Melting Curve of ^{4}He: No Sign of a Supersolid Transition down to 10 mK

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We have measured the melting curve of ^{4}He in the temperature range from 10 to 400 mK with the accuracy of about 0.5 μbar. Crystals of different quality show the expected T^4 dependence in the range from 80 to 400 mK without any sign of the supersolid transition, and the coefficient is in excellent agreement with available data on the sound velocity in liquid ^{4}He and on the Debye temperature of solid ^{4}He. Below 80 mK, we have observed a small deviation from T^4 dependence, which, however, cannot be attributed to the supersolid transition, because instead of decrease the entropy of the solid rather remains constant, about 2.5×10^{-6} R.

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In 1969, Andreev and Lifshitz proposed that, owing to the large zero-point motion of the atoms, helium crystals may contain a finite concentration of vacancies even at absolute zero temperature [1]. These vacancies are delocalized and do not violate the crystalline symmetry. At sufficiently low temperature, the vacancies may Bose condense, in which case the crystal phase would manifest quite unusual properties, such as a nondissipative mass current.

This possible "supersolid" state was a subject of great interest in the 1970s and 1980s, when several experimental groups tried to detect the superflow of vacancies by various methods (see [2] for a review). While all these attempts were unsuccessful, they did put an upper limit for the possible superfluid fraction at 5×10^{-6} and for the value of the critical velocity at $<5 \times 10^{-8}$ cm/s down to 25 mK [2]. The only exceptions were the ultrasonic experiments with ultrapure (1.5 ppb of ^{3}He) solid ^{4}He by Lengua and Goodkind [3], who observed an increase of the sound attenuation at low temperatures. They attributed this phenomenon to the interaction between phonons and vacancies and obtained a superfluid fraction $\rho_s/\rho \sim 10^{-3}$ and a condensation temperature of the order of 0.1 K.

Interest in the problem of the supersolid was renewed with the observation by Kim and Chan [4] in 2004 of the reduction in the rotational inertia of a cell containing solid ^{4}He below about 0.2 K. The authors named this phenomenon "nonclassical rotational inertia" and interpreted it in terms of superfluidity of the solid, possibly caused by Bose-Einstein condensation of vacancies [5], estimating a superfluid fraction ρ_s/ρ to be from 0.5% to 1.5%, depending on the density of the solid and purity of the ^{4}He. Their observations were recently confirmed by Rittner and Reppy [6], who also pointed out that this effect could be observed only in very nonuniform samples grown at relatively high temperatures and then rapidly cooled. If such samples are annealed by thermal cycling, the effect disappears. However, recent experiments by Kim and Chan [7] did not confirm the annealing effect.

Most of the previous searches for the supersolid have been via attempts to detect unusual features in the dynamic behavior of the solid sample, yielding various interpretations [8–10]. Our motivation was to check for the peculiarities of the equilibrium thermodynamical properties of solid ^{4}He, its entropy, in particular, which should manifest an anomaly at the transition (if it really is a phase transition in the bulk solid).

The thermodynamical properties of solid ^{4}He at relatively high temperatures were intensively investigated during the 1960s and 1970s and have been thought to be well understood for more than 30 years. The hcp solid ^{4}He is well described by the "classical" concept of phonons, with an effective Debye temperature $\Theta \approx 26$ K. The temperature dependence of Θ becomes negligible below 0.5 K [11]. This implies that below 0.5 K the heat capacity of solid ^{4}He varies as T^3, $C_S = (12/5)\pi^4 R(T/\Theta)^3$. The slope of the melting curve is proportional to the difference of the entropies of the liquid and solid $dp/dT|_{\mathrm{MC}} = (S_L - S_S)/(v_L - v_S)$, where v_L and v_S are molar volumes of liquid and solid ^{4}He, respectively. The heat capacity of superfluid ^{4}He below ~0.5 K is dominated by phonons, $C_L = 2\pi^2 RT^3/(15\hbar^3 nu^3)$, where n is the density and $u = 366$ m/s is the sound velocity in liquid ^{4}He at the melting pressure [12]. Thus, the melting pressure should vary basically as T^4 but should deviate from this dependence near any possible supersolid transition. Corrections due to rotons, thermal expansion, etc., become negligible below 0.45 K [11,13,14].

