³He melting curve below 15 mK

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We have performed new measurements of the P-T relation along the ³He melting curve for temperatures between 0.4 and 15 mK in zero magnetic field. The temperature was determined by a Pt-wire nuclear-magnetic-resonance thermometer calibrated against the National Bureau of Standards scale (1983) above 15 mK. Three distinct points on the melting curve (the two superfluid transitions and the nuclear-spin ordering in the solid phase) were observed at temperatures lower than the currently accepted values by about 10%. Our results are in good agreement with the P-T relation recently proposed by Greywall using a La-cerium magnesium nitrate thermometer, but differ seriously from the thermodynamic measurements by Halperin *et al.* From the measured melting curve, we could determine the ground-state energy of a nuclear spin in solid ³He to be −1.24 mK at the melting density. This value can be quantitatively explained by the current four-spin exchange theory.

The low-temperature melting curve of ³He has been recognized as the most reliable temperature standard in the millikelvin region. It has a number of advantages over other thermometric methods such as (i) a wide and continuous temperature range (1–300 mK) available for thermometry with high resolution and reproducibility, (ii) insensitivity to sample purity, and (iii) existence of three fixed points of pressure and temperature below 3 mK, i.e., the superfluid A transition (P_A, T_A), the superfluid B transition (P_B, T_B), and the nuclear-spin ordering in the solid phase (P_S, T_S).

Until now two major measurements of the melting-curve between T_S and 15 mK, each based on different methods of thermometry, are reported. Halperin, Rasmussen, Archie, and Richardson[1] used a thermodynamic method of measuring the latent heat for solidification of ³He to determine the temperature. Their temperature scale has been believed to be proportional to the absolute temperature. On the other hand, Greywall[2] employed a La-cerium magnesium nitrate (CMN) thermometer. It was calibrated against the National Bureau of Standards scale (NBS-1983)[3] at 15.6 mK, and was done at the lower temperatures based on the following assumptions: (i) the susceptibility of La-CMN follows the Curie-Weiss law down to 0.93 mK, (ii) the normal-phase specific heat of liquid ³He at zero pressure measured by this thermometer is linear in temperature. Unfortunately, these two measurements differ from each other by as much as 18%. Since the Weiss temperature (−0.121 mK) is not negligible, the first assumption in Greywall's work is not necessarily obvious at the lowest temperatures. There is also a report contradictory to the second assumption.[4] In addition to the difference in thermometry, sintered powder with a large surface area was employed in Greywall's experiment and its influence on his results is not known. In this report we present new measurements of the ³He melting curve in zero magnetic field using a Pt-NMR thermometer for a temperature region between 0.4 and 15 mK. The nuclear susceptibility of platinum is expected to obey the Curie law, since the spin interactions are three orders of magnitude smaller than the temperatures to be studied.

The ³He cells used in this experiment are similar to that of Greywall and Busch.[5] The melting pressure was measured by a capacitive strain gauge with a long term stability of 10 μbar. The capacitance-bridge readings were calibrated at 1 K against a high-precision pressure gauge[6] with an absolute accuracy of a few mbar. A niobium superconducting tube was placed around the cell to shield the ³He from any stray magnetic fields.

The nuclear susceptibility of platinum was obtained from integration of the free-induction-decay (FID) signal at a Larmor frequency of 250 kHz with a standard pulsed NMR spectrometer.[7] The platinum sample (99.999% pure) consists of 2000 wires with diameter of 20 μm. After annealing at 500 °C for 1 h in air (resultant residual-resistivity ratio is 1200), the wires were welded to a pure silver plate which is attached to the ³He cell. Measured decay time T_2^* of the FID signal is 1.05 ± 0.05 msec and is independent of temperature between 0.18 and 20 mK. The calibration of this thermometer was carried out against the melting curve itself between 15 and 45 mK where the P-T relation has been well established.[8] Also, we have made our own measurement of the melting curve between 25 and 100 mK using a carbon resistance thermometer, which was previously calibrated against the NBS-1983 scale by means of a CMN thermometer and a superconducting fixed-point device.[9] Our results followed the P-T relation determined in Ref. 8 within an experimental accuracy of ±1%. Cooling was achieved by a powerful nuclear refrigerator which consists of copper (70 moles) precooled to 12 mK in a magnetic field of 7.4 T. The demagnetization appeared to be ideal at least down to 2 mK. We can, therefore, exclude the possibility of anomalous behavior in susceptibility of our platinum wire as was reported by Ling, Dobbs, and Saunders,[10] for a powder specimen. We believe no measurable nonlinearity in our thermometer remains in the temperature range studied here.

