Crystallization waves in He^4

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The spectrum of crystallization waves in He^4 and the frequency and temperature dependences of their damping are determined. The surface energy on the liquid–crystal interface exhibits a noticeable anisotropy and depends little on temperature in the 0.36–1 K range. It is established that below 1.2 K the equilibrium shape of the He^4 crystal contains both rounded and flat parts.

Experimental investigations of capillary phenomena in ordinary classical crystals are fraught in principle with difficulties due primarily to the excessively long time required for the crystal to assume an equilibrium shape. The physical reason why ordinary crystals grow exceedingly slowly under conditions close to equilibrium is the following. Upon crystallization, as in any first-order phase transition, the states of the two phases are separated from each other by some energy barrier that ensures stability of each phase. For the phase transition to proceed at a finite rate, it is necessary to disturb the phase equilibrium in one way or another. As a result, the phase transition is always accompanied by energy dissipation, and it is this which limits in the upshot the rate of establishment of phase equilibrium, and in particular the rate of establishment of the equilibrium shape.

The situation is entirely different when the crystallization does not proceed as usual, i.e., by random transition of individual particles from one phase to another, but constitutes a coherent process unconnected in principle with any energy dissipation whatever.[1] The conditions needed in practice for this purpose might be realized in the growth of helium crystals from the liquid phase at sufficiently low temperatures. In nondissipative crystallization it becomes possible to observe all the capillary phenomena that are characteristic of ordinary liquids. In particular, weakly damped oscillations of the surface with macroscopic amplitude are possible, similar in many respects to ordinary capillary waves (in this case they are due to periodic melting and crystallization). These oscillations—crystallization waves—were experimentally observed[2] in He^4.

We present here the result of an investigation of the crystallization waves in He^4, and of the frequency and temperature dependences of their damping. The surface energy exhibits a noticeable anisotropy and depends little on temperature. It has been established that at temperatures below 1.2 K the equilibrium shape of the He^4 crystal contains both rounded and flat sections (the latter correspond to the most closely packed faces). Above 1.2 K, flat surface sections do not occur at equilibrium, but they do appear if the growth is fast enough.

1. APPARATUS

We used in our experiments an optical cryostat with He^3, constituting a modification of apparatus previously employed[3] to study the properties of solid helium. Four pairs of plane-parallel windows (K-8 glass at 300 K, single-crystal sapphire at 77 K, chemical and quartz glasses at 1.2 K) permitted observation of the crystal growth, photography, and simple optical measurements. The He^4 crystals were grown in a ferrochrome container (1, see Fig. 1) of rectangular 12 × 15 mm cross section with two chemical glass walls measuring 12 × 28 × 3 mm, so that the entire volume of the container could be observed. The glass was secured to the ferrochrome by Stycast-1266 epoxy resin. When carefully constructed (the gap between the glass and the ferrochrome was approximately 50 μm over the entire perimeter) this structure can withstand repeated cooling from room to helium temperature, as well as pressures up to 60 bar. On the side wall inside the container was mounted a capacitor (2) intended to excite oscillations of the crystal surface. The capacitor constituted two kapron-insulated copper wires of 30 μm diameter, found bifilarly (150 turns) on a bakelite plate; it could withstand (in He II) a voltage not less than 3 kV, corresponding to a maximum field intensity $(2-3) \times 10^6$ V/cm. In the upper part of the container were fused a capillary 3 and four electric leads 4, while in the lower part was fused a copper cold finger 5 leading to the He^3 bath. The capillary was in good thermal contact with the He^3 bath.

The temperature was measured with a carbon resistance thermometer mounted on a copper cold finger fused into the side wall of the container. The thermometer was calibrated against a cadmium standard[7] (T_{cr}
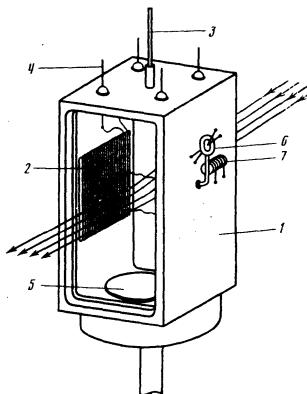
FIG. 1. Construction of container. 1) Housing, 2) capacitor, 3) capillary, 4) electric lead-in, 5) cold finger, 6) thermometer 7) cadmium standard. The arrows indicate the direction of the light beam.

=0.515 K) mounted on the same cold finger as the thermometer. When the container was filled, the total heat flow into the He³ bath, including that by radiation through the windows, did not exceed 10^{-4} W.

