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Positive Ion Induced Solidification of ^{4}He

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We have observed bulk solidification of ^{4}He induced by nucleation on positive alkali ions in pressurized superfluid helium. The ions are extracted into the liquid from alkali-doped solid He by a static electric field. The experiments prove the existence of charged particles in a solid structure composed of doped He that was recently shown to coexist with superfluid helium below the He solidification pressure. This supports our earlier suggestion that the Coulomb interaction of positive ions surrounded by a solid He shell (snowballs) and electrons trapped in spherical cavities (electron bubbles), together with surface tension, is responsible for the stability of that structure against melting. We have determined the density of charges in the sample by two independent methods.

^{4}He is a unique substance that becomes superfluid at low temperatures and that solidifies only under an external pressure in excess of 25 bar, at the absolute zero of temperature. Both features are manifestations of the quantum nature of condensed helium, due to the small He mass and the weak interatomic He-He interaction. Condensed ^{4}He is a model system for studying crystal growth, because of its low heat of fusion and the high speed at which heat and mass are transported, in contrast to any other substance. Therefore, many fundamental aspects of the formation of a solid from the liquid phase can be, and have indeed been studied in solid He in their purest form (for a review see, e.g., [1,2]). In the case of ^{4}He, uncontrolled nucleation usually sets on at rough surfaces. Controlled solidification is conventionally triggered by the attractive force exerted by strong electric field gradients near charged tips or thin wires [2]. This force locally compresses the polarizable liquid (electrostriction effect) slightly above the solidification pressure.

It has been known for a long time that positive alkali ions [3] in liquid He are surrounded, due to electrostriction, by a shell of solid He—a structure known as ''snowball'' [4]. Cole and Sluckin have argued [5] that the surface tension at the snowball boundary limits the snowball growth and that crystal nucleation from a solitary snowball is only possible at overpressures of several bar. In this Letter we present evidence that embedded atomic ions lead to the formation of macroscopic solid structures that coexist with superfluid He, slightly below its solidification pressure. We also show that a significant amount of Cs^+ and Rb^+ ions which are field extracted into superfluid He, induce the growth of macroscopic crystallites along the electric field lines.

Recently, we have observed a macroscopic solid structure that coexists with HeII below its solidification pressure [1]. This structure, which we have named ''iceberg'', appears during the melting of solid ^{4}He doped with alkali (Rb or Cs) atoms and clusters. The doped portion of the matrix remains solid under pressure and temperature conditions for which the pure matrix is completely molten. Because neutral alkali atoms and clusters repel He, we have argued in [1] that the He atoms in the iceberg are bound to positively charged ions, for which there had been, so far, no experimental evidence. The observations reported here support this interpretation.

A helium crystal of ≈ 200 cm^3 is grown in a copper pressure cell immersed in a liquid He bath kept at 1.5 K. Windows provide optical access to the cell from four sides and from the top. The second harmonic of a pulsed Nd:YAG laser ($\simeq$100 mJ) is focused from above onto an alkali-metal target at the bottom of the cell. The deposited heat locally melts the helium solid and the ablated material is distributed in a cylindrically-shaped liquid region. Typically a thousand laser pulses are required for the implantation. When the ablation laser is switched off, the helium resolidifies and the impurity particles become trapped in the solid. Details of the doping process are given in [6,7].

Two vertical square electrodes 4×4 cm^2 spaced by 10 mm are mounted above the ablation target in the pressure cell in a way similar to the one used in our recent study [8] of the Stark effect in matrix-isolated Cs atoms. One electrode is connected to a high voltage power supply and the other is grounded via a 100 kΩ resistor. Voltages up to 16 kV of either polarity could be applied to the capacitor. The temperature in the cell is measured with a germanium resistor, and the helium pressure is determined by a pressure gauge installed at the warm end of the line connecting the cell with a high pressure He storage bottle at room temperature. Video recordings of the interior of the cell are taken during the measurements from a direction parallel to the electrodes.

In the cell filled with superfluid helium, a static electric field of several kV/cm produces a dc leakage current of $\approx$100 nA, even in the absence of dopants. This current is due to field emission from the electrodes. It decreases with rising helium pressure and becomes lower than the detec-

tion limit of our system (1 nA) when the He in the cell is solidified. We assign this effect to the reduced mobility of electrons in the denser liquid [9] and, in particular, in the solid [10,11]. For a study of laser ablation we filled the lower part of the cell with solid He and the upper part with liquid He at 1.5 K at 26.9 bar (at the bcc-HeII melting line). The ablation target was located in the He solid (as in [1]), and the gap between the electrodes was filled with liquid He in order to collect the charge carriers produced by the ablation. On top of the dc current, laser ablation in the presence of an electric field produces current pulses as shown in Fig. 1(a). We inferred the number of charge carriers produced during the ablation by integrating the ac component of the current. Each of the laser pulses used for implantation [1], produces $\approx 10^{11}$ electron-ion pairs. A typical sample, prepared by shooting approximately 1000 laser pulses, may thus contain up to 10^{14} positive ions. The actual number may be lower due to partial recombination of the charge carriers during their diffusion through helium.