Experiments were conducted in three sample cells with

different heat exchangers. Two of them contained sintered silver powders with surface areas of 0.5 and 1.2 m^2. Assuming that the particles are spherical, the diameter is estimated to be 3400 Å from the measured specific surface area. The third one contains a sintered sponge of an admixture of platinum and silver powders. The total surface area of 6.3 m^2 comes mainly from platinum particles whose estimated diameter is 100 Å. The amount of ^{3}He (containing less than 3 ppm of ^{4}He) in each cell is about 0.1 cm^3, and roughly 25% is inside the sinter. The sample with appropriate average density was confined by the blocked-capillary method in order to leave a very small volume fraction (less than 3%) of solid at zero temperature. The temperature difference, estimated from the measured thermal resistance, between the ^{3}He cell body and the Pt-NMR thermometer is less than 3 μK at 1 mK.

The measured P-T data between 0.91 and 45 mK obtained with the Pt-NMR thermometer are shown in Fig. 1 as deviations from the least-squares-fitted expression of 152 data points:

$$P = P_S + \sum_{i=0}^{9} a_i T^i ,$$ (1)

with

$a_0 = 2.4347306 \times 10^{-2}$, $a_1 = -2.3240817 \times 10^{-2}$,

$a_2 = -4.1457509 \times 10^{-3}$, $a_3 = 5.2228032 \times 10^{-4}$,

$a_4 = -3.8574492 \times 10^{-5}$, $a_5 = 1.7667759 \times 10^{-6}$,

$a_6 = -5.0066193 \times 10^{-8}$, $a_7 = 8.4854888 \times 10^{-10}$,

$a_8 = -7.8444028 \times 10^{-12}$, $a_9 = 3.0303608 \times 10^{-14}$.

The rms deviation is 0.7%. Here P is in bar and T is in mK. P_S was measured to be 34.393 ± 0.008 bars. Most of the data points were taken after waiting for equilibrium
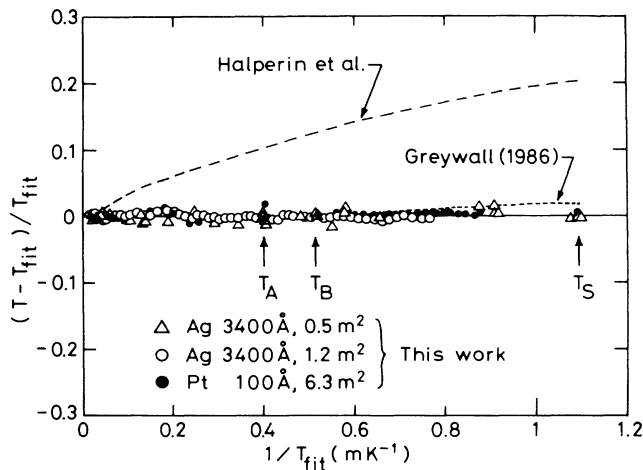

FIG. 1. ^{3}He melting-curve data between 0.91 and 45 mK plotted as deviations from Eq. (1). T_{fit} is the temperature calculated from Eq. (1) for a given melting pressure. The long- and short-dashed curves represent the data of Halperin et al. (Ref. 1) and of Greywall (Ref. 2), respectively.

between the melting pressure and the thermometer reading both on cooling and on warming. The data taken during slow warming at about 10 μK/h at 1 mK, however, do not differ from the equilibrium ones within experimental uncertainty. We would like to emphasize that all of the data obtained for the various heat exchangers fall on the single curve expressed in Eq. (1). This indicates all of the solid probably exists outside of the heat exchangers, because the melting pressure in the small pores is elevated due to absence of the continuous nucleation of solid ^{3}He on the silver and the platinum powders. This is consistent with the previous finding[5] at higher temperatures. Therefore, we believe the measured melting curve is that for bulk ^{3}He.

