Measurement of the surface stiffness of ^{4}He with a small ^{3}He impurity

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The angular and temperature dependence of the surface stiffness of helium single crystals grown from a solution with a small ^{3}He impurity ($x_3 = 8 \times 10^{-5}$) has been measured in the temperature range 0.45–0.91 K. An upper bound has been determined for the energy of adsorption of ^{3}He on the crystal–liquid interface: $E_a \leqslant 4$ K. A small concentration of the impurity does not have a significant influence on the temperatures of the roughening transition on both basal and lateral faces. © *1995 American Institute of Physics.*

1. INTRODUCTION

The thermodynamics and kinetics of the growth of the ^{4}He crystal–liquid interface have been investigated actively during the past 15 years since the theoretical prediction[1] and experimental observation[2] of crystallization waves, and since the discovery of two-dimensional roughening transitions.[3,4] The bulk of the work was performed on pure helium single crystals, and the influences of a small ^{3}He impurity was studied experimentally in only a few investigations.[3,5,6] It was noted in Ref. 3 that the crystal in a solution containing 0.1% ^{3}He at a temperature of 0.4 K, unlike the crystal in pure helium, has large planar sections, i.e., faces. This change in shape was attributed to adsorption of the impurity on the surface. Assuming that the crystal in a solution has an equilibrium shape, Castaing, Greenberg, and Papoular[7] calculated the decrease in the surface energy α due to adsorption: $\Delta\alpha = -0.03$ erg/cm^2. Substituting the parameters reported in that paper into the equations derived in the lattice-gas approximation for adsorbed atoms [Eq. (11) in Ref. 7], we find the adsorption energy $E_a \approx 0.8$ K. In Ref. 5 the shape of crystals was studied during growth in solutions with ^{3}He concentrations equal to 8×10^{-7} to 1.5×10^{-4} at 1–1.3 K. On the basis of the change in the form of the growth shape, Carmi et al. concluded that the temperature of the first roughening transition drops from 1.28 K to 1.08 K and attributed this effect to a decrease in the surface energy due to the adsorption of ^{3}He on the liquid–crystal interface. Assuming that the adsorbed atoms form a nondegenerate two-dimensional gas, they obtained the value $E_a = 10$ K. No dependence of the transition temperature on the impurity concentration was discovered. The influence of the impurity on the surface stiffness was investigated by the crystallization-wave method in Ref. 6 at lower temperatures in the 0.02–0.05 K range and ^{3}He concentrations equal to 4.5×10^{-9} to 47×10^{-9}. The concentration dependence of the stiffness gave the following value of the adsorption energy for the adsorbed atoms in the two-dimensional degenerate-gas approximation: $E_a = 3.4$ K.

The adsorption of ^{3}He on a crystal of ^{4}He was treated theoretically by Treiner.[8] According to his calculations, a ^{3}He atom near the crystal surface has a bound state with an energy of 2.9 K.

As is seen from the foregoing material, at the present time there is a spread of values of the adsorption energy covering an order of magnitude. From the methodological standpoint, the change in the surface energy should be determined under equilibrium conditions, for which the chemical potential of the adsorbed atoms is equal to the well known chemical potential of the impurity atoms in the bulk. Only in this case are the equations used to treat the results in Refs. 3, 5, and 6 applicable. The question of whether this condition was satisfied during the growth of the crystal in Ref. 5 and during the motion of the crystallization waves (Ref. 6) remains open. In addition, as follows from the theoretical evaluations in Ref. 9 and the experiment in Ref. 6, even such a small quantity of impurities can significantly alter the growth kinetics of a surface and, therefore, the shape of the crystal during growth due to the additional dissipation accompanying diffusion of the impurities. This casts some doubt on the correctness of the determination of the roughening temperature from the growth shape[5] and, therefore, on the magnitude of the change in the surface stiffness found from the theory of phase transitions.[10]

In the present work we measured the temperature dependence of the surface stiffness of a crystal grown from a solution with a small ^{3}He impurity under quasisteady conditions in order to determine the energy of adsorption of ^{3}He atoms on atomically rough crystal surfaces.

