

## Magnetization of hcp Solid $^3\text{He}$

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The nuclear magnetization of hcp solid  $^3\text{He}$  has been measured for molar volumes ranging from 18.1 to 19.4 cm<sup>3</sup>/mol and at temperatures down to 43  $\mu\text{K}$ . The magnetization follows the Curie-Weiss law with a positive Weiss temperature, indicating that the dominant spin interactions are ferromagnetic.

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The thermodynamic properties of solid  $^3\text{He}$  at low temperatures are dominated by the nuclear-spin degree of freedom. Aside from the very small dipole interaction of order 0.1  $\mu\text{K}$ , the interaction between the spins arises solely from the atomic motion due to quantum effects and should be extremely sensitive to the lattice symmetry. In the bcc phase,  $^3\text{He}$  orders antiferromagnetically at temperatures below 1.1 mK. Thermodynamic measurements around the