Assuming the superfluid fraction to be about 1% at low temperatures, which would correspond to the concentration of vacancies of 1% at the condensation temperature, one would expect the excess entropy in the solid of the order of 0.01R above the transition temperature, with a rapid fall in this excess entropy below the transition [15]. For more detailed calculations, see [9]. Such a big excess entropy has never been observed in helium crystals. To rule out this discrepancy, Anderson *et al.* [16] recently proposed a new model of the solid state of ^{4}He, where the vacancies and interstitials are assumed to be incorporated in a highly correlated quantum state of the crystal, and the only modes giving large contribution to thermodynamics are phonons. In this model, there is no direct connection between the superfluid density and the excess entropy above the transition, which behaves as T^7 at temperatures up to 1 K and thus may be much smaller than in the case of weakly interacting Bose gas. In view of such a possibility, it seems very important to look for any possible anomaly in the entropy of solid ^{4}He below 0.2 K with high accuracy.

The heat capacity measurements of solid ^{4}He have been carried out down to 140 mK by Castles and Adams [17], who have observed a deviation from the T^3 behavior already at 0.4 K. The melting pressure of ^{4}He has been measured indirectly by Hanson *et al.* [18], who found it to vary as T^4 down to 100 mK. Two groups have measured the melting pressure of ^{4}He at ultra low temperatures. Van de Haar *et al.* [19] have found that below 100 mK the melting curve is flat with the accuracy of 20 μbar. Measurements with better accuracy by Ruutu *et al.* [20] have shown that the variation of the melting pressure from 100 to 2 mK is much larger than the expected 3.5 μbar due to phonons. Unfortunately, Ruutu *et al.* had very poor thermometry above $\sim$10 mK. These results demonstrate that accurate measurements of the melting curve of ^{4}He in the whole temperature range which covers the region of the possible supersolid transition and continues down to the lowest temperatures have been urgently needed.

In this Letter, we present our direct high-precision measurements of the melting pressure of ^{4}He in the range from 10 to 400 mK. With the accuracy of about 0.5 μbar, we do not see any deviation from the expected T^4 behavior from 80 up to 400 mK. The variation of the melting pressure obtained -34.2 ± 0.2 mbar/K^4 is in good correspondence with the value of the heat capacity of the solid measured at higher temperatures and with the sound velocity in the liquid. We have also observed an anomaly below 80 mK, where the T^4 dependence changes to much weaker, almost linear dependence.

Our capacitive pressure gauge, of a standard Straty-Adams design [21], is made of beryllium bronze and has the sensitivity $dC/dp = 44$ pF/bar at the melting pressure (25.31 bar) yielding the accuracy of about 0.5 μbar. The time and temperature stability measured at zero pressure is of the order of 10^{-6} pF. The ^{4}He sample, supplied by Oy Woikoski AB, Finland, contained less than 0.1 ppm of ^{3}He impurities. The temperature was measured by a ^{3}He melting curve thermometer thermally anchored to the sample cell. The conversion of ^{3}He melting pressure to temperature was made according to the provisional low temperature scale, PLTS-2000 [22].

The first sample crystal was nucleated and grown at a rather high temperature, 1.4 K, and then rapidly cooled below 0.6 K. Crystals grown in this way are known to contain dislocations, which facilitates crystal growth at low temperatures, which can take place without significant overpressures [20]. Indeed, our pressure data taken during warming, when the crystal is growing, do not show any systematic excess over that taken on cooling (melting). Instead, we have observed a small hysteresis with opposite sign, which becomes smaller at slower cooling (warming) rates, apparently due to the relatively high heat capacity of ^{3}He in the melting curve thermometer (see Fig. 1).

On the other hand, the melting pressure at 1.4 K is by about 1 bar higher than at low temperatures. This pressure difference leads to large nonuniform stresses in the sample crystal after cooling down, which may affect the measured melting pressure [23,24]. To check the possible role of these effects in our measurements, another sample was grown at $T = 1.1$ K, at a pressure of only $\sim$0.1 bar higher than the melting pressure at low temperatures. Despite the fact that such a crystal should be of much better quality, no systematic difference was found between the data taken with this crystal and those of the crystal grown at 1.4 K. This demonstrates that the measured melting curve does not depend significantly on the concentration of defects in the sample.

Indeed, the contribution of defects such as dislocations to the melting pressure can be shown to be negligible. At low temperatures, the entropy of dislocations is due to phononlike oscillations of dislocations and can be estimated in a way similar to the calculation for the usual phonons in a bulk solid, $S_d \sim \sigma v_S k_B (T/\Theta_d)/d$. Here σ is the density of dislocations, v_S is the molar volume, d is the lattice constant, and the Debye temperature of dislocations Θ_d can be taken the same as for a bulk solid. The concentration of dislocations can be obtained from the observed threshold for the crystal growth. According to Ruutu *et al.* [20], thresholds of the order of 1 μbar correspond to the density of dislocations of about 100 cm^{-2}. The corre-