The He⁴ crystals were grown at constant temperature (0.4–1.3 K) and pressure (25 bar) and at a controllable flow, which determined the crystallization rate, of the helium through the container. The container was first filled with liquid helium at an approximate pressure 25 bar from an external gasifier, which was subsequently disconnected. The growth and melting of the crystals were effected by varying the temperature of an external ballast volume (300 cm³; $\Delta p/\Delta T = 25/300$ bar/K). When necessary, the grown crystal could be melted completely within less than 1 minute, by merely lowering the pressure in the ballast volume to 0.1–0.2 bar below the melting curve. Next by raising the pressure, the growth process could be repeated at any desired rate. Continuous visual control ensured the possibility of not only repeated the growth process many times in one experiment, but also of partially melting and growing the crystal, retaining in the container a seed of size ~1 mm³ for the next growth of a large crystal, etc. Once the required crystal was grown, the ballast volume was disconnected and the position of the interphase boundary could be maintained constant accurate to 0.1–0.2 mm for many hours.

2. FEATURES OF He⁴ CRYSTAL GROWTH AT LOW TEMPERATURES

Visual observation of the He⁴ crystal growth reveals a great variety of crystal shapes and of the growth dynamics, depending on the temperature, the nucleation point, and the orientation of the seed. It must be noted that the gravitational field influences significantly the growth dynamics and the crystal shape both during the growth and at equilibrium, in the entire investigated temperature range (0.4–1.3 K). We must emphasize even here that direct observation of the He⁴ crystal during its growth at low temperatures makes it possible not only to fix its orientation, but also to control effectively the degree of perfection, since the crystal surface, during the growth and especially at equilibrium, is highly sensitive to the crystal defects, including those that are practically unobservable by other methods (see the later discussion in this section).

At temperatures below 1.2 K the crystal grows as a rule from one seed, and during its growth the crystal is faceted in one manner or another. The faceting is pronounced more strongly the faster the growth and the lower the temperature. The observed faceting always corresponds to a hexagonal prism having various types of faces, depending on the place where the seed was produced, on the crystal dimension, and on its orientation relative to the container walls (see Fig. 2). The crystal symmetry (hcp structure, space group D_{6h}^4) makes it possible to identify the base of the prism with the basal plane (0001), and the side faces perpendicular to it with planes of either the $\{11\bar{2}0\}$ or $\{10\bar{1}0\}$ type.

Figure 2 shows clearly all the characteristic features of the growth of He⁴ crystals at low temperature: a
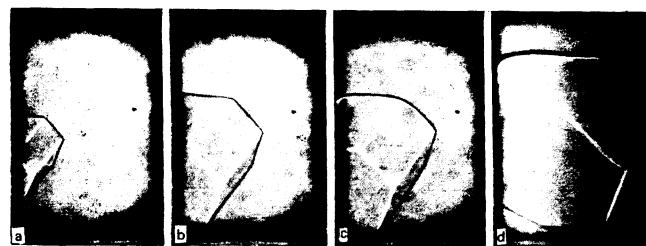
FIG. 2. Different stages of the growth of one of the samples at 0.5 K.

distinct faceting at relatively rapid growth (~0.1 mm/ sec, frames a and b), the onset of rounded sections in the upper part of the surface when the growth slows down (c) with a transition to the characteristic meniscus (d). During the course of melting the crystals usually have the shape of a drop.

The dependence of the crystal shape on the growth rate can be naturally attributed to the anisotropy of the growth coefficient K, defined by the relation

$$V(\bar{n}, \Delta\mu) = K(\bar{n}, \Delta\mu)\Delta\mu, \qquad (1)$$

V is the growth rate along the normal $\bar{n}$ to the given face, and $\Delta\mu$ is the difference between the chemical potentials of the two phases. Namely, K is a minimum for directions determined by the faces of the growth prism (and has a singularity of the type-4 kink in these directions); the lower the temperature, the stronger the anisotropy.

The growth rates are particularly slow in the case of the (0001) face. At the lowest temperatures (0.4–0.6 K) and at not too large $\Delta\mu$, the growth rate in the [0001] direction is so small that when suitably oriented the crystal can be suspended for several hours from the container wall in contact with the (0001) face (Fig. 3). The rounded sections of the surface, and only they, show clearly the oscillations produced by even insignificant vibrations of the apparatus; the amplitude of these oscillations increases rapidly with decreasing temperature (see also Fig. 1 of Ref. 2). This fact, in our opinion, indicates unequivocally that the previously postulated[1] quantum state of the surface is indeed realized for all its orientations except the singular ones, namely (0001) as well as $\{11\bar{2}0\}$ (or $\{10\bar{1}0\}$). It is obvious that at the very lowest temperatures the singular surfaces
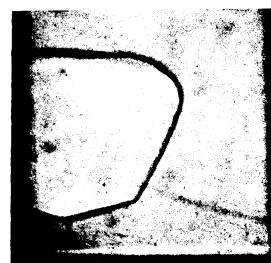
FIG. 3. Crystal under conditions close to equilibrium at 0.5 K. The lower face is represented by the (0001) plane. A crystallization wave due to vibration of the cryostat can be seen on the upper rounded surface.
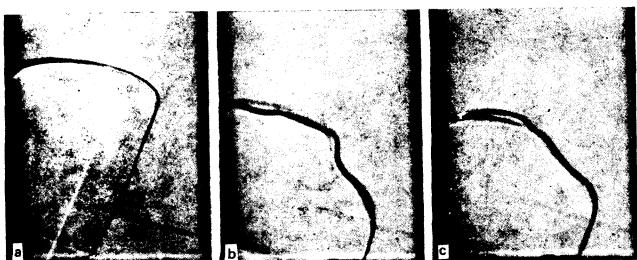
FIG. 4. Motion picture of the "shakedown" of the crystal obtained at 24 frames/sec.