We have also observed a time-dependent current during the melting of the doped crystal exposed to an electric field [typical recording shown in Fig. 1(b)]. Helium is released from the cell in several steps via a needle valve at the room temperature end of the filling capillary. The melting proceeds from top to bottom in the cell. Current starts to flow when the liquid-solid interface drops below the upper edge

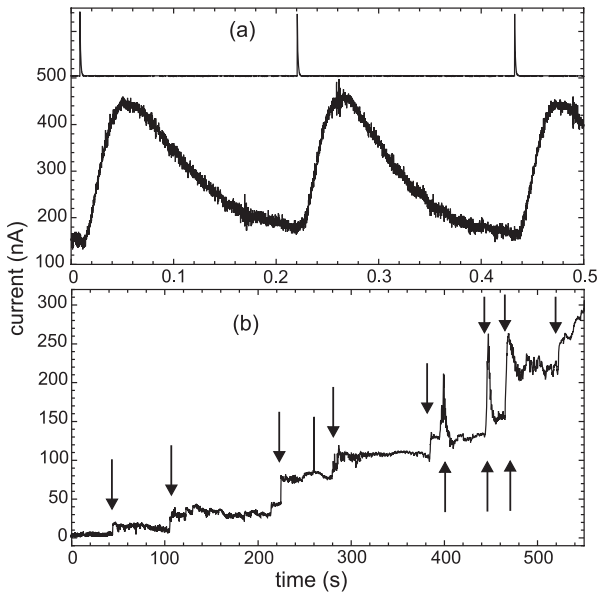

FIG. 1. Time dependence of the electric current measured during (a) laser ablation in a field of 5 kV/cm, and (b) melting of the doped crystal in a field of 12 kV/cm. The uppermost trace shows the laser pulses recorded with a photodiode. In (b), the ↓-arrows mark the moments at which pressurized He was partly released from the cell, and the ↑-arrows the spikes that were integrated for inferring the number of ions. After the last release only liquid helium remained in the cell. $T = 1.5$ K, $p = 26.9$ bar.

of the electrodes and increases as the interface moves further down. Each opening of the valve induces a partial melting of the crystal which is accompanied by a fast current increase. After closing the valve, the current stabilizes at a value that is probably due to field emission from the surface of the positive electrode in contact with liquid helium. The spikes in Fig. 1(b) appearing during each decrease of pressure originate from trapped charges in the crystal that are released during melting. The three spikes at 400, 445, and 470 s in Fig. 1(b) contain approximately 2.5×10^{13} electron-ion pairs. The total number of charged particles trapped in the crystal could eventually be higher, since some ions and electrons may diffuse out of the iceberg between consecutive valve openings.

The two methods described above give comparable results, so that we conclude that the number density N_i of positive ions trapped in the iceberg lies between 10^{14} and 10^{15} cm^{-3} (iceberg volume $\simeq 0.1$ cm^3 [1]). The density of alkali atoms trapped in the He crystal as individual atomic bubbles is about 10^8–10^9 cm^{-3} [6]. However, our spectroscopic study [1] has shown that the total density of neutral alkali atoms produced by the ablation is about 10^{16}–10^{17} cm^{-3}. Most of those atoms are aggregated into clusters, each containing about 10^6–10^7 atoms. The ions thus represent only $\approx 1\%$ of the mass of the ablated material, but their number density is significantly higher than that of neutral isolated atoms and clusters. Positive ions and electrons are therefore the most abundant impurities in the doped samples and their concentration is high enough to influence the macroscopic properties of solid He.

In contrast to positive alkali ions, which form snowballs, free electrons in condensed He form nanometer-sized cavities, so-called electron bubbles [12], as a consequence of the Pauli repulsion between the electron and the He atoms. Because of their large size, the diffusion velocity of electron bubbles and snowballs is very low, in particular, in solid He. Moreover, in order to recombine, an electron bubble would have to pass a potential barrier in order to penetrate into the snowball. This barrier strongly suppresses charge recombination.

We have speculated [1] that the Coulomb interaction between snowballs and electron bubbles in the sample leads to the formation of the iceberg structure. The radius R_S of a Cs^+ snowball in liquid helium at saturated vapor pressure is 8.4 Å [3], much smaller than the average distance ($d \simeq \sqrt[3]{N_i} \simeq 100$ nm) between snowballs in the iceberg. One expects a critical value ρ_c of the ratio $\rho = d/R_S$, below which a macroscopic conglomerate of snowballs and electron bubbles, bound by Coulomb forces and surface tension, is stable. To our knowledge this question has never been addressed in model calculations.

