\mu^{(0)}$ corresponding to the emergence to the surface of the crystal face in question should gradually go over into a flattening point, i.e., into a point at which one or both of the eigenvalues of the matrix $\partial^2 z/\partial x_\mu \partial x_\nu$ vanish.

On account of the formula (6), this implies the vanishing on the face in question of one or both of the eigenvalues of the matrix $\partial^2\tilde{f}/\partial\eta_\mu\partial\eta_\nu$ or the matrix $\partial h_\mu/\partial\eta_\nu$. Then for the transition to be continuous it is necessary that the well-known[2] stability criterion requiring the positive definiteness of the quadratic form

$$\frac{\partial^2 f}{\partial h_\mu \partial h_\nu}\delta h_\mu \delta h_\nu = \frac{\partial\eta_\mu}{\partial h_\nu}\delta h_\mu \delta h_\nu$$

for all δh_μ remain fulfilled for all the faces close to the one in question at the very critical point.

Equivalent to this criterion is the one stipulating the positive definiteness of the expression

$$\frac{\partial h_\mu}{\partial\eta_\nu}\delta\eta_\mu\delta\eta_\nu \tag{7}$$

for all $\delta\eta_\mu$ or the fulfillment of the two inequalities

$$\frac{\partial h_1}{\partial\eta_1} > 0, \quad \frac{\partial h_1}{\partial\eta_1}\frac{\partial h_2}{\partial\eta_2} > \left(\frac{\partial h_1}{\partial\eta_2}\right)^2. \tag{8}$$

It is easy to see that a continuous faceting transition is possible for faces perpendicular to threefold symmetry axes. In this case, on account of the symmetry of the face, the eigenvalues of the matrix $\partial^2\tilde{f}/\partial\eta_\mu\partial\eta_\nu$ coincide, and therefore both are equal to zero at the critical point. Since the face under consideration corresponds to the values $\eta_\mu = 0$, the potential $\tilde{f}$ of the adjacent faces is determined by the third-order invariants:

$$\tilde{f} = f_0 + a(\eta_1^3 - 3\eta_1\eta_2^2) + b(\eta_2^3 - 3\eta_1^2\eta_2),$$

where a and b are constants. The derivatives $\partial h_1/\partial\eta_1$ and $\partial h_2/\partial\eta_2$, which should be positive at small η_μ, do, however, contain sign-variable linear—in η_μ—terms when computed with the aid of this formula. The presence of a symmetry plane passing through the axis clearly does not save the situation. In this case a reflection in the plane can be represented as the transformation $\eta_1 \to -\eta_1$, so that $a = 0$. But the terms with b do, as before, violate the criterion for stability.

In the majority of cases, however, the faceting transitions can, as we shall see below, be second-order phase transitions.

2. SIXFOLD SYMMETRY AXIS

Let the face under consideration be perpendicular to a sixfold symmetry axis. The potential $\tilde{f}$ for the adjacent faces, i.e., for the faces with small η_μ, is in this case isotropic at the required accuracy. It can be written in the form

$$\tilde{f}(t, \eta_\mu) = f_0(t) - \frac{1}{2}at\eta_\mu^2 - \frac{1}{4}b(\eta_\mu^2)^2, \tag{9}$$

where $t = T - T_c$ (T_c is the critical temperature of the faceting transition) and a and b are constants, both of which should be positive in order for the stability criterion (8) for $t \geq 0$ to be fulfilled for all η_μ.

By differentiating the expression (9), we find that

$$h_\mu = at\eta_\mu + b\eta^2\eta_\mu. \tag{10}$$

It follows from (9) and (10) that, for $t > 0$ and sufficiently small h_μ, the surface energy is equal to

$$f(t, h_\mu) = f_0 + h^2/2at, \tag{11}$$

i.e., its second derivatives with respect to the angle variables h_μ go to infinity on the face in question (i.e., at $h_\mu = 0$) in inverse proportion to $T - T_c$.