stay in an atomically smooth state.

Under these conditions the crystal growth in the [0001] direction is due only to the appearance of seeds of new atomic layers at the points of contact of the (0001) face with the container walls. This is frequently accompanied by a very fast (within less than 0.1 sec) avalanche-like recrystallization, as a result of which the crystal previously attached, say, to one of the side walls is "thrown down" into the lower part of the container without any change in its orientation (Fig. 4). As a rule this process is accompanied by the onset of one or several planar defects [most frequently in the (0001) plane], which are apparently the stacking faults well investigated in ordinary close-packed structures. These defects appear at equilibrium in the form of "ravines" at the points where the defect plane emerges to the outer surface of the crystal [Fig. 5(a)]. The onset of the ravines is obviously due to the excess defect energy, which is proportional to the defect area (the observed depth of the ravines yields for this energy and estimate of 0.1–0.2 erg/cm². When the growth of a crystal with such defects is resumed, the ravines are rapidly filled, and the resultant faceting does not differ in any way from that of a defect-free crystal [Fig. 5(b)]. We emphasize the orientations of the blocks on both sides of the stacking-fault plane are strictly identical.

The possibility of growing a large crystal without visible defects depends not only on the temperature (the best results are obtained at 0.8–1.0 K) but also on the orientation of the seed. As a rule, when the growth process is repeated many times during one experiment, all the seeds have the same or nearly the same orientation, even if they are produced at different points in the container.[1] In the overwhelming majority of the
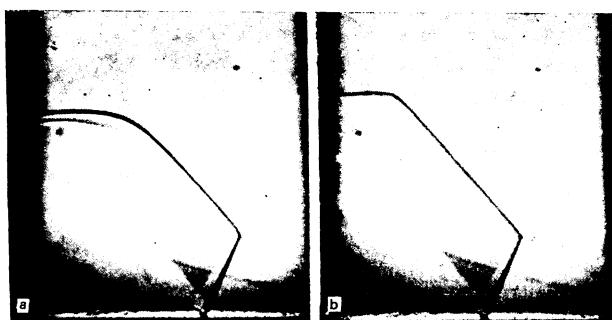
experiments the "singular" faces made an appreciable (not less than 20°) angle with the horizontal plane. Under these conditions, to prevent the already mentioned falling of the crystal, it was necessary to seek painstakingly in each experiment the best growing regime. It must be noted that when a sample grown, say, at 0.8 K is heated to 1.1 K or more its surface shape is irreversibly altered, apparently because of the crystal plastic deformation due to the change of the equilibrium pressure by an amount of the order of 0.1 bar (cf. Ref. 5). Only a sufficiently slow (not faster than 0.1 K/hr) change of the temperature is apparently not accompanied by plastic deformation of the crystal.

At temperatures 1.2–1.3 K the crystals have usually a droplike shape both when they grow and when they melt. As a rule, several seeds are produced simultaneously and "climb over" gradually (taking dozens of seconds) into the lower part of the container and ultimately fill this part. A similar picture was already observed by Shal'nikov.[6] The crystal grown in this manner has a hilly shape which does not change significantly during the growth or the melting. In addition to the defects that emerge to the surface, it is frequently possible to note also directly in the bulk of the crystal defects in the form of cords and clusters of minute liquid bubbles. A crystal without visible defects could not be grown above 1.3 K.

3. EQUILIBRIUM SHAPE AND ELECTROCAPILLARY PHENOMENA

The surfaces of the crystals grown by the method described in the preceding section, with all the precautions taken, have (except for the special cases discussed below) the shape of a convex meniscus (Fig. 6). The contact angles are approximately the same for a great variety of materials (copper, ferrochrome, glass, kapron insulation of capacitor wires), and range from 30° to 60°, depending on the crystal orientation. The shape of the photographed meniscus can be described with sufficient accuracy (everywhere except in the vicinity of about 1 mm of the side walls) by the formula

$$z(x) = z_0 \operatorname{ch}(x/a),$$

where a has the meaning of the capillary constant and is independent of temperature within the accuracy limits. In other words, the surface energy α (more accurately the quantity $\tilde{\alpha} = +\partial^2 \alpha / \partial \varphi^2$, where φ is the angle between the normal to the surface and the z axis) exhibits no noticeable temperature dependence. Thus, for one of the investigated samples $\tilde{\alpha} = 0.19 \pm 0.02$ erg/cm² in the temperature interval from 0.5 to 1.0 K. It must be noted that the values of $\tilde{\alpha}$ obtained in this manner must

FIG. 5. External view of crystal with defect: a) at equilibrium, b) during growth.