2. EXPERIMENTAL

Helium crystals with an impurity concentration $x_3 = 8 \times 10^{-5}$ were grown in an optical container placed in a ^{3}He bath. The following technique was employed to grow high-quality crystals which make minimal contact with the inner surface of the container. The point of a tungsten needle (see Fig. 1), to which a high voltage was applied to create additional pressure near it, was placed at the center of the container. Then the pressure in the container was increased until the solidification point was attained. Owing to the electrostatic pressure, the original seed formed at the tip of the needle. The subsequent growth of the crystal to the necessary size took place almost freely. At the conclusion of the growth process, the crystal remained suspended on the needle without touching the walls of the container, since at temperatures below the second roughening transition the rate of growth of the faces is very small. For this reason, the range of tempera-
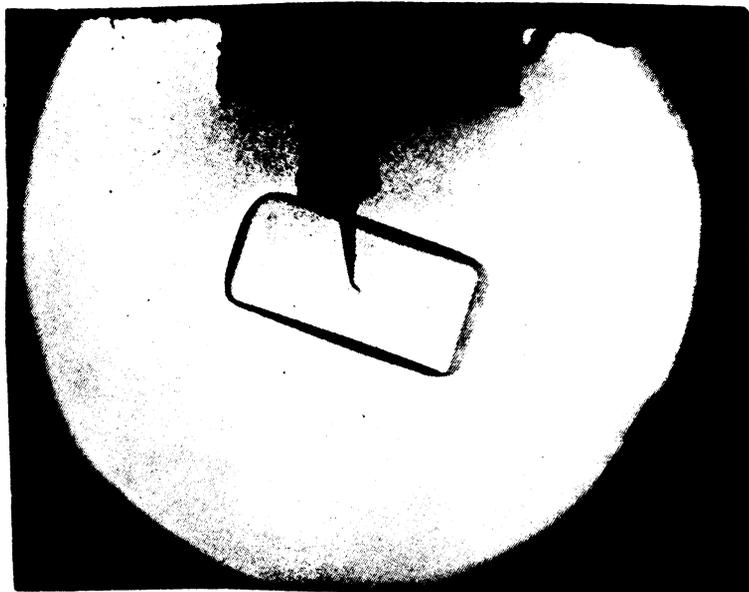
FIG. 1. Helium single crystal at 0.562 K. The curvature of the top surface is considerably smaller than the curvature at equivalent points on the lower surface—a manifestation of the hydrostatic pressure gradient.

tures investigated on the freely suspended crystal was boarded above by the roughening transition on a lateral face: $T = 0.45–0.9$ K. The container design and the technique for growing crystals were described in detail in Ref. 11.

We note that the growth of helium crystals in the presence of small impurity concentrations differs from the growth of pure crystals. For example, in our experiments we were unable to obtain a single crystal in the case in which it began to form on the wall: a nodule of crystals or, at best, a bicrystal grew. The technique described for growing crystals on the point of a needle with minimal deformation during growth, nevertheless, produced several crystals in about half the cases. The growth shape of the single crystals with impurities differed appreciably from the form for pure crystals.

The time for establishing the equilibrium shape of the atomically rough surfaces of the crystal over the entire temperature range was only a few minutes. At high temperatures in the 1.1–1.4 K range the rate of growth of the rough sections determined from the time for the establishment of the equilibrium shape was close to the growth rate of a pure helium crystal. At low temperatures, at which crystallization waves were observed in pure helium, the impurity suppressed this phenomenon. This makes it possible to evaluate the upper bound for the kinetic growth rate, $K < 100$ s/m.

We attempted to grow a crystal from a solution with a ^{3}He concentration equal to 2×10^{-4}. The growth of the crystal at this concentration exhibited the same features that were noted above. Unfortunately, after 20 attempts we were unable to grow a crystal of suitable orientation and to perform measurements of its shape.