At the critical point itself we have

$$\eta_\mu = (bh^2)^{-1/6} h_\mu,$$

which corresponds to a nonanalytic angle dependence of the surface energy of the form

$$f = f_0 + {}^3/_4 (h^4/b)^{1/3}. \tag{12}$$

On account of the general relations (4) and (6), the crystal shape at $t \geq 0$ is determined directly by the expression (9).

At $t < 0$ the dependence (10) of η_μ on h_μ is many-valued. It, however, becomes single-valued if it is noticed that for the values $\eta^2 < a|t|/b$ the stability criterion (8) is violated, so that these η_μ values do not have any physical meaning. As a result, as $h_\mu \to 0$ the quantities η_μ tend to the finite value $\eta_\mu = \eta_0 (h_\mu/h)$, where $\eta_0 = (a|t|/b)^{1/2}$. On account of the relations (4), this implies that there appears on the crystal surface a planar section of circular shape with radius proportional to η_0, i.e., to the square root of $T_c - T$. The shape of the planar section differs from the circular shape only when allowance is made for terms of higher order in $T_c - T$. The dependence of the surface energy on the angles and temperature at $t < 0$ and $h \to 0$ is given by the formula

$$f(t, h_\mu) = f_0 + \frac{a^2}{4b} t^2 + \eta_0 h. \tag{13}$$

The jump in the angle derivatives at $h = 0$ is equal to $2\eta_0$.

Thus, in the considered simplest case, the faceting transition is described by formulas quite similar to those of the Landau theory of phase transitions if the quantities η_μ are regarded as the order parameter and angle variables h_μ as the external field. Let us, however, draw attention to the negative signs in the formula (9).

3. FOURFOLD SYMMETRY AXIS

Assume that the face under consideration is perpendicular to a fourfold symmetry axis and has, moreover, two mutually perpendicular symmetry planes passing through this axis. Among the faces with a fourfold axis this case is of greatest interest from the experimental point of view. The point is that, as noted above, the most convenient objects for the investigation of faceting transitions are crystals of the helium isotopes. The ^{4}He isotopes on the melting curve at low temperatures form hexagonal close-packed crystals whose basal planes undergo a faceting transition described by the formulas of the preceding

section. The crystals of ^{3}He under the same conditions are body-centered cubic crystals. The basal planes of these crystals have symmetry planes.

In the present case we can form from the quantities η_μ two independent fourth-order invariants. If we choose as the x_1- and x_2-coordinate axes the lines of intersection of the symmetry planes with the face, then we can choose as these invariants the quantities $\eta_1^4 + \eta_2^4$ and $\eta_1^2 \eta_2^2$. The potential $\tilde{f}$ has the form

$$\tilde{f} = f_0 - {}^1/_2 at(\eta_1{}^2 + \eta_2{}^2) - {}^1/_4 b(\eta_1{}^4 + \eta_2{}^4) - {}^1/_2 c\eta_1{}^2\eta_2{}^2, \tag{14}$$

where a, b, and c are constants. From the stability conditions for $t \geq 0$ we have the inequalities $a > 0$, $b > c/3 > 0$.

By differentiating the potential $\tilde{f}$, we find the angle variables

$$h_1 = \eta_1(at + b\eta_1{}^2 + c\eta_2{}^2), \quad h_2 = \eta_2(at + b\eta_2{}^2 + c\eta_1{}^2). \tag{15}$$

To determine the structure of the facet at $t < 0$, let us note the following. The potential $\tilde{f}$ for a fixed direction of the vector η_μ is an increasing function of the absolute value of η for small η and a decreasing function for large η. On the other hand, the dependence of $\tilde{f}$ on the direction of η_μ has different characters in the parameter regions $b > c$ and $b < c$. First let $b > c$, then the potential $\tilde{f}$ as a function of the direction of η_μ for a fixed absolute value of η has minima along the coordinate axes $\eta_1 = 0$ and $\eta_2 = 0$. Since the sections with zero curvature should arise at those places where the original potential $\tilde{f}$ [and, on account of (6), the coordinate z] has its minima, these sections with $b > c$ should be located along the coordinate axes. As the first of the formulas (15) shows, the quantity h_1 for fixed η_2 $(\eta_2^2 < a|t|/c)$ vanishes for the two values