FIG. 6. Equilibrium shape of meniscus.

be regarded only as tentative, since the employed formula, of course, is not the result of an exact solution of the problem of the equilibrium shape of the crystal in the gravitational field; all that matters to us here is the absence of a temperature dependence.

The foregoing pertains to crystals having a certain arbitrary orientation relative to the gravitational field. A qualitatively different picture is observed in cases when one of the singular surfaces (i.e., prism growth faces) is close to a horizontal plane. In these cases, at sufficiently low temperatures, the equilibrium meniscus contains a perfectly flat section (Fig. 7) (the possible curvature radius of this "mirror" is not less than l^2/λ, where l is the dimension of the mirror and λ is the wavelength of the visible light). The mirror is surrounded on all sides by a the rounded surface of the meniscus, which has the usual form, and no noticeable breaks are observed on the boundary between the flat and rounded sections. If crystallization waves are excited on the surface of such a crystal in some manner, then the plane of the mirror remains perfectly immobile, and only its boundary is subject to oscillations caused by the vibrations of the rounded sections. The plane of the mirror coincides exactly with one of the faces of the growth prism, a fact easily established when such a crystal is grown.

It became possible to grow a crystal with practically horizontal basal plane (or lateral face of the growth prism) by using the following procedure. In those cases when the seed is produced on one of the walls in the central or upper part of the container, it is frequently possible to "shake it down" to the copper bottom by melting the crystal at the point of its contact with the wall. It suffices for this purpose to apply a small heat pulse to the wall by some external source, say by a flash from a pocket flashlight; the container temperature should in this case be 0.8 K or very slightly higher. Next, during the time of its fall, amounting to a fraction of a second, the crystal should grow somewhat and as a result acquire a faceting. The crystal, like a gambling die, lands therefore on one of its flat faces [most probably on the (0001) face]. In this manner it is possible to "lay" the basal plane horizontally within less than 1°, whereas the best "casting" terminated with the "dropping" of the lateral face of the prism, the angle with the horizontal was 2.3°.

In those cases when this procedure does not succeed directly, for example because of an inappropriate place-ment of the seed, it helps to turn on an electric field. When the voltage on the capacitor exceeds 700–800 V, seeds are always produced in its surface,[2] from which they can be shaken down in most cases. To be sure, several seeds are produced as a rule in this case almost simultaneously and the operation described above must be performed very rapidly.[3]
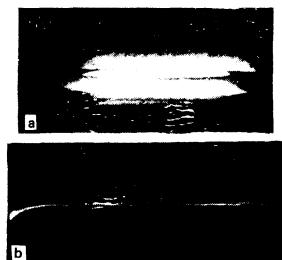
The growth of crystals from seeds oriented in this manner encounters the same difficulties as the growth of crystals with other orientations. The presence of visible defects greatly distorts the shape of the flat mirror, decreases its dimensions, and may cause it even to vanish completely. In addition, the shape and position of the mirror are quite sensitive to even weak (several degrees) inclinations relative to the gravitational field.

When the temperature is raised the mirror decreases in size and vanishes completely at a certain temperature T_c. The values of T_c for a given face vary noticeably (by 0.1–0.2 K) from sample to sample, probably as functions of the perfection of the crystal. It appears that the maximum values of T_c are reached in the most perfect crystals (prolonged maintanance of a crystal temperature near T_c leads to an increase of T_c). The largest registered T_c equal 1.17 for the basal plane and 0.9 for a lateral face of the prism. We were unable to attain good reproducibility of the measurements of the temperature dependence of the mirror size.

Figure 8 shows the results of one such experiment. A basal plane "laid" horizontally with accuracy better than 0.5° was grown at a temperature close to 1.15 K and was kept at 1.15–1.18 K for 15 hours. The dimension l was determined from the angular width of the principal diffraction maximum in reflection (at an angle 5°) of a plane-parallel light beam from the meniscus with the mirror (Fig. 8). Each measurement was performed after the temperature was stabilized accurate to 10^{-4} K for at least a half-hour. After cooling the crystal to below 1 K, the measured size was 9–10 mm. The reasons for the observed scatter of the points as at present not clear enough; it may be due to fluctuations of the amount of helium in the container or even to mechanical vibrations of the apparatus (we emphasize that a mirror is observed on the surface of a growing crystal also at temperatures much higher than T_c for the given face). More profound physical causes can, however, not be ruled out.