Our results, as clearly seen in the figure, are in excellent agreement with the P-T relation measured by Greywall above 1.6 mK. As the temperature further decreases, he finds slightly higher temperatures than ours. Although the difference at T_S is about 1.9% which is larger than the rms deviation in the fitting of our data to Eq. (1), it is within the combined experimental uncertainties in both the measurements. On the other hand, the disagreement with the result of Halperin et al. is serious. Though not so far from ours at the highest temperatures, their result deviates more and more as the temperature is lowered. At T_S it gives higher temperatures than ours by 20%. We speculate that the applied heat was not entirely absorbed by the solidification of ^{3}He at the liquid-solid interface within the time interval in their latent heat measurements (a few minutes; see Fig. 15 in Ref. 1). The presence of solid ^{3}He on the heater wire, coupled with its low thermal conductivity and high specific heat, was likely to cause a significant temperature gradient within it and a long thermal relaxation time at lower temperatures.

The three phase transitions at T_A, T_B, and T_S were easily identified by clear signatures on the time evolution of the melting pressure. Those were recorded at 2.477 ± 0.026 mK, 1.933 ± 0.021 mK, and 0.914 ± 0.012 mK, respectively. The pressure differences between them are determined as $P_S - P_A = 52.72 \pm 0.26$ mbar and $P_S - P_B = 32.50 \pm 0.19$ mbar, which are in excellent agreement with the previous measurements.[1,2] We defined T_B as the transition temperature from the superfluid B to A phase upon warming. Significant supercooling was always observed at the $A \rightarrow B$ transition on the first cooling through the normal liquid. The supercooled transition occurs in a narrow temperature range between 0.7 and $0.8 T_B$, and is not affected by the cooling rate between 2.3 and 14.9 μK/min as shown in Fig. 2. These features are consistent with the previous report on lower pressure liquids by Hakonen, Krusius, Salomaa, and Simola[11] if we extrapolate their data to the melting pressure taking into account the pressure dependence of the transition temperatures. The newly acquired knowledge about this unsolved phenomenon is its insensitivity to the pore size or surface area of heat exchanger. This suggests that the nucleation of B phase occurs in the bulk liquid instead of the liquid confined inside of the small pores. When the A-phase liquid passed through the last $B \rightarrow A$ transition and was cooled back again, only very little supercooling of $0.02 T_B$ was detected. Some textural
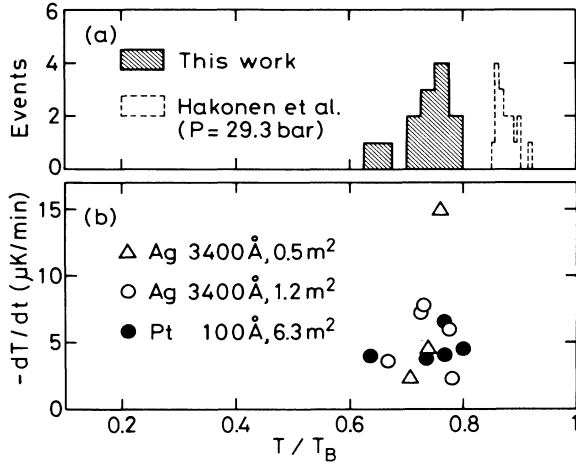
FIG. 2. (a) Histogram of the observed supercooled B-transition temperatures. The dashed-line data are from Hakonen et al. (Ref. 11). (b) The supercooled B-transition temperatures plotted as a function of the cooling rate.
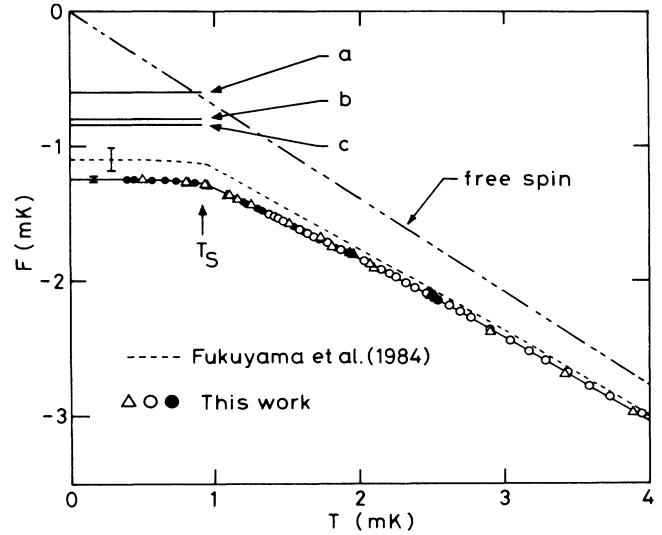