$$\eta_1^{(1,2)} = \pm[(a|t| - c\eta_2{}^2)/b]^{1/2}.$$

The potential $\tilde{f}$ (and, hence, the coordinate z), which depends only on η_1^2, assumes equal values at these two points. It is clear therefore that in fact the entire region $\eta_1^{(2)} < \eta_1 < \eta_1^{(1)}$ should correspond to a constant, zero value of the angle variable h_1. Similarly, for fixed η_1 $(\eta_1^2 < a|t|/c)$ the region $\eta_2^{(2)} < \eta_2 < \eta_2^{(1)}$, where $\eta_2^{(1,2)} = \pm[(a|t| - c\eta_1^2)/b]^{1/2}$, should correspond to zero h_2. Thus, the facet should have the following structure. Inside the ellipse

$$b\eta_1{}^2 + c\eta_2{}^2 = a|t|$$

the crystal surface has zero curvature along the η_1 axis. Correspondingly inside the ellipse

$$c\eta_1{}^2 + b\eta_2{}^2 = a|t|$$

the curvature is equal to zero along the η_2 axis. Inside the region common to the two ellipses there arises a plane section of the surface in the form of a square with its vertices coinciding with the points of intersection of the ellipses. Adjoining it are four regions with zero curvature only in one direction.

In the $b < c$ case the potential $\bar{f}$ as a function of the direction of η_μ has minima along the bisectrix $\eta_1 = \pm \eta_2$. Along these directions should be located sections with zero curvature. The resulting structure should be similar to the preceding structure, but rotated as a whole through an angle $\pi/4$. Indeed, if we carry out a rotation through $\pi/4$, i.e., if in place of η_1 and η_2 we introduce the new variables

$$\eta_1' = (\eta_1 + \eta_2)/\sqrt{2}, \quad \eta_2' = (\eta_1 - \eta_2)/\sqrt{2},$$

then the potential $\bar{f}$, expressed in terms of the new variables, will have the former form, but with the new coefficients $a' = a$, $b' = (b + c)/2$, and $c' = b' - (c - b)$. The condition $b' > c'$ is satisfied in terms of the new variables.

As in the preceding section, all the linear dimensions of the facet structures vary with temperature in proportion to the square root of $T_c - T$.

It is easy to understand that the existence on the crystal surface of areas with only one zero curvature implies the appearance at $t < 0$ of discontinuities in the surface energy $f(h_\mu)$ as a function of the angles not only at $h_1 = h_2 = 0$, but also over the segments of the coordinate axes of the (h_1, h_2) plane, determined by the conditions $h_1 = 0$, $|h_2| < h_0$ and $h_2 = 0$, $|h_1| < h_0$, where $h_0 = (a^3|t|^3/c)^{1/2} \times (b/c - 1)$. The surface $f = f(h_1, h_2)$ has a conical shape with kinks of finite length located along the four generatrices in the region close to the vertex.

4. FACES OF THE GENERAL TYPE, SYMMETRY PLANES, TWOFOLD AXES

For faces of the general type, i.e., not possessing any symmetry properties, the faceting transition can be continuous. This case is characterized by the fact that the transition is accompanied by the vanishing of not both, as in the preceding sections, but only one of the eigenvalues of the matrix $\partial^2 \bar{f}/\partial \eta_\mu \partial \eta_\nu$. The second, weaker inequality in (8) should then become an equality at the transition point:

$$F(\eta_1, \eta_2, T) = \frac{\partial h_1}{\partial \eta_1} \frac{\partial h_2}{\partial \eta_2} - \left(\frac{\partial h_1}{\partial \eta_2}\right)^2 = 0. \tag{16}$$