Avron et al.,[7] using a holographic technique, have

FIG. 7. Shape of meniscus for a crystal with horizontal (0001) plane: a) overall view, b) profile.
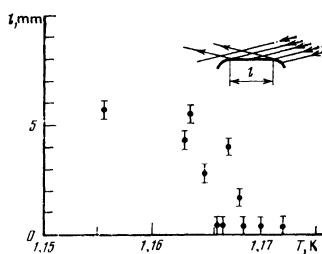
FIG. 8. Temperature dependence of the size of the flat section.

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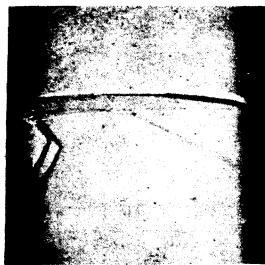
FIG. 9. Onset of bubbles in an electric field. The upper half of the container is filled with liquid helium and the lower with the crystal. Two faceted bubbles are seen on the condenser below the meniscus.

recently observed a jumplike change in the area of the flat (0001) section at $T = 1.08$ K. These data, as seen from the foregoing, do not contradict our observations; it is clear, however, that the question of the suggested phase transition[7,8] calls for further study.

A voltage applied to the capacitor produces a visible change in the contact angle and a corresponding rise of the meniscus edge adjacent to the capacitor. This rise can reach 1-2 mm. At low voltage the rise is approximately proportional to the square of the voltage, and starting with 0.8-1 kV this dependence saturates rapidly. The saturation is apparently due to the already mentioned appearance of minute crystallites on the capacitor surface; these crowd out the main crystal from the regions with maximum field.

We note finally a curious phenomenon that can be observed by applying to the capacitor a sufficiently high (~1 kV) 50-100 Hz voltage. Under these conditions there are produced on the surface of the capacitor, below the main meniscus, bubbles that are obviously filled with liquid helium and reach several millimeters in size (Fig. 9). The bubbles have a clearly pronounced faceting which is the same for all bubbles and coincides with the outer faceting of the crystal as the latter grows; they are very mobile, appear and disappear rapidly (within a fraction of a second), "climb" upwards over the surface of the capacitor, etc. Those that are particularly large can sometimes break up, so that one or several bubbles remains frozen inside the crystal; such bubbles lose practically all their mobility.

4. SPECTRUM AND DAMPING OF CRYSTALLIZATION WAVES

By applying to the capacitor an alternating voltage of suitable frequency ω it is possible, as shown earlier,[2] to excite a plane crystallization wave with wave vector **k** normal to the capacitor surface. The $\omega(k)$ dependence for such waves, when account is taken of the gravitational field and the damping due to the finite growth coefficient K, is determined by the expression[1]

$$\omega^2 - \frac{\bar{\alpha}\rho_2}{(\rho_1-\rho_2)^2}k^3 - \frac{\rho_2}{\rho_1-\rho_2}gk + i\omega k\frac{\rho_1\rho_2}{mK(\rho_1-\rho_2)^2} = 0. \quad (2)$$

Here $\bar{\alpha} = \alpha + \partial^2\alpha/\partial\varphi^2$ (the angle φ is reckoned along **k**), ρ_1 and ρ_2 are the densities of the crystal and of the liquid, respectively, g is the acceleration due to gravity, and m is the mass of the atom. In our pre-

ceding paper[2] we measured the crystallization wavelengths by using the diffraction of light from an He–Ne laser by these waves. This method is not convenient in practice, primarily because of the presence of random surface oscillations due to the vibrations of the apparatus; in addition, it cannot be used to measure the damping.

In the present paper we used a method in which a narrow beam of an LG-66 laser (with a width much smaller than the measured wavelength) scans slowly the oscillating surface and remains practically parallel to the wave front. The vertical beam dimension is about 2 mm, the wave amplitude is estimated at 0.01-0.5 mm, and the amplitude of the random oscillations is of the same order or even somewhat larger. The lower part of the beam is refracted by the slightly curved surface and is deflected downwards considerably; the remaining light passes over the surface and is incident on an FD-3 photodiode.

The light intensity at the photodiode thus contains an alternating component proportional to the vertical displacement of the surface at the given point. The signal from the photodiode is amplified by a selective amplifier tuned to the excitation frequency, and after synchronous detection (at a constant phase shift between the exciting and reference signals) is fed to the Y input of an x–y recorder. The actual voltage on the capacitor consisted of a dc component U_1 and an ac component (frequency ω) U_2, with $U_1 \gg U_2$. The X input of the plotter received simultaneously a signal from a multiturn potentiometer connected to the micrometric screw used for the scanning. Figure 10 shows one of the plots obtained in this manner.