FIG. 3. The free energy of a nuclear spin in solid ³He derived from the measured melting curve data. The double-dotted line represents $F(T) = -\ln 2T$ for a free spin. The dashed line is the result from the pressure measurements (Ref. 14) on all-solid samples. The vertical bars show the experimental errors. The three horizontal lines labeled as a, b, and c are the calculated mean-field energies with the following exchange parameter sets: a, $j_t = -0.167$ mK and $K_P = K_F = -0.264$ mK (Ref. 16); b, $j_{NN} = -0.377$ mK, $j_t = -0.155$ mK, and $K_P = -0.327$ mK (Ref. 17); c, $j_t = -0.130$ mK, and $K_P = -0.385$ mK (Ref. 15). See Ref. 15 for the definition of the exchange parameters.

"memory" of the B phase might be maintained in the A phase.

The temperature variation of the melting pressure is determined by the Clausius-Clapeyron equation:

$$dP/dT = (S_1 - S_s)/(V_1 - V_s) , \qquad (2)$$

where S_1 and V_1 are entropy and molar volume of the liquid phase and S_s and V_s are those of the solid phase. After integration of Eq. (2) in temperature, the free energy $F(T)$ of the solid phase at a given temperature is described by

$$F(T) - F(T_0)$$
$$= (V_1 - V_s)[P(T) - P(T_0)]/R - \int_{T_0}^{T} S_1 dT . \qquad (3)$$

Here R is the gas constant and T_0 is an arbitrary temperature below which $V_1 - V_s$ is temperature independent. Figure 3 shows the temperature dependence of the free energy of solid ³He obtained from our melting curve data through Eq. (3). We defined $T_0 = 15$ mK and $V_1 - V_s = 1.314$ cm³/mole[1] here. The data below T_S are consistent with the result of Osheroff and Yu[12] if their T_S is adjusted to ours. A kink in the free energy at T_S clearly indicates the first-order phase transition. The second term in the right-hand side of Eq. (3) was evaluated[13] from the measured specific heat of liquid ³He by Greywall.[2] The value of F (15 mK) can be determined from other thermodynamic measurements[14] off the melting curve at high temperatures. To make our data along the melting curve consistent with those at a constant volume of 24.21 cm³/mole, a small correction, which increases $F(T)$ by 1.1% at most, has been applied. Consequently, the ground-state energy E (the energy at the absolute zero) of a nuclear spin in solid ³He can be determined as $E = -1.24 \pm 0.02$ mK. The only other experimental determination of E in literature is given in the pressure

measurements on all-solid samples by Fukuyama, Sawada, Miwa, and Masuda.[14] The present value is in reasonable agreement with their result of $E = -1.10 \pm 0.09$ mK which is extrapolated to the melting density (see Fig. 3).

Although most of the magnetic properties in solid ³He can be explained by a spin Hamiltonian including up to four-spin exchange,[15] so far we have no definitive description of what kind of exchange processes are dominant or how large they are. Several authors[15-17] proposed possible exchange parameter sets satisfying various experimental aspects. The calculated ground-state energies with these parameter sets based on the mean-field approximation are also shown in Fig. 3, where we assume the $u2d2$ spin structure[18] as the ordered phase. All of those are considerably higher than the measured value. This means that the zero-point fluctuation of spins causes a large energy gain up to 100% of the mean-field energy. Almost the same amount of energy reduction is predicted in the calculations based on the spin-wave approximation[16] or on the numerical diagonalization of a finite size of spins.[19] Our experiments, therefore, support these calculations quantitatively.

In conclusion, we determined the P-T relation along the ³He melting curve from 0.91 to 15 mK. Our results strongly support the temperature scale recently proposed by Greywall at least above 1.6 mK, but are in serious conflict with the thermodynamic one measured by Halperin et al. If the NBS-1983 scale, on which our Pt-NMR

thermometer stands, is accepted, the current temperature scales widely used in the millikelvin region should be lowered more than by 10%. From the measured melting curve we deduced the ground-state energy of a nuclear spin in solid ^{3}He with little uncertainty. This quantity would serve as a criterion for testing various exchange Hamiltonians or approximations describing this quantum solid.

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