For the transition to be continuous, it is necessary that the quantity F be positive for all η_μ at $T > T_c$ and first vanish at some $\eta_\mu^{(0)}$ at the critical point itself. It is clear that, as a function of η_μ, the quantity F should have a minimum at $\eta_\mu = \eta_\mu^{(0)}$ and $T = T_c$, i.e.,

$$\partial F/\partial \eta_1 = \partial F/\partial \eta_2 = 0. \tag{17}$$

The three conditions (16) and (17) constitute three equations that determine the transition point T_c and the critical face $\eta_\mu = \eta_\mu^{(0)}$. If we choose the η_1 coordinate axis along the direction in which the curvature vanishes, then the equalities (16) and (17) imply that the conditions

$$\partial^2 \bar{f}/\partial \eta_1^2 = \partial^2 \bar{f}/\partial \eta_1 \partial \eta_2 = \partial^3 \bar{f}/\partial \eta_1^3 = \partial^3 \bar{f}/\partial \eta_1^2 \partial \eta_2 = 0. \tag{18}$$

are fulfilled at the point $\eta_\mu^{(0)}$ at $T = T_c$.

Furthermore, it can always be assumed that the angle variables, $h_\mu^{(0)}$, corresponding to the critical face are equal to zero at $T = T_c$. The potential $\bar{f}$ can thus be written in the form of the following expansion:

$$\bar{f} = f_0 - \alpha t \eta_1 - \beta t \eta_2 - {}^1\!/_2 a t \eta_1^2 - {}^1\!/_2 c \eta_2^2 - {}^1\!/_4 b \eta_1^4 - e \eta_1 \eta_2^2 - {}^1\!/_3 p \eta_1^3 \eta_2 - {}^1\!/_2 q \eta_1^2 \eta_2^2, \tag{19}$$

where α, β, a, b, c, e, p, and q are some constants. For brevity of notation, here and below under η_μ we mean the deviations of the quantities η_μ from the critical values $\eta_\mu^{(0)}$. The angular variables are equal to

$$h_1 = \alpha t + a t \eta_1 + b \eta_1^3 + e \eta_2^2 + p \eta_1^2 \eta_2 + q \eta_1 \eta_2^2,$$
$$h_2 = \beta t + c \eta_2 + 2 e \eta_1 \eta_2 + {}^1\!/_3 p \eta_1^3 + q \eta_1^2 \eta_2. \tag{20}$$

From the stability conditions (8) for $t \geq 0$ we obtain for the coefficients of the expansion (19) the following inequalities:

$$a > 0, \quad b > 0, \quad c > 0, \quad q - 4e^2/c - p^2/3b > 0.$$

The facet structure at $t < 0$ should be obtained by joining certain pairs of points $x_\mu^{(1)}$ and $x_\mu^{(2)}$ on the initial unstable crystal surface between which the region of the z minimum is located by tangents along which the angle variables h_μ are constant. The difference $\Delta z = z(x_\mu^{(2)}) - z(x_\mu^{(1)})$ is then equal to $\Delta z = h_\mu \Delta x_\mu$, where $\Delta x_\mu = x_\mu^{(2)} - x_\mu^{(1)}$. On account of the formulas (4) and (6), this means that the values, $\eta_\mu^{(1)}$ and $\eta_\mu^{(2)}$, of the variables η_μ at the ends of the straight lines should satisfy the condition

$$\Delta \bar{f} + h_\mu \Delta \eta_\mu = 0, \tag{21}$$

where $\Delta \eta_\mu = \eta_\mu^{(2)} - \eta_\mu^{(1)}$, $\Delta \bar{f} = \bar{f}(\eta_\mu^{(2)}) - \bar{f}(\eta_\mu^{(1)})$, and $h_\mu = h_\mu(\eta_\mu^{(1)}) = h_\mu(\eta_\mu^{(2)})$. Since the variable η_2 is not singular, the points $\eta_\mu^{(2)}$ and $\eta_\mu^{(1)}$ can be joined by a continuous curve along which h_2 is constant everywhere, and not only at the ends. On this curve the equality (21) can be regarded as an equation for the determination of the variable $\Delta \eta_1$ for fixed $\eta_1^{(1)}$, h_2, and $h_1 = h_1(\eta_1^{(1)}, h_2)$. Let us introduce the potential $f' = \bar{f} + \eta_2 h_2$. Its differential is equal to $df' = -h_1 d\eta_1 + \eta_2 dh_2$, so that