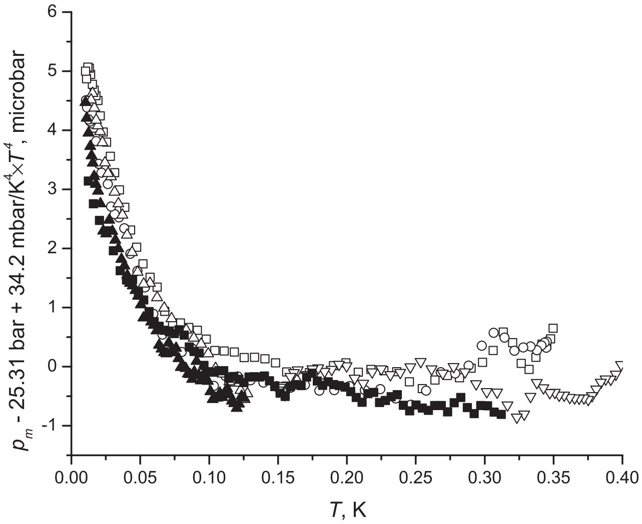

FIG. 1. Melting pressure of ^{4}He after substracting the T^4 term found from the fit of the data at $T > 100$ mK. Data have been taken with the crystals grown at 1.4 and 1.1 K. Open symbols correspond to cooldowns and solid ones to warmups. Different symbols correspond to different runs. In the vicinity of the ^{3}He melting curve minimum at 0.32 K, the scatter of experimental points is somewhat larger because of the smaller sensitivity of the melting curve thermometer. Note that the substracted T^4 term varies by about 1 mbar in this temperature range.

sponding additional term to the melting pressure $\Delta p_{\mathrm{MC},d} \approx 10\sigma k_B(T^2/\Theta_d)/d$ would give a contribution of the order of 10^{-7} μbar/K$^2T^2$.

The measured melting pressure could also be affected by ^{3}He impurities. According to the ^{3}He-^{4}He phase diagram calculated by Edwards and Balibar [25], the concentration of ^{3}He in solid ^{4}He, $c_{3,S}$, at a constant concentration in liquid, $c_{3,L}$, quickly falls down below 0.6 K:

$$c_{3,S}/c_{3,L} \approx \exp(-\Delta/T), \Delta \approx 1 \text{ K}. \quad (1)$$

This means that at low temperatures almost all ^{3}He atoms are in liquid, which has a much larger volume than the crystal, and thus the concentration of ^{3}He in liquid is the same as in the whole helium sample, $c_{3,L} < 10^{-7}$, and $c_{3,S} \ll c_{3,L}$. The corresponding contribution to the slope of the melting curve is positive and less than 10 μbar/K. We should note, however, that Eq. (1) has not been proven experimentally at low temperatures.

Our results are shown in Figs. 1 and 2. As one can see, the melting pressure measured during different runs is reproduced within about 1 μbar. In the temperature range from 80 to 400 mK, the measured melting pressure of ^{4}He shows the expected T^4 behavior with the coefficient, -34.2 ± 0.2 mbar/K^4, which is in very good agreement with the earlier measurements of melting pressure and heat capacity of solid ^{4}He at higher temperatures by different experimental groups. Indirect measurements of the melting pressure by Hanson *et al.* [18] give the variation of the melting pressure -36 mbar/K^4, and from the heat capacity measurements of solid ^{4}He by Gardner *et al.* [11] the coefficient -34.7 mbar/K^4 can be found.

Within the accuracy of about 0.5 μbar, we do not see any manifestation of the transition which Kim and Chan [4] and Rittner and Reppy [6] have observed with torsional oscillations technique. Kim and Chan have stated that their data measured at 26 bar are consistent with a supersolid fraction of about 1% [4] and the supersolid transition temperature about 200 mK, but we do not see any anomaly in the entropy above 80 mK with an accuracy of about $3 \times 10^{-7}R$ which has to be compared with the expected drop of entropy of the order of $0.01R$ below the transition temperature.

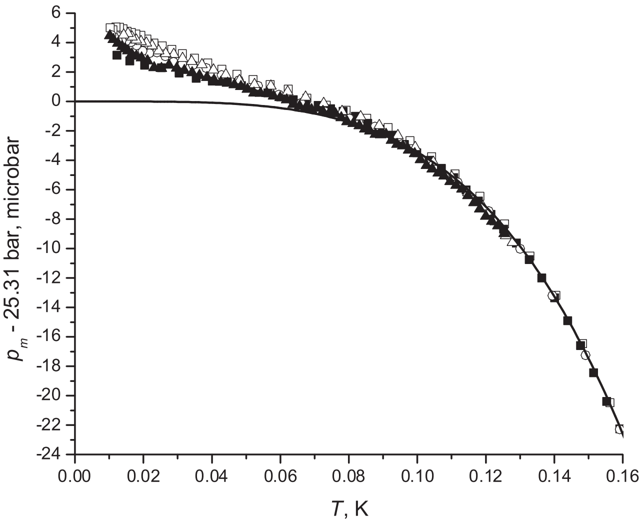

FIG. 2. Melting pressure of ^{4}He at low temperatures measured with the crystal grown at 1.1 K. Open symbols correspond to cooldowns and solid ones to warmups. Different symbols correspond to different runs. The solid line is the T^4 fit to the data at $T > 100$ mK extended down to 0 K.