The distance between the signal zeros along the X axis determines the crystallization wavelength, and the ratio of the amplitudes of the neighboring maxima determines its damping. Figure 11 shows the measured spectrum for one of our samples at two temperatures, 0.360 and 0.505 K. The dashed line corresponds to the relation $\omega \sim k^{3/2}$, while the solid curve is the theoretical $\omega(k)$ dependence given by Eq. (2) with allowance for the gravitational term (the correction for damping can be neglected) and with $\bar{\alpha} = 0.21$ erg/cm². Thus, within the accuracy limit (5%), $\bar{\alpha}$ remains unchanged when the temperature is raised from 0.360 to 0.505 K.

The data for the other samples agree essentially with the foregoing, except that the entire curve is shifted somewhat in accord with the change of the value of $\bar{\alpha}$.
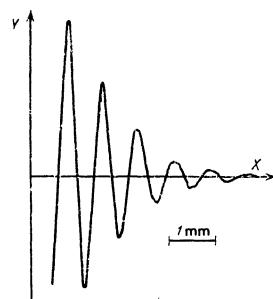
FIG. 10. Typical experimental plot.

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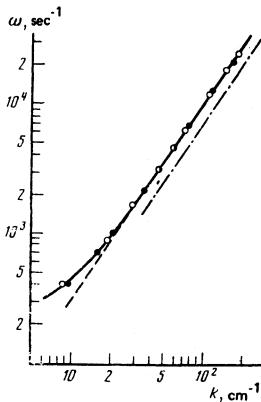
FIG. 11. Spectrum of crystallization waves for two samples. Sample No. 1: ●) $T = 0.505$ K, O) $T = 0.360$ K, $\tilde{\alpha} = 0.21$ erg/cm^2. Sample No. 2—dash-dot line, $\tilde{\alpha} = 0.097$ erg/cm^2.

In addition to the forgoing, we registered $\tilde{\alpha}$ values 0.18, 0.15 and 0.097 erg/cm^2 (dash-dot line on Fig. 11). The spectrum presented in the preceding paper[2] corresponds to $\tilde{\alpha} = 0.23 \pm 0.4$ erg/cm^2. These data point to a substantial anisotropy of the surface energy $\tilde{\alpha}$, but give, of course, a far from complete idea of the magnitude and character of this anisotropy, since all the surfaces investigated by this method had a certain random orientation made angles not less than 20° with all of the singular surfaces.

Balibar, Edwards, and Laroche[9] (see also Ref. 8) investigated the value of α by the capillary rise method. Neglecting anisotropy, they obtained $\alpha = 0.107-0.145$ erg/cm^2 at $T = 1.3$ K, in good agreement with our data (the temperature difference hardly matters, in view of the already mentioned weak temperature dependence of α). At lower temperatures, the method used in Ref. 9, as noted by the authors themselves (see Ref. 8), is unsuitable even for the estimate of the angle-averaged values of α, since the crystal acquires a faceting in the course of the measurement.

In measurements of the spectrum, and particularly of the damping, of the crystallization waves, it is necessary to satisfy a number of rather stringent requirements. First, the amplitude of the wave must be low, and the usual requirement that it be small compared with the wavelength is insufficient: at high voltages, as already mentioned, crystallization takes place over the entire surface of the capacitor above the main meniscus, the total volume of the liquid in the container varies periodically, and the resultant oscillation of the surface is a superposition of the investigated wave and of a quasi-homogeneous oscillation having the same frequency. In addition, at large excitation amplitudes the results are no longer reproducible, probably because of irreversible changes that take place in the crystal under the prolonged action of a large-amplitude electric field. Next, the wavelength must be small compared with the container dimension L, but large compared with the diameter of the capacitor-winding wire (~0.04 mm). Finally, the damping must not be too large ($\varkappa \lesssim k_0$, where $\varkappa$ and k_0 are respectively the imaginary and real parts of the wave vector $\mathbf{k}$), but not too small ($\varkappa L$

$\gtrsim 1$), to be able to neglect the reflected wave.

In measurements of the damping (i.e., of $\varkappa$), which are connected with the measurements of the amplitude, another difficulty is encountered, due to the imperfection of our optical system (mainly dirt on the glasses). Namely, the measured values of $\varkappa$ can contain an uncontrollable additive increment due to the impossibility of exact calibration of the transmission over the entire optical channel in each experiment.

