

^3He Impurity Effects on the Growth Kinetics of ^4He Crystals

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We report the growth kinetics of the ^4He crystals with a small amount of ^3He impurities around 0.8 K. The growth resistance was measured using the response of the charged interface with respect to an externally applied voltage. In 5 ppm and 10 ppm ^3He mixtures, it is found that (1) the relaxation process can be expressed as an exponential behavior, (2) the growth resistance becomes larger compared to pure ^4He and does not have a strong ^3He concentration dependence, and (3) the temperature dependence of the growth resistance is much the same as pure ^4He . We discuss several possible explanations of the present experiment.

1. INTRODUCTION

From early visual observations¹⁻³ it is known that adding a small amount of ^3He impurities drastically affects the shape of ^4He crystals. Carmi *et al.*³ reported that the *c*-facet roughening transition temperature T_R is subjected to a 20% reduction when even about 1 ppm ^3He is added. They related the lowering of T_R to the lowering of the surface stiffness as resulting from the adsorption of ^3He at the solid-liquid interface. The binding energy of ^3He ε_S was estimated to be on the order of 10 K.

In 1984 Graf *et al.*⁴ first carried out a quantitative experiment on the interface of dilute ^3He mixtures. They measured the Kapitza resistance below 0.4 K, and found that the interface is mobile and atomically rough.

In 1992 Wang and Agnolet⁵ used the crystallization wave technique in the low temperature regime to measure the surface stiffness of ^4He crystals which contain ^3He impurities. Their values are considerably smaller than those previously reported by Keshishev and Andreeva.⁶ From the comparison they obtained $\varepsilon_S \approx 3.4$ K, which is distinctly smaller than that of

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Carmi *et al.* Rolley *et al.*⁷ recently performed a systematic study on the adsorption of ³He on ⁴He crystals. They also used the crystallization wave technique and found that the surface stiffness of a 130 ppb ³He mixture below 0.3 K deviates from ultrapure ⁴He (0.4 ppb ³He). The temperature dependence of the deviation is consistent with the existence of two-dimensional bound states for ³He atoms at the solid-liquid interface with a binding energy $\varepsilon_S = 4.3 \pm 0.3$ K and a ³He density saturating around the 0.4 monolayer.

Although Graf *et al.*⁴ revealed that the mobility of the interface is high, there are very few experiments on the ³He impurity effects on the growth resistance $(m_4K)^{-1}$, defined by

$$v = -(m_4K) \Delta\mu \quad (1)$$

where v is the interface growth velocity, and $\Delta\mu$ is the difference of the chemical potential per unit mass between the solid and the liquid. In pure ⁴He, the growth resistance of atomically rough surfaces is attributable primarily to the scatter at the solid-liquid interface of the elementary excitations in the liquid, i.e. phonons and rotons.⁸⁻¹⁰ In particular, in the high temperature regime, the roton contribution becomes more dominant, the temperature dependence of which is expressed as $(m_4K)^{-1} \propto \exp(-\Delta'/k_B T)$, where Δ' is in close agreement with the energy gap of rotons Δ .¹¹⁻¹³

Regarding dilute ³He mixtures, Bowley and Edwards⁹ in 1983 evaluated the ³He impurity effects on the basis of the idea that the reflection of ³He atoms in the liquid at the solid-liquid interface creates additional growth resistance,

$$(m_4K)^{-1}_{\text{He}} = \frac{n_3}{\rho_C} \left(\frac{8m_3^* k_B T}{\pi} \right)^{1/2} \quad (2)$$

where n_3 is the number density of ³He, m_3^* is the effective mass of ³He, and ρ_C is the density of the solid.

In 1993 Burmistrov and Dubovskii¹⁴ pointed out the importance of ³He mass flow in front of a moving solid-liquid interface. For a case in which the interface moves at a constant velocity, they developed the formula

$$(m_4K)^{-1}_{\text{He}} = \frac{(X_S - X_L)^4 \left(\frac{k_B T}{m_3^* X_L} \right)^2}{2D} \frac{L}{\Delta\mu} \quad (3)$$

where D is the mass diffusion coefficient of ^3He , X_S and X_L are the ^3He concentration in the solid and the liquid and L is the displacement of the interface.