The surface stiffness was determined from the shape of the crystal after it ceased to grow and reached an equilibrium state. The equation of the equilibrium shape of a surface with consideration of the hydrostatic pressure gradient has the form[12]

$$\rho_l g(z_0 - z) = \frac{\rho_l}{\rho_s - \rho_l} \left(\frac{\tilde{\alpha}_1}{R_1} + \frac{\tilde{\alpha}_2}{R_2} \right), \tag{1}$$

where $\rho_{l,s}$ are the densities of liquid and solid helium, g is the gravitational acceleration, z is the coordinate in the vertical direction, z_0 is the height at which the planar boundary of the crystal would be in equilibrium with the liquid, and $\tilde{\alpha}_{1,2}$ and $R_{1,2}$ are the surface stiffnesses and radii of curvature in the directions of principal curvature of the surface. A crystal oriented with a lateral face parallel to the line of sight of the camera with a deviation of $3.4°$ was selected for treatment. In this orientation the cylindrical surface adjoining the basal and lateral faces is observed along the generatrix, the radius of curvature of the profile of the crystal coincides with the principal radius of curvature R_1 in the plane in which the normals to the lateral and basal faces lie, and the second principal curvature is close to zero. It can be shown that the second principal curvature decreases exponentially with increasing distance L from the apex of the crystal: $1/R_2 \approx 1/R_1 \exp(-\text{const} \cdot L/R_1)$, and const~ 1 (a numerical calculation for a cubic crystal gives const≈ 1.6). The correction was largest for the upper left-hand edge of the crystal (see Fig. 1) and did not exceed 12% in our experiments. The image of the crystal was fed into a computer, and after median filtration it was treated by a Roberts filter to isolate the boundary of the crystal. The orientation of the boundary, i.e., the angle θ relative to the C_6 axis of the crystal, and curvature of the profile were determined by numerical differentiation with averaging over a $4°$ angle. Such a method is suitable for determining the curvature of the profile for sections not directly adjacent to the faces of the crystal. A check revealed that this algorithm gives correct values of the curvature for the orientations of a surface at an angle of at least $10°$ to the faces.

In relation (1) the parameter z_0 is still unknown, and we shall determine it by the method previously developed by Parshin et al.[13] This method takes advantage of the fact that sections of a surface with the same crystallographic orientation on different edges of the crystal have the same value for the surface stiffness, but are located at different heights with different hydrostatic pressures and consequently have differ-

ent curvatures (see Fig. 1). Knowing the coordinate z at these points and assuming that the values of $\tilde{\alpha}$ are identical, we obtain the value of z_0 from relation (1). To verify the accuracy of the method, the value of z_0 was determined for the surface orientations $\theta = 20-70°$ with $4°$ spacing, and its mean value and standard deviation were calculated.

The surface stiffness was calculated using Eq. (1). The total error was determined from the spread of the values of $\tilde{\alpha}$ with consideration of the standard deviation of z_0. The results of the treatment of the profile of the crystal whose photograph is shown in Fig. 1 are presented in Fig. 2.

As follows from theory[14] and experiment,[15] the heat fluxes in liquid helium cause redistribution of the impurities in the bulk of the container. The concentration gradient is related to the temperature gradient by the expression (see Ref. 15)

$$(k_B T/m_3)\nabla c_3 = -\sigma_0 \nabla T, \qquad (2)$$

where k_B is Boltzmann's constant, m_3 is the mass of the ^{3}He atom, c_3 is the mass concentration, $c_3 \cong x_3 m_3/m_4$ (m_4 is the mass of the ^{4}He atom), and σ_0 is the entropy of a unit of mass of pure ^{4}He. The temperature gradient is related to the heat flux q by the usual formula