The damping, as follows from Eq. (2), is given by

$$\varkappa = \tfrac{1}{3}\rho_1\rho_2^{1/3}(\rho_1-\rho_2)^{-1/3}\tilde{\alpha}^{-1/3}(mK)^{-1}\omega^{1/3} \tag{3}$$

(the gravitational correction can be neglected in the investigated frequency range). Figure 12 shows the measured frequency dependences of $\varkappa$ for two different temperatures for the sample whose spectrum is shown in Fig. 11. It is seen that the relation $\varkappa \sim \omega^{1/3}$ is indeed satisfied, i.e., the observed damping is indeed due to the finite nature of the growth coefficient K.

According to Ref. 1, at low temperatures, when the energy dissipation accompanying the motion of the interphase boundary is due to its collision with the phonons, the temperature dependence of the growth coefficient takes the form $K \propto T^{-4}$, and at higher temperatures, when the number of rotons in the liquid becomes large enough, it is given mainly by the relation $K \propto \exp(\Delta/T)$, where Δ is the roton gap. Figure 13 demonstrates the temperature dependence of the quantity $1/mK$ calculated from the measured values of $\varkappa$ for three different samples.

It can be stated that at low temperature the damping decreases more slowly than in the case of a pure phonon mechanism. When comparing the experimental data with the theory, however, it must be borne in mind that in a real experiment there are always factors that lead to a residual damping, i.e., to a finite damping at arbitrarily low temperatures. These include various processes involving scattering of the crystallization waves by crystal defects and by surface oscillations due to the vibration of the apparatus, the influence of the geometry of the light source and of the curvature of the meniscus, and others. This residual damping can obviously vary greatly from sample to sample and, depending on the actual scattering mechanism, can vary with frequency in accordance to one law or another. From this point of view it is easy to explain the systematic discrepancy between the data corresponding to the two
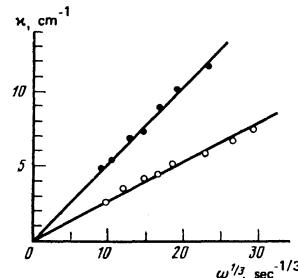
FIG. 12. Frequency dependence of the damping of crystallization waves at two temperatures: O) $T = 0.360$ K, ●) $T = 0.505$ K.
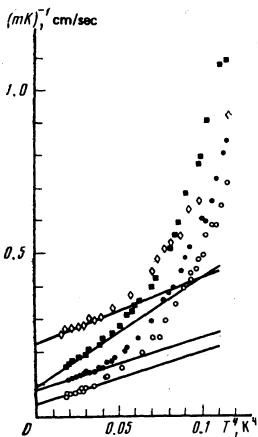
FIG. 13. Temperature dependence of the damping of crystallization waves for three samples: sample No. 3, O) 1118 Hz, ●) 232 Hz; sample No. 4, ■) 827 Hz; sample No. 5, ◊) 837 Hz.

different frequencies for sample No. 3 on Fig. 13 (the aforementioned uncontrollable increment of the damping is not enough to explain this discrepancy).

The foregoing arguments lead to the following interpretation of the data of Fig. 13. We assume that the measured damping consists of three independent terms: residual damping and the phonon and roton damping:

$$1/mK = A(\omega) + BT^4 + Ce^{-\Delta/T}, \qquad (4)$$

and according to the foregoing the coefficient A can vary from sample to sample, and can furthermore depend on the frequency. The phonon damping B, owing to the strong anisotropy of the speed of sound in crystalline He^4, can vary significantly with the sample orientation. As for the roton contribution C, which depends principally on the characteristics of the rotons of the liquid, it should apparently be approximately the same for all samples.

In accordance with this interpretation, Figure 13 shows the lines representing the contribution of the first two terms of Eq. (4). The roton contribution determined by this method is shown in Fig. 14. It is seen that all these
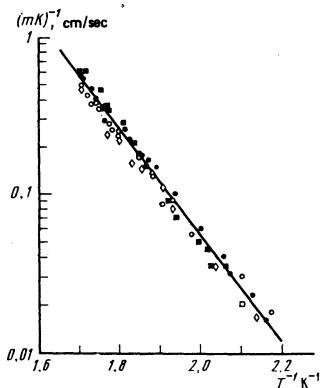
FIG. 14. Roton contribution to damping of crystallization waves. The notation is the same as in Fig. 13. The straight line corresponds to $\Delta = 7.8$ K.

data can be fitted in practice to the single relation $\exp(-\Delta/T)$. This is in essence the strongest argument favoring the proposed interpretation. The obtained value $\Delta = 7.8$ K is somewhat higher than that obtained by neutron diffraction (7.0–7.2 K).[10] This difference, however, may be only illusory, since the coefficient C can have a certain power-law temperature dependence, as have most quantities determined by the roton spectrum (heat capacity, normal density, and others).