$$h_1 = -(\partial f'/\partial \eta_1)_{h_2}. \tag{22}$$

For fixed h_2 we have $\Delta f' = \Delta \bar{f} + h_2 \Delta \eta_2$, and Eq. (21) can be rewritten in the form

$$\Delta f' + h_1 \Delta \eta_1 = 0. \tag{23}$$

Since the straight lines in question are common tangents at the points $\eta_\mu^{(1)}$ and $\eta_\mu^{(2)}$, Eq. (23) should possess the following property (see Fig. 1) that allows us to determine $\eta_1^{(1)}$ along with $\Delta \eta_1$. To wit, the actual value of $\eta_1^{(1)}$ should be the smallest among those for which Eq. (23) for $\Delta \eta_1$ possesses a solution.

On account of (19) and (20), the potential f' is equal to

$$f' = f_0 - \alpha t \eta_1 + {}^1\!/_2 a |t| \eta_1^2 + {}^1\!/_2 c \eta_2^2 - {}^1\!/_4 b \eta_1^4 + e \eta_1 \eta_2^2 + {}^1\!/_2 q \eta_1^2 \eta_2^2. \tag{24}$$
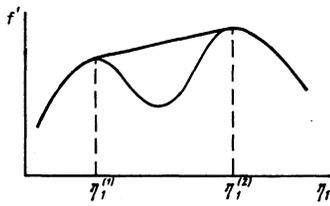
Expressing η_2 with the aid of the second of the Eqs. (20)

FIG. 1.

with the required accuracy in terms of h_2 and η_1, and substituting the result into (24), we obtain

$$f'=f_0-\alpha t\eta_1+{}^1\!/_2 a|t|\,\eta_1{}^2-{}^1\!/_4 b\eta_1{}^4+{}^1\!/_2 cs^2-{}^1\!/_3 ps\eta_1{}^3-es^2\eta_1-{}^1\!/_2(q-4e^2/c)s^2\eta_1{}^2,$$

(25)

where $s=(h_2-\beta t)/c$.

On account of (22), the terms linear in $\Delta\eta_1$ in Eq. (23) cancel each other out. After being divided through by $(\Delta\eta_1)^2$, it assumes the following form:

$$\left[\Delta\eta_1+2\left(\eta_1+\frac{p}{3b}s\right)\right]^2$$
$$+2\left[\eta_1{}^2+\frac{2p}{3b}s\eta_1\right.$$
$$\left.+\frac{s^2}{b}\left(q-\frac{4e^2}{c}-\frac{2p^2}{9b}\right)-\frac{a|t|}{b}\right]=0,$$

from which we find

$$\Delta\eta_1=-2\left(\eta_1+\frac{p}{3b}s\right),$$

$$\eta_1{}^{(1,2)}=-\frac{p}{3b}s$$
$$\mp\left[\frac{a|t|}{b}-\frac{s^2}{b}\left(q-\frac{4e^2}{c}-\frac{p^2}{3b}\right)\right]^{1/2}.$$

Since to within the dominant terms $\eta_2\approx s$, the second of the Eqs. (26) defines an ellipse,

$$b\eta_1{}^2+\frac{2}{3}p\eta_1\eta_2+\left(q-\frac{4e^2}{c}-\frac{2p^2}{9b}\right)\eta_2{}^2=a|t|,$$

inside which the section of the surface with singular curvature is located.

The surface energy $f(h_1, h_2)$ possesses a discontinuity of the derivatives on the segment of the curve in the (h_1, h_2) plane with the equation $h_1 \approx \alpha t + es^2 \approx \alpha t + (e/c^2)h_2^2$. The derivative jump is determined by the formula

$$\Delta\frac{\partial f}{\partial h_1}'=2\left[\frac{a|t|}{b}-\frac{h_1{}^2}{bc^2}\left(q-\frac{4e^2}{c}-\frac{p^2}{3b}\right)\right]^{1/2}.$$

It vanishes at a finite value of $|h_2|$, and is equal to zero everywhere at higher values of $|h_2|$.