However, below 80 mK a deviation from T^4 dependence is seen, such that the derivative $-dp/dT$, which is proportional to the entropy difference between the solid and liquid, stops decreasing as T^3 and saturates at a roughly constant value down to our lowest temperature of 10 mK (see Fig. 2). Note that the entropy of the liquid is about 5 times less than the phonon entropy of the solid, and its contribution to the melting pressure is small, less than 0.5 μbar at 80 mK. Thus, we have an excess entropy in the solid, which decreases with increasing temperature and disappears around 80 mK. Such rather unusual behavior of entropy (additional specific heat is *negative*) is difficult to understand, but it certainly cannot be attributed to a supersolid transition, because in this case the additional entropy would *increase* when temperature increases. Also, as was pointed out in previous paragraph, the amplitude of this anomaly is more than 4 orders of magnitude smaller than expected for the Bose condensation of weakly interacting vacancies.

In the following, we discuss possible sources of errors in our measurements. The measured pressure could be influenced by dynamic and capillary effects and by the hydrostatic pressure change. If the crystal quality is so good that there is no even single dislocation crossing a facet, then such a facet is practically immobile, and the corresponding overpressure for its growth may reach $10, \ldots, 100$ μbar [20]. Indeed, when we created crystals very carefully at low temperatures, 0.6 K and below, the measured ^{4}He pressure traces typically had significant temperature hysteresis, up to $10, \ldots, 20$ μbar. Measurements with the crystal grown at 1.4 K were much better in this sense, with hysteresis of the order of 1 μbar and with a tiny drift to smaller pressures with time, of the order of -2×10^{-6} μbar/s. In turn, the crystal grown at 1.1 K with better quality, but still with a finite number of dislocations, showed even better reproducibility and no measurable time drift. The time drift of the pressure measured with 1.4 K crystal we thus interpret as the sign of structural disorder in the crystal which slowly becomes smaller. The relaxation time of such a process was found to be very long, of the order of a month. On the other hand, all measured sample crystals of different quality (altogether seven) have shown the anomaly below 80 mK.

The capillary contribution to the total equilibrium pressure on the crystal, being proportional to the surface stiffness γ, could reach as much as 10 μbar. For pure ^{4}He, temperature dependence of γ is very weak at low temperatures [26], even when taking into account possible new roughening transitions [24], and does not contribute to the slope of the measured melting curve. Because of the adsorption of ^{3}He impurities at low temperatures, γ may decrease by about 20% [27], which would produce a decrease of the measured pressure by a few μbar at most with decreasing temperature.

Finally, the change of the hydrostatic pressure due to the temperature variation is negligible in our experimental conditions. Indeed, both 1.4 and 1.1 K crystals were grown up to $\sim$200 mm^3 in volume, which means that their lateral sizes were much larger than the capillary length $\lambda \approx$ 1 mm. The dependence of the equilibrium height of such a big "crystal on a table" on its volume is exponentially weak; the crystal grows from its sides. The hydrostatic pressure difference between the crystal and the pressure gauge thus changes very little due to growth or melting of the crystal in the course of warming or cooling. At low temperatures, where the melting curve is almost flat, this effect is negligible. Moreover, the sign of the effect is opposite to what we observe: When cooling, the crystal melts, and the pressure of the liquid in the pressure gauge decreases, while we have observed the excess of the melting pressure over the expected T^4 dependence.

To summarize, the measured melting pressure of ^{4}He obeys the expected T^4 law at temperatures above 80 mK with an accuracy of about 0.5 μbar, which is in good agreement with previous measurements done at higher temperatures [11,13,18]. No sign of the supersolid transition has been observed. Below about 80 mK, the T^4 dependence changes to a roughly linear one, which would correspond to about $2.5 \times 10^{-6} R$ constant entropy in solid ^{4}He. However, this anomaly cannot be attributed to the supersolid transition, because instead of a drop below the possible transition the entropy of the solid rather remains constant. Also, the size of the anomaly is by 4 orders of magnitude smaller than one would expect for the supersolid transition. The origin of this residual entropy remains unclear.

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