In another experiment we have observed an interesting phenomenon during the melting of a Rb-doped He crystal exposed to a static electric field (Fig. 2, left). In order to

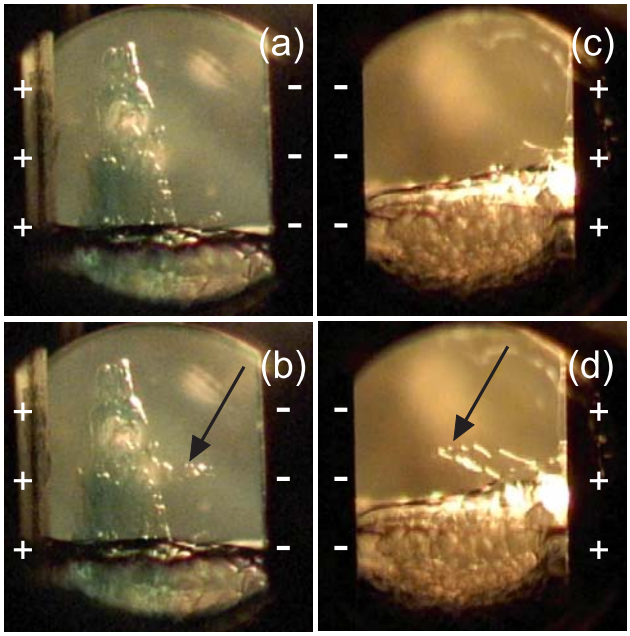

FIG. 2 (color online). Video frames of a doped helium crystal at $T = 1.5$ K and $p = 26.9$ bar in a static electric field: (a), (b) a crystal branch grows from the Rb-doped iceberg at constant pressure towards the negative electrode in a field of 12 kV/cm; (c), (d) a crystal branch grows from the positive electrode ($E = 10$ kV/cm) in Cs-doped helium as more helium is admitted into the cell. The field of view is limited on the left and right by the vertical plate electrodes spaced by 10 mm.

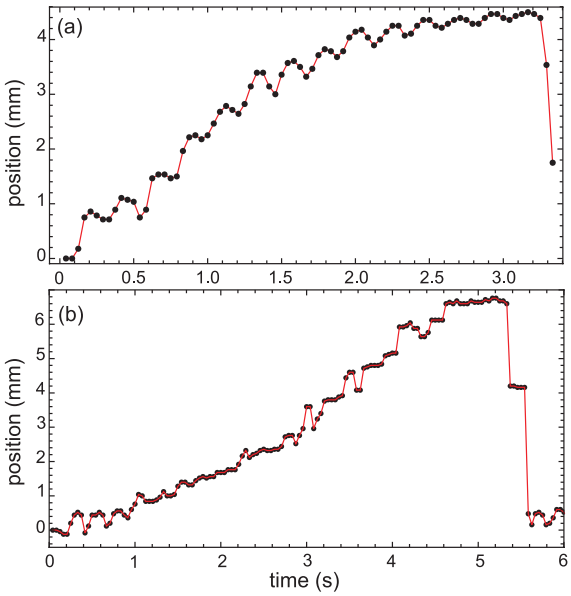

FIG. 3 (color online). Horizontal position of the tip of a crystal branch growing at $T = 1.5$ K and $p = 26.9$ bar. (a) branch growing from a Rb-doped iceberg in the cell disconnected from the reservoir at 12 kV/cm; (b) branch growing from the electrode in Cs-doped helium as more helium is admitted into the cell at 10 kV/cm.

study the evolution of the iceberg in the electric field, the release of helium from the cell was stopped at the moment when all undoped helium was molten so that only the iceberg remained solid. This situation is illustrated in Fig. 2(a). In general, a field of 12 kV/cm does not affect the iceberg structure. However, as can be seen in Fig. 2(b), a new horizontal structure may eventually grow out of the iceberg towards the *negatively* charged electrode. This crystal branch extends over several millimeters in a few seconds, after which it either melts (due to heat dissipated by flowing charges), or it breaks off and sticks laterally to the iceberg's main body, or it drifts to the *positive* electrode. This process may repeat several times, as long as the iceberg prevails and the electric field is applied. A polarity change of the electric field reverses the crystallite growth direction. In Fig. 3(a) we plot the position of the tip of one such branch as a function of time. Each point was inferred from a single frame of a video recording taken through a side window of the cryostat.

We have observed a similar growth process during laser ablation in a cell partially filled with solid He in absence of an iceberg structure. Branch growth in that case was triggered by admitting a small portion of helium into the cell via the needle valve. Under those conditions the branches start to grow from the surface of the positive electrode and reach a length of up to 1 cm, with their tips touching the negative electrode. The process is illustrated by the photographs in Figs. 2(c) and 2(d). The time-evolution of the length of such a branch in Cs-doped liquid He is shown in Fig. 3(b).