From the damping of the crystallization waves Wang and Agnolet⁵ found that a very small amount of ^3He impurities (12 ppb ^3He) drastically increases the growth resistance (compared to 4.5 ppb ^3He). Although this technique is very useful, the measurement may be confined to the low temperature regime because the crystallization waves are strongly damped at higher temperatures ($T > 0.5$ K). In order to deduce the ^3He impurity effects in the high temperature regime we measured the growth resistance using the response of the charged interface with respect to electrostatic pressure. In this paper, we also discuss several possible explanations for the present experiment.

2. EXPERIMENTAL

The experimental technique has been reported in detail previously^{13, 15} so we provide only a short description of it here.

An experimental cell was assembled in a ^3He cryostat with optical access from the bottom, and worked as an interferometer. The change in crystal height was detected by a shift of the interference fringes. After growing the crystal, electron bubbles were introduced into the liquid by a field emission tip and pulled downwards to the solid-liquid interface by the externally applied field. These were trapped at the interface. In equilibrium, the electrostatic pressure is balanced by the hydrostatic pressure, so that the height of the charged interface is lower than that of the uncharged part of the interface. When changing the externally applied field, the position of the charged interface approaches a new equilibrium. In a case where the growth resistance $(m_4 K)^{-1}$ is constant with respect to $\Delta\mu$, i.e., the velocity of the interface is proportional to the difference of the chemical potential, the approach of the charged interface to the new equilibrium position shows an exponential behavior. Thus the relaxation time τ is simply related to the growth resistance,

$$\tau^{-1} = (m_4 K) g \frac{\Delta\rho}{\rho_C} \quad (4)$$

where $\Delta\rho = \rho_C - \rho_L$ is the difference in density between the solid and the liquid, g is the acceleration due to gravity.

Two different dilute ^3He mixtures, 5 ppm and 10 ppm ^3He , were prepared at room temperature. A single crystal was grown slowly at

around 0.8 K, and atomically rough surfaces, i.e., neither the c - nor a -axis being vertical, were chosen for measurement. The ratio of the ^3He concentration in the solid, X_S , to the liquid, X_L , can be expressed as

$$\frac{X_S}{X_L} = 2 \left(\frac{1.696}{T} \right)^{3/2} \exp \left(- \frac{1.36}{T} \right) \quad (5)$$

at low concentrations and temperatures.¹⁶ The parameters in Eq. (5) are chosen at $T_0 = 0.61$ K (the endpoint of the azeotropic line), so that this may apply to the temperature range where the melting pressure does not have a strong temperature dependence. We estimate the ^3He concentration in the solid to be $X_S \approx 1.1X_L$ at 0.8 K.

3. RESULTS AND DISCUSSION

A typical relaxation process with respect to the change in the externally applied voltage is shown in Fig. 1. To improve the data we averaged 30 events and reached a resolution of the crystal height of about $0.1 \mu\text{m}$. This process can be well expressed as an exponential behavior in the range of the interface velocity from $v = 1.1 \times 10^{-3} \text{ cm sec}^{-1}$ to $2 \times 10^{-5} \text{ cm sec}^{-1}$, which means that the growth resistance does not show a nonlinear behavior with respect to $\Delta\mu$. In addition, no difference between the crystallization and the melting is observed. From Eq. (4) the growth resistance obtained is $93 \pm 9 \text{ cm sec}^{-1}$. In general, without respect to either ^3He concentration or temperature (between 0.7 K and 0.9 K), the relaxation process between the crystallization and the melting shows an exponential behavior and has the same relaxation time within experimental error.