Recently Castaing, Balibar, and Laroche,[11] in an investigation of the passage of sound through an interphase boundary in He^4 at 0.4–1 K, were able to measure a quantity equivalent to the growth rate K (Ref. 12) and obtained an exponential dependence with Δ ranging from 5 to 7.8 K for different samples. For a final answer to the question, a theory must be developed containing a quantitative calculation of the roton contribution to the damping, as well as possibly other effects.[11]

5. CONCLUSIONS

The existence of weakly damped helium-crystal surface oscillations due to periodic melting and crystallization means that quantum effects play a decisive role in helium crystallization at low temperatures. It can thus be states that a theory based on the notation of quantum-mechanical localization of surface defects[1] describes on the whole correctly the observed phenomena. On the other hand, the existence, at low temperatures, of atomically smooth surfaces corresponding to symmetry-preferred crystal faces makes it possible to refine the hypotheses advanced in Ref. 1. Namely, the free energy β of the delocalized steps on the singular surfaces (and only on them) turns out to be positive. The value of β can be determined in principle by measuring the equilibrium dimension l of the mirror (for a strictly horizontal mirror we can use the formula $\beta = \tilde{\alpha} a_0 l/2R$, where a_0 is the height of the step and R is the radius of curvature of the meniscus near the edge of the mirror). Thus, it follows from Fig. 5(b) that for the (0001) plane we have in order of magnitude $\beta \sim 5 \times 10^{-9}$ erg/cm (at $a_0 \approx 3 \times 10^{-8}$ cm); we note that this value is lower by one order than that obtained by Balibar and Castaing[8] from other considerations.

When the temperature is raised, the quantum effects assume as a rule a smaller role. It is of interest to estimate the temperature range in which the quantum effects in the crystallization of helium are significant. To this end we use the following simple arguments. We note that the quantum effects cannot be neglected at any rate if, at a given temperature, there exists a wavelength region where the crystallization waves are weakly damped. The temperature T_0 above which the damping is large for all wavelengths down to atomic can be estimated by extrapolating the data of Fig. 14, using relation (3). Such an estimate yields $T_0 = 1.5$ K. In other words, everywhere, all the way to the transition to the bcc phase (and possibly even higher), the processes that take place on the helium-crystal surface have essentially a quantum character. This means, in particular, that a successive examination of the phase

transition from an atomically smooth to an atomically rough surface,[12] which manifests itself in the vanishing of the mirror, cannot be carried out in purely classical terms in the case of helium.

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Addendum (12 September 1980). We have recently learned of work by Landau *et al.*[14] in which it is indicated that flat sections are present in equilibrium He⁴ crystals below 1 K, and which reports also the results of measurements of $\bar{\alpha}$ for the rounded sections ($\bar{\alpha} = 0.1$–0.2 erg/cm² for different samples, and is independent of temperature in the range 0.4–1.45 K). These results, as seen from the text, are in full agreement with ours.

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[1] We have no coherent explanation of this fact at present.
[2] The reflectivity of the capacitor surface under grazing illumination changes abruptly immediately prior to formation of visible seeds. This is due, in all probability, to the formation of a large number of minute (1–10 μm) crystallites in regions with maximum field intensity.
[3] We note that in this case, too, all the seeds have as a rule the same orientation, which differs in general from the orientation of the seeds prior to application of the electric field (see footnote 1).

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Anharmonicity of local vibrations of Be in Cu–Be alloy

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The local-vibration (LV) spectra in Cu–Be alloys with Be impurity density from 0.5 to 9.5% are investigated in the 100–515 K temperature range by the methods of inelastic incoherent scattering of slow neutrons. The width of the spectral density of the LV is determined by the temperature and concentration broadenings. The weak temperature dependence of the LV frequency is due to the mutual cancellation of the volume expansion of the lattice (i.e., of the anharmonicity of the lattice vibrations) and the anharmonicity of the LV. It is shown that the principal process that determines the temperature broadening and the LV shifts is the third-order anharmonicity, namely the decay of the LV into two phonons of the main spectrum.

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1. INTRODUCTION

The appearance of anharmonicity of local vibrations (LV) of a light substitutional impurity is a little-investigated question even though it is just for the LV that the observation of the real and imaginary parts of the frequency shift is greatly facilitated because the LV are located in a spectral region forbidden to the main spectrum. An exception is the case of ionic crystals, for which the shifts and broadening of the LV of various impurity atoms were investigated by optical methods.[1,2] It was observed in particular that in alkali-halide crystals with H⁻ and D⁻ impurities the width of the LV level of the hydrogen isotopes increases approximately tenfold when the sample temperature is raised from 100 to 400 K.[1] To our knowledge, no such investigations were made for metallic impurity systems to date.

The width of the LV in metallic systems is determined, besides by the anharmonicity, also by the interaction of the impurity atoms with one another and by the electron-phonon interaction. In a preceding study[3] the concentration dependence of the energy position $\varepsilon_{l,V}$ and of the width $\Delta\varepsilon_{l,V}$ of the LV level were investigated for a system