In Fig. 3(a) one can see that the relatively slow growth of the crystal is modulated with a frequency of ≈ 4 Hz. The same modulation can also be seen in the initial growth stage of Fig. 3(b). We believe that thermoacoustic oscillations, discussed, e.g., in [13] are at the origin of such oscillations in the capillary that connects the inner cell volume to room temperature He gas. A pressure gauge at the warm end indicates synchronous pressure modulations with an amplitude of 15 mbar that induce solidification-melting cycles around the solidification pressure.

In both growth mechanisms the direction of the field-induced growth coincides with the direction of positive ion drift. The speed of growth inferred from Figs. 3(a) and 3(b) lies in the range of 0.7–2.6 mm/s, which can be compared to the drift velocities of positive ions in pressurized condensed He. The mobilities $\mu(Cs^+)$ and $\mu(Rb^+)$, measured only in unpressurized HeII at $T = 1.4$ K [3], have comparable values that are 10% below $\mu(He^+)$. From the comprehensive mobility data of He^+ in liquid [9,14] and solid [10,11] He one finds that $\mu(He^+) = 7 \times 10^{-2}$ cm^2/V $\cdot$ s in liquid and 10^{-5} cm^2/V $\cdot$ s in solid He near the solidification point ($T = 1.5$ K). Assuming that alkali ions move at a 10% lower speed than He^+, their corresponding velocities in liquid and solid He (at 12 kV/cm) would be 760 cm/s and 0.1 cm/s, respectively. The growth rates measured here are significantly smaller than the estimated

mobilities in liquid He, but sufficiently close to the mobilities in solid He to suggest that they are largely due to ions moving in solid He.

We suggest the following qualitative model of the observed phenomena. In the cell completely filled with solid He positive alkali ions and free electrons are produced by laser ablation and are trapped in the region that forms the iceberg after melting. During ablation in the cell partially filled with solid He, ions are also adsorbed on the electrode surface. The Coulomb interaction between the electrons and the ions in the iceberg together with the polarization interaction between the charges and He atoms provide a potential barrier that does not allow the charges to escape from the iceberg. In the external electric field the ions at some spots overcome the barrier and start to drift towards the *negative* electrode. Within the solid part of the sample they move with a speed of about 1 mm/s. As they approach the solid-liquid interface (side of the iceberg), electrostriction causes the helium density to increase in the liquid near the interface and then to solidify. This onset of macroscopic solidification will occur only near surface spots, where the mean separation between the ions is smaller than its critical value $d_c = \rho_c R_S$. The ions remain trapped in the growing crystal branch, where they continue to drift. Liquid He around the iceberg contains electron bubbles produced by laser ablation and by field emission from the electrodes. These electrons will be attracted by the positively charged growing crystallite and become bound therein. The crystal growth will stop when the average snowball separation near the tip drops below d_c. In that case positive ions will move from the crystallite into the liquid without inducing a further growth, and the crystallite will become negatively charged. If the electrostatic force on the residual electron bubbles becomes sufficient to break off the structure, the fragment will be attracted to the *positive* electrode, i.e., in the opposite direction of growth.

A directional helium crystal growth in an electric field was reported in [15], where the growth of an undoped helium crystal towards a positively charged needle was observed. In that experiment no impurities other than field-emitted electrons from the tip were introduced into helium. The authors of [15] assumed that the injected electron bubbles generate a He flow along the crystal surface which induces instabilities of the latter. Such a mechanism can be ruled out in our experiment, in which the crystallites grow towards the electrode's center, while field emission is expected to originate from the edges of the electrode.

We have measured the number of electrons and positive ions produced by laser ablation from an alkali-metal target in liquid helium and subsequently trapped in a helium crystal. The results support our hypothesis that charged particles are responsible for stabilizing the doped helium crystal against melting. In addition we have observed that a static electric field induces the growth of crystallites along field lines directed to the negative electrode. We assign this effect to the nucleation of solid He on positive ions that are extracted from the doped matrix into the surrounding superfluid.

So far, very little is known about the solidification and melting properties of ^{4}He containing neutral or charged atomic or molecular dopants. Macroscopic impurity-He solids, consisting of neutral hydrogen, nitrogen, or noble gas clusters, each surrounded by a van der Waals bound layer of solid He, have been well studied [16,17]. Recently, the modification of the properties of condensed He by defects, and, in particular, by atomic impurities such as ^{3}He, has also received interest in the context of understanding supersolidity [18]. The possibility to control the solidification of He by guiding positive ions with electric fields is a novel approach for studying the growth of quantum solids.

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