Figure 2 shows the growth resistance of 10 ppm ^3He of several measurements as a function of temperature as well as the extrapolated lines of pure ^4He (which is not a purified but a commercial one) from Ref. 13. The two extrapolated lines are considered as the fastest and the slowest axes of pure ^4He . (Before measuring the mixtures, we checked the growth resistance of pure ^4He around 1 K and found that the data fall between these two lines.) The scatter of the growth resistance of different measurements at the same temperature is attributed primarily to the difference in crystal orientation. However, the growth resistance is about three times larger than that of pure ^4He , and the temperature dependence is nearly expressed by $(m_4 K)^{-1} \propto \exp(-\Delta/k_B T)$, which is much the same as pure ^4He .

Figure 3 shows the growth resistance at 0.83 K as a function of ^3He concentration. As stated, the scatter of the growth resistance is attributed

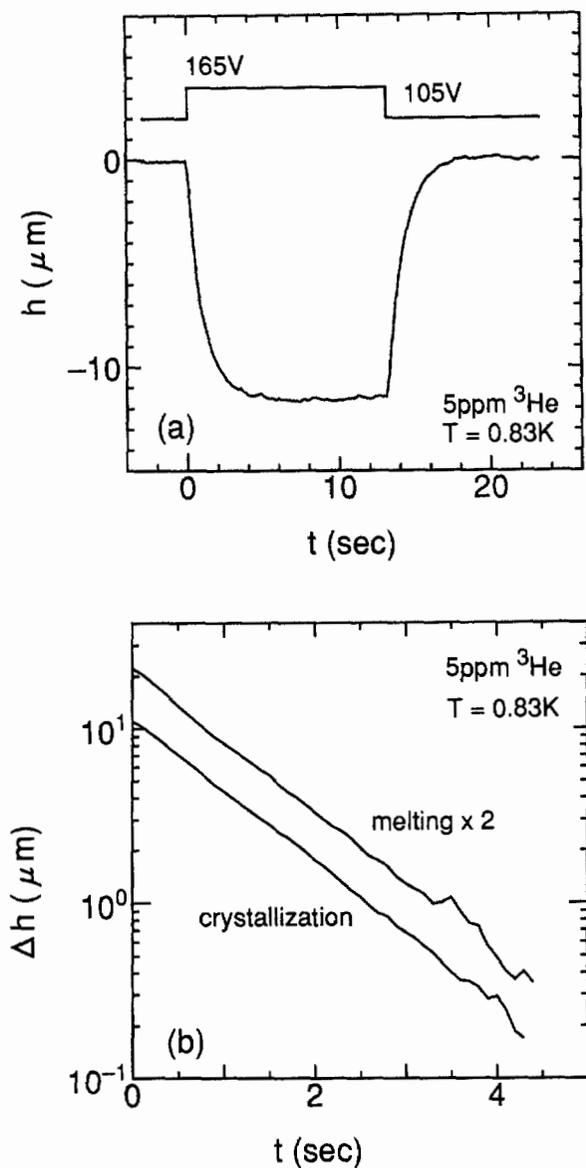


Fig. 1. (a) Typical relaxation process with respect to the change in applied voltage. By increasing the applied voltage from 105 to 165 V, the crystal melts by $11.5 \mu\text{m}$, and recrystallizes as the voltage is reduced to 105 V again. This sample contains 5 ppm ^3He . (b) Same relaxation process on a log scale. The melting curve is multiplied by 2 for clarity.