The obtained formulas describe, in particular, continuous faceting transitions at the faces possessing symmetry planes and twofold axes.

There exists in the presence of a symmetry plane a one-parameter family of faces the normals to which lie in this plane. There are two possibilities here. The first of them corresponds to the situation in which the curvature vanishes along the direction perpendicular to the symmetry plane (a reflection in the plane changes the sign of η_1, but does not change η_2). In this case, on account of the symmetry of the faces, the derivatives $\partial^2\!f/\partial\eta_1\partial\eta_2$ and $\partial^3\!f/\partial\eta_1^3$ vanish identically. The remaining two of the conditions (18) constitute equations for the determination of the transition temperature and the critical face. The transition is described by the above presented formulas, in which we should, on account of the symmetry, set $\alpha=e=p=0$. The second possibility is the vanishing of the curvature along a direction in the symmetry plane (the symmetry transformation is the substitution $\eta_2\to-\eta_2$). In this case $\partial^3\!f/\partial\eta_1^2\partial\eta_2$ and $\partial^2\!f/\partial\eta_1\partial\eta_2$ vanish identically and, furthermore, $\beta=p=0$.

For faces perpendicular to a twofold axis, $\partial^3\!f/\partial\eta_1^3$ and $\partial^3\!f/\partial\eta_1^2\partial\eta_2$ vanish identically. As in the case of a face of the general type, the remaining two conditions in (18) constitute, in fact, a single equation (the second equation is a condition on the choice of the coordinate system) determining the critical temperature. The transition is described by the above-presented formulas with $\alpha=\beta=e=0$.

Of special interest from the experimental point of view are faces perpendicular to twofold axes in hexagonal close-packed [4]He crystals and body-centered cubic [3]He crystals. In both of them a twofold axis lies along the intersection of two perpendicular symmetry planes. In this case p vanishes along with α, β, and e.

In all the transitions considered in the present section, only one of the curvatures of the surface vanishes. Plane regions do not arise. Such regions should appear as a result of another phase transition at a temperature $T_c' < T_c$. The second transition may also be continuous, and then it is described by similar formulas. In the case of faces with a twofold axis, for example, the faceting transition in question is one on an initially cylindrical surface with $h_1 = 0$. The potential $\bar f$ as a function of the variable η_2 in the vicinity of the critical temperature T_c' can be written in the form

$$\bar f(\eta_2, \tau)=f_0(\tau)-{}^1\!/_2 u\tau\eta_2{}^2-{}^1\!/_4 v\eta_2{}^4,$$

where u and v are positive constants and $\tau = T - T_c'$. The angle variable h_2 is equal to

$$h_2=(u\tau+v\eta_2{}^2)\eta_2.$$

There arises at $\tau < 0$ along the generatrix of the cylindrical surface a plane section with $h_2 = 0$ in the form of a belt of width $2(u|\tau|/v)^{1/2}$.

5. EDGES AND CONICAL POINTS

At the above-considered critical points of the faceting transitions the curvature of the crystal surface vanishes. This, as can be seen, for example, from the formula (11), leads to a situation in which the coefficients of the expansion of the surface energy f in powers of the angle parameters h_μ become infinite. The situation should clearly be the opposite near the critical points corresponding to the appearance of edges or conical points. If such a critical point is a

second-order phase transition point, then the curvature of the surface should become infinite and, consequently, at least one of the eigenvalues of the matrix $\partial^2 f/\partial h_\mu \partial h_\nu$ should vanish in its neighborhood. Then, as before, depending on the symmetry of the face on which the singularity first appears, one or both of the eigenvalues will vanish, the first case corresponding to the appearance of an edge; the second, of a conical point.

In both cases the coefficient in the expansion,

$$f = f_0 + \frac{1}{2} a t h^2 \tag{27}$$

of the surface energy in powers of at least one of the h_μ components (denoted here simply by h; a is a constant and $t = T - T_c$) vanishes at the critical point. At small t the fluctuations in the variable h grow on the critical face. As usual,[13] to investigate the possibility of a second-order phase transition, we must generalize the formula (27) to the case in which the critical parameter h depends on the coordinates x_μ by allowing for the spatial dispersion of the expansion coefficient. As a result, we obtain in place of (27) the expansion

$$f = f_0 + \frac{1}{2} \sum_{k_\nu} [at + \varphi(k_\nu)] |h(k_\nu)|^2, \tag{28}$$

where the $h(k_\nu)$ are the Fourier transforms of the function $h(x_\nu)$ and $\varphi(k_\nu)$ is some function of the wave vector with the property $\varphi(0) = 0$. For a second-order phase transition to be possible, the function $\varphi(k_\nu)$ should have a minimum at $k_\nu = 0$. It is easy to see, however, that in our case this condition is not met, owing to the distinctive strictional interaction of the fluctuations on the crystal surface via the lattice-deformation field in the volume. Indeed, the existence of the x-coordinate (the coordinate system has been chosen such that $h = h_1$) dependent parameter h indicates the appearance on the surface of an excess number, $|n(x)| = |h(x)|/l$, of steps of one or another sign per unit length along the x axis (l is the step height; see Fig. 2). Let us define the function $n(x)$ so that its sign coincides with that of $h(x)$, i.e., with the sign of the excess steps. It is important for the determination of the behavior of the function $\varphi(k)$ at small $k \equiv k_1$ that we take the long-range interaction of the steps into consideration. It is well known[14] that the interaction $v(x)$ of the steps over fairly long distances is largely determined by the interaction via the lattice-deformation field, and falls off in inverse proportion to the square of the distance $|x|$ between the steps. The total interaction energy U of the system of steps is given by the integral

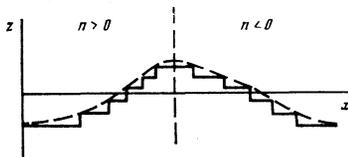$$U = \frac{1}{2} \int v(x-x') n(x) n(x') dx dx',$$

FIG. 2.

where the function $v(x - x')$ for large $|x - x'|$ is equal to

$$v(x-x') = A/(x-x')^2,$$

where $A > 0$, since steps of the same sign repel, while those with unlike signs attract, each other. Going over to Fourier transforms, we obtain

$$U = \frac{1}{2} S \sum_k v(k) |n(k)|^2 = \frac{S}{2l^2} \sum_k v(k) |h(k)|^2,$$

where S is the area of the surface.

The asymptotic form, $v(k) \approx -\pi A |k|$, of the Fourier transforms of the function $v(x)$ for $k \to 0$ is evident from the obvious equality

$$\lim_{\delta \to +0} \int_{-\infty}^{+\infty} |k| e^{ikx - |k|\delta} \frac{dk}{2\pi} = -\frac{1}{\pi x^2}.$$

As a result, the contribution of the long-range elastic interaction between the steps to the surface energy is equal to

$$f = \frac{U}{S} = -\frac{\pi A}{2l^2} \sum_k |k| |h(k)|^2,$$

from which we obtain the following asymptotic form of the function $\varphi(k)$ for small k:

$$\varphi(k) = -\frac{\pi A}{l^2} |k|. \tag{29}$$

Thus, this function has at $k = 0$ not a minimum, but a maximum, so that a second-order phase transition is indeed not possible. A formula of the type (29) can also be derived (see Ref. 15) purely macroscopically by taking into account the dependence of the surface energy on the lattice deformation.

Let us note in conclusion that, if by chance the elastic interaction between the steps is weak compared to the other types of interaction, then the result obtained indicates the possibility of the appearance on the critical face at a temperature slightly higher than T_c of a superstructure with a macroscopically large period (see Ref. 15).

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