$$q = \kappa_m \nabla T, \qquad (3)$$

where κ_m is the effective thermal conductivity. We evaluate the concentration nonuniformity caused by the parasitic supply of heat at the minimum temperature of the experiment, 0.45 K, at which the influence of such nonuniformity on the adsorption is greatest. The total supply of heat evaluated from the cooling efficiency was less than 50 μW, which gives a heat flux $q \leqslant 600$ erg/cm^2·s. The entropy of helium[16] is equal to 1.56×10^{-4}J/g· K. We determine the lower bound of the effective thermal conductivity from the data in Ref. 17 by means of linear extrapolation toward lower concentrations, $\kappa_m \geqslant 2 \times 10^6$ erg/cm· K. Substituting the values of the parameters into (2) and (3), we find that when the dimensions of the crystal equal about 1 cm, the concentration difference does not exceed $10^{-5}\%$, which is considerably less than the mean concentration of $8 \times 10^{-3}\%$, i.e., the nonuniformity of the concentration is small.

3. ANGULAR AND TEMPERATURE DEPENDENCE OF THE SURFACE STIFFNESS

As is seen from Fig. 2, the angular dependence of the surface stiffness is in satisfactory agreement with the results of the measurements of this parameter by the crystallization-wave method performed in Ref. 18 and 19 on pure helium single crystals. A broad minimum is observed near the orientation with $\theta = 35°$ in the impure crystal, as well as in the pure crystal. This orientation was selected for constructing the temperature dependence of the stiffness, since at this value of θ the error in the determination of $\delta\theta$ makes a small contribution to the error in the calculation of $\tilde{\alpha}$. In addition, small variations in the stiffness are more noticeable at small values of $\tilde{\alpha}$. Figure 3 presents the temperature dependence of the stiffness of a surface with the orientation indicated for the crystal shown in Fig. 1. It is seen that within the range of
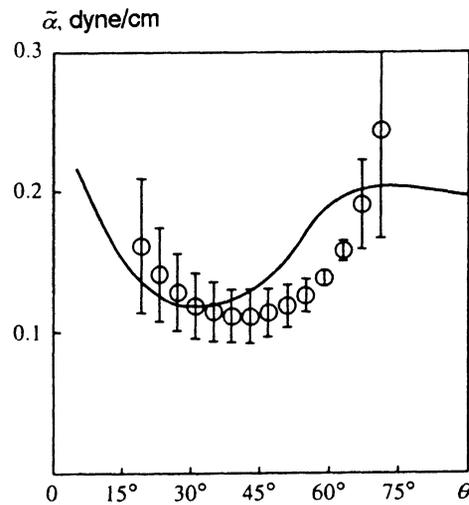

FIG. 2. Angular dependence of the surface stiffness of the crystal shown in Fig. 1. Solid curve—angular dependence of the stiffness in a pure ^{4}He crystal from Ref. 19.

accuracy of the experiment, there is no temperature dependence of the stiffness above 0.54 K and that its value is close to the value for pure helium.

4. DISCUSSION OF RESULTS

The variation of the surface energy α is related, according to the Gibbs equation, to the surface concentration n_s by the expression

$$\alpha - \alpha_0 = -T n_s. \qquad (4)$$

The surface concentration of the impurity under equilibrium conditions is determined by equating the chemical potentials
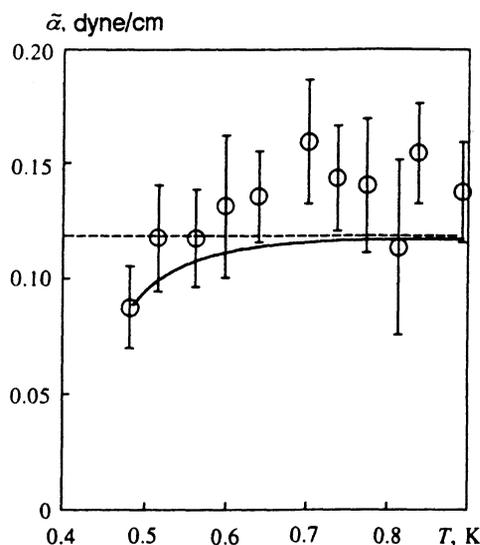

FIG. 3. Temperature dependence of the stiffness for a surface at a 35° angle to the C_6 axis. Dashed line—value of the stiffness in pure helium. Solid line—results of a calculation of the temperature dependence of the stiffness using Eq. (5) with the value $E_a = 3.8$ K.

of the ^{3}He atoms on the surface and in the interior. If the adsorbed layer forms a lattice gas, for the concentration n_s we obtain the expression[20]

$$n_s = N_s \left[1 + \exp\left(-\frac{E_a}{T} \right) \middle/ \left(\frac{x_3}{2} \frac{N_A}{V_m} \left(\frac{2\pi\hbar^2}{m_3^* T} \right)^{3/2} \right) \right]^{-1},$$
(5)

where x_3 is the volume density of the impurity, N_s is the number of adsorption sites on the surface, $N_s \approx (N_A/V_m)^{2/3}$, N_A is Avogadro's number, V_m is the molar volume of the liquid, m_3^* is the effective mass of the ^{3}He atom, and $m_3^* \approx 3m_3$. A similar expression was used in Ref. 7. In the limit of small concentrations, for which relation (4) holds, the concentration varies according to an exponential law:

$$n_s = N_s \exp\left(\frac{E_a}{T} \right) \frac{x_3}{2} \frac{N_A}{V_m} \left(\frac{2\pi\hbar^2}{m_3^* T} \right)^{3/2}.$$
(6)

If the ^{3}He atoms form a two-dimensional gas on the surface, their chemical potential includes an addition due to the kinetic energy (the expressions used in Refs. 5 and 6), and, assuming that the gas is noninteracting, in the limit of small concentration we obtain the relation

$$n_s = x_3 \frac{N_A}{V_m} \left(\frac{2\pi\hbar^2}{m_3^* T} \right)^{1/2} \exp\left(\frac{E_a}{T} \right).$$
(7)

Expressions (6) and (7) have different pre-exponential factors, which cause a numerical difference between the values of the adsorption energy amounting to $\Delta E \approx T^* \ln T^*$, where T^* is the measurement temperature, when the data are treated with these equations; at $T^* \approx 0.4$ K the difference has a value approximately equal to 0.4 K.

We note that the equations presented describe the variation of the surface energy, rather than the stiffness measured in the experiment. The stiffness is related to the energy by the expression

$$\tilde{\alpha}_i = \alpha + \partial^2 \alpha / \partial \phi_i^2,$$
(8)

where ϕ_i denotes the angles in the planes of the principal cross sections. On surfaces with large Miller indices, where the concentration of steps is high and the anisotropy of the stiffness is small (the minimum on the curve in Fig. 2), adsorption of the impurity does not give rise to additional strong anisotropy of $\tilde{\alpha}$. Then the variation of the stiffness is proportional to the variation of the surface energy, and Eqs. (4)–(7) are suitable for determining the adsorption energy from the temperature dependence of the surface stiffness.

Approximation of the temperature dependence shown in Fig. 3 by Eqs. (5)–(6) gives an approximately identical upper bound for the adsorption energy. For a lattice gas $E_a \leqslant 3.4$ K, and for a two-dimensional gas we obtain $E_a \leqslant 4$ K. Figure 3 presents the results of the calculation using Eq. (6) for $E_a = 3.8$ K. This value does not contradict Treiner's theoretical estimate[8] or the value obtained from Ref. 7 and is consistent with the value determined in Ref. 6. The value of the adsorption energy $E_a = 10$ K in Ref. 5 contradicts the experimental results.

Let us discuss the method for determining the adsorption energy in Refs. 3 and 7. Castaing et al.[7] calculated the decrease in the surface energy due to adsorption, assuming that the crystal grown for a 0.1% solution[3] has an equilibrium shape. At low temperatures the rates of growth of the faces and the rough sections differ strongly. This causes the round sections to shrink sharply even when the inflow of helium into the container is insignificant. Special measures, for example, installation of a bellows valve,[13] must be taken to obtain the true equilibrium shape. Since such measures were not taken in Ref. 3, the question of the equilibrium state of the shape remains open, casting some doubt on the correctness of the value of the adsorption energy obtained.

Wang and Agnolet obtained the value $E_a = 3.4$ K from the concentration dependence of $\tilde{\alpha}$ (see Fig. 2 in Ref. 6). We note that the results of the theoretical calculation presented in that figure are more likely at variance than in agreement with the experimental data. This casts some doubt on the correctness of the value obtained. Unfortunately, Wang and Agnolet[6] did not indicate the temperature at which they performed these measurements and did not present the temperature dependence of the stiffness. For an adsorption energy $E_a = 3.4$ K and an impurity concentration $\approx 50 \times 10^{-9}$, an increase in stiffness should have been observed at ≈ 0.2 K due to desorption of the impurity from the surface, which could have been used to verify the value presented.

It is seen from Fig. 3 that the contribution of impurities to the surface energy is negligibly small at temperatures above the second and, even more so, the first roughening transition. Thus, a small ^{3}He impurity does not significantly alter the surface energy at the temperatures of the first ($T_{R1} \approx 1.3$ K) and second ($T_{R2} \approx 0.9$ K) roughening transitions, and, therefore, according to the theory in Ref. 10, the temperatures of the roughening transitions should not vary significantly.

This conclusion was tested experimentally by measuring the temperatures of the roughening transitions, which were identified on the basis of the presence of a planar section under equilibrium conditions, as was previously done in Ref. 4. Such an approach differs qualitatively from the method previously used in Ref. 5 to determine the phase transition point from the growth shape.

The crystal grown on the point of a needle melted a little before slipping off the needle and dropping to the bottom of the container. After several attempts, we were able to orient the crystal so that the required face would be horizontal and parallel to the line of sight. Then the temperature was raised slowly, at a rate no greater than 2 mK/s. The shape of the crystal was photographed during the warming process. The profile of the crystal was then treated on a computer using the code previously described, and the presence of a face was identified on the basis of the existence of an extended section with a zero curvature. This method did not make it possible to determine the presence of a face on a crystal measuring about 4 mm, if the face measured less than 0.2 mm. In addition, pure helium[4] exhibited hysteresis phenomena, which may be due to mechanical strains appearing in the crystal as a result of thermal expansion upon warming. All this taken together made it possible to restrict the temperature of the

first roughening transition to the 1.18–1.28 K range. This value coincides within the range of error with the data obtained in pure helium.[4] Thus there is no basis to assert that a small ^{3}He impurity significantly lowers the transition temperature.

Similar measurements were performed for a lateral face, for which there are no data on the transition temperature in a solution. Using the procedure described, we obtained the range $0.87 \leq T_{R2} \leq 0.91$ K, which is also consistent with the value in pure helium. Another method was also used to measure the transition temperature. As was previously noted, the single crystal remained on the needle owing to the slow rate of growth of faces at such degrees of supersaturation. As the temperature increased, the size of the lateral faces decreased, and when the transition temperature was achieved, the entire lateral surface became atomically rough with a high rate of growth. This resulted in "spreading" of the crystal along the basal planes, which was clearly observed. This technique made it possible to reduce the hysteresis in the data and to improve the accuracy of the determination of T_{R2}: $0.892 \leq T_{R2} \leq 0.905$ K. We stress the qualitative difference between the "spreading-out" method and the method used in Ref. 5 to determine the roughening transition from the growth shape. In fact, in our case the crystal began to spread out (i.e., to melt) above the roughening transition after the lateral face disappeared, while in Ref. 5 the crystal grew below the roughening transition. Our method fixed the moment when the face vanished, since up to that moment the crystal was immobile and existed under quasistationary conditions, in contrast to the situation with a growing crystal described in Ref. 5.

Thus, direct measurements of the surface stiffness give an upper bound for the energy of adsorption of ^{3}He on the crystal–liquid interface: $E_a \leq 4$ K. The small concentration of the impurity does not significantly influence the temperatures of the roughening transitions on the basal and lateral faces.

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