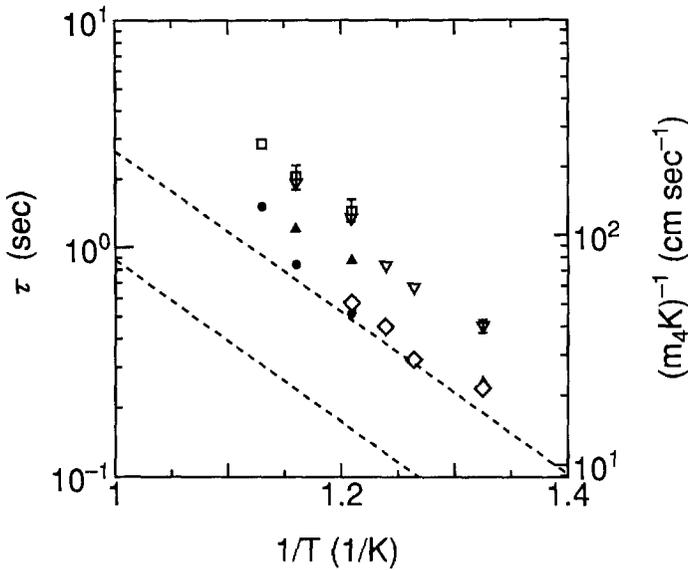


Fig. 2. Temperature dependence of the growth resistance of a 10 ppm ^3He mixture. Different symbols correspond to different crystals. Two dashed lines represent the extrapolated lines of pure ^4He with [0001] and [1010] orientations in Ref. 13.

to the crystal orientation, and the growth resistance is not drastically influenced by ^3He concentration.

The following points should be kept in mind from the present experiment: (1) The relaxation process of dilute ^3He mixtures can be expressed as an exponential behavior, i.e., no nonlinear effects are observed. (2) The growth resistance increases about three-fold over pure ^4He and does not have a strong ^3He concentration dependence. (3) The temperature dependence of the growth resistance is much the same as for pure ^4He .

There are several possibilities to explain these properties:

(a) The first one is the contribution of the reflection of ^3He quasi-particles at the interface, which is evaluated by Eq. (2). Using the typical values of this experiment, $T = 0.8\text{ K}$, $m_3^* = 3m_3$ and $n_3 = 2.7 \times 10^{17}\text{ cm}^{-3}$ (10 ppm ^3He), the contribution of ^3He to the growth resistance, $(m_4K)^{-1}_{^3\text{He}}$ is estimated to be 0.1 cm sec^{-1} . Since the growth resistance of pure ^4He at 0.8 K is about 20 cm sec^{-1} , this correction is too small to explain the enhancement of the growth resistance of dilute ^3He mixtures.

(b) The second possibility is the contribution of the ^3He mass flow in front of a moving interface. Although Eq. (3) cannot be applied directly

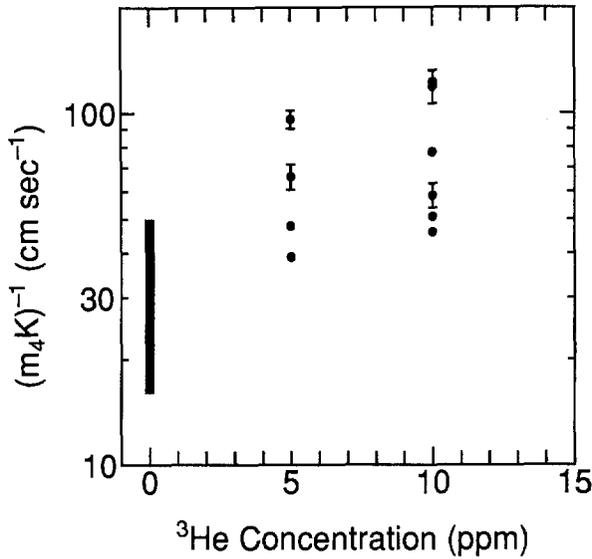


Fig. 3. Concentration dependence of the growth resistance at 0.83 K. The line at 0 ppm ^3He indicates the extrapolated values of pure ^4He in Ref. 13.

to the present experimental conditions, it would give a rough estimate. From Eq. (5) the ^3He concentration difference is estimated to be $X_S - X_L \approx 0.1X_L$. Concerning the ^3He mass diffusion coefficient, we use the value $D \approx 4 \times 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$,^{17, 18} which was measured around 1.2 K. (The mass diffusion coefficient is considered to be inversely proportional to the number of rotons, so that we may expect the value at 0.8 K is rather large compared to the adopted value.) By substituting into Eq. (3) the typical values, $m_3^* = 3m_3$, $\Delta\mu/L = 980 \text{ cm sec}^{-2}$ and $X_L = 10^{-5}$ (10 ppm ^3He), respectively, we obtain $(m_4 K)^{-1}_{^3\text{He}} \approx 0.2 \text{ cm sec}^{-1}$, where the growth resistance of pure ^4He at 0.8 K $(m_4 K)^{-1} \approx 20 \text{ cm sec}^{-1}$. The estimated value is again too small to explain the present experiment. In this calculation, the estimated value is so sensitive to the ^3He concentration difference, that this may have large ambiguity.

However, the theory of Burmistrov and Dubovskii suggests that the growth resistance depends strongly on ^3He concentration, and that the relaxation process shows a nonlinear behavior with respect to the interface velocity because $\Delta\mu/L$ is not constant during the relaxation. But these suggestions are contradictory to our results, the present experiment therefore does not seem to support their theory.

(c) The third possibility is the effect of the adsorbed ^3He atoms at the interface. It is found that the temperature dependence of the growth resistance of dilute ^3He mixtures is closely similar to that of pure ^4He , which may suggest that even in the case of the mixtures the main contribution to the growth resistance is the roton scattering at the interface. The enhancement of the growth resistance may be explained by the change in the scattering potential of rotons associated with the addition of a small amount of ^3He impurities. This means that ^3He atoms are adsorbed at the interface.

The condition of the surface adsorption is that the chemical potential of ^3He in the bulk, μ_3 , becomes larger than the binding energy ε_S ($\mu_3 > -|\varepsilon_S|$). Here, the chemical potential in the liquid can be calculated by $\mu_3 = k_B T \ln\{n_3/2 (2\pi\hbar^2/m_3^*k_B T)^{3/2}\}$. By substituting the conditions of the present experiment, $T = 0.8$ K, $n_3 = 2.7 \times 10^{17}$ cm $^{-3}$ (10 ppm ^3He), we obtain $\mu_3 = -6.0$ K.

Rolley *et al.*⁷ recently made a systematic study on the adsorption of ^3He below 0.4 K, and found that the binding energy ε_S is 4.3 ± 0.3 K and the saturated ^3He density is about 0.4 monolayer. If we adopt their results, few ^3He atoms are adsorbed at the interface (about 0.05 monolayer). Therefore, this idea is not promising. However, there might be a possibility that a very small amount of adsorbed ^3He affects the roton scattering at the interface.

(d) As discussed in detail by Balibar *et al.*,¹⁹ the measured value of the growth resistance differs from the isothermal growth resistance $(m_4 K_T)^{-1}$. The effective growth resistance $(m_4 K_{\text{eff}})^{-1}$ increases due to the finite thermal conductivity, which is given by

$$(m_4 K_{\text{eff}})^{-1} = (m_4 K_T)^{-1} + \left(\frac{\rho_C R_K}{T} \right) \left(\frac{J_E}{J} + \frac{b}{c} \right)^2 \quad (6)$$

where $J = \rho_C v$ and J_E/T are the currents of mass and entropy crossing the interface, and R_K is the Kapitza resistance. Here, we use the same notations for the coefficients b and c as used in Ref. 19.

In the high temperature experiment of pure ^4He by Bodensohn *et al.*¹³ the Kapitza resistance is small enough and the heat propagates very efficiently in the superfluid ^4He . Then, the heat flows mainly through the liquid, and the correction to $(m_4 K_T)^{-1}$ by the second term in Eq. (6) is not large compared to the scatter of the data. Their measured values of the growth resistance are considered to be the isothermal ones.

In the case of dilute ^3He mixtures, on the other hand, the behavior of the heat flow is completely different. In the liquid the effective thermal conductivity (including both the diffusive and the counterflow contributions)

decreases drastically by adding ^3He impurities. The effective conductivity in the liquid of 10 ppm ^3He mixture around 0.8 K is estimated to be $\sim 0.1 \text{ W cm}^{-1} \text{ K}^{-1}$,¹⁷ while the thermal conductivity in the crystal is $\sim 0.5 \text{ W cm}^{-1} \text{ K}^{-1}$.²⁰ (The thermal conductivity of the crystals which contain ^3He impurities is slightly suppressed. In the case of 10 ppm mixture, however, the impurity effect is negligible.) Thus the main channel of the heat flow seems to be the crystal rather than the superfluid ^3He - ^4He mixture.

To roughly estimate the correction due to heat flow, let us suppose that the heat current density in the liquid is neglected and the heat propagates efficiently in the crystal. In this case, Eq. (6) can be applied with $J_E/J = TS_L$, where S_L is the entropy of the liquid. Since b/c is small enough compared to J_E/J , we may neglect this term.

Graf *et al.*⁴ measured the Kapitza resistance of the interface of dilute ^3He mixtures. From their results, the Kapitza resistance of 10 ppm ^3He is considered to be comparable to that of pure ^4He . The Kapitza resistance is thus given by $R_K = (4/3)(\rho_L S_{\phi L} c_L \bar{\tau})^{-1}$, where c_L is the sound velocity in the liquid, $S_{\phi L}$ is the phonon contribution to the liquid entropy, and $\bar{\tau}$ is the mean phonon transmission coefficient. Therefore, from Eq. (6) we obtain

$$(m_4 K_{\text{eff}})^{-1} = (m_4 K_T)^{-1} + \frac{4}{3} \frac{\rho_c S_L^2 T}{\rho_L S_{\phi L} c_L \bar{\tau}} \quad (7)$$

Here, the sound velocity in the liquid is $c_L = 3.662 \times 10^4 \text{ cm sec}^{-1}$,²¹ the entropy of the liquid $\rho_L S_L = [2767T^3 + 7.505 \times 10^6 T^{1/2} (\Delta/k_B T + \frac{3}{2}) \exp(-\Delta/k_B T)] \text{ erg cm}^{-3} \text{ K}^{-1}$ with $\Delta = 7.21 \text{ K}$,²² $\rho_L S_{\phi L} = 2767T^3 \text{ erg cm}^{-3} \text{ K}^{-1}$ and the mean phonon transmission coefficient $\bar{\tau} \approx 0.8$ at 0.8 K.²³ One finds that the second term in Eq. (7) is 20 cm sec^{-1} at 0.8 K, where the growth resistance of pure ^4He is also about 20 cm sec^{-1} . Since the transmission coefficient $\bar{\tau}$ varies slowly with respect to temperature, the temperature dependence of the second term in Eq. (7) is dominated by the exponential behavior of the roton entropy in $\rho_L S_L$. Thus, the correction varies as $\exp(-\Delta/k_B T)$ just like the growth resistance of pure ^4He .

From the above estimate the effective growth resistance of dilute ^3He mixtures becomes about twice as large as the isothermal growth resistance of pure ^4He and has much the same temperature dependence as pure ^4He . Furthermore, the correction due to heat flow does not depend strongly on ^3He concentration. The observed properties of the growth resistance can thus be well explained by the effect of heat flow.

Finally, we comment on the current of ^3He crossing the interface, which contributes to the dissipation. In the above estimate, the currents of

^4He mass J and entropy J_E/T are considered with respect to the entropy production. In the case of mixture, there is an additional contribution, i.e. the current of ^3He which is driven by a difference in ^3He chemical potential. It is difficult to estimate this contribution to the growth resistance. However, in the present experimental conditions, this could be negligible since the entropy of ^3He per unit volume is adequately small compared to that of the liquid $\rho_L S_L$.

In summary, we found that a small amount of ^3He impurities has drastic effects on the growth kinetics of ^4He crystals around 0.8 K. In 5 ppm and 10 ppm ^3He mixture, the growth resistance increases to about three-fold that of pure ^4He . This enhancement may be attributable to the effects of heat flow, i.e. since the effective thermal conductivity of the superfluid ^3He - ^4He mixtures is poor, the observed growth resistance includes a large correction to the isothermal growth resistance.

This experiment was only exploratory and many questions remain. Wang and Agnolet⁵ observed a drastic increase in the growth resistance in the low temperature regime. The mechanism of their observed enhancement seems different from what we found. More systematic experiments, especially those over a wide temperature range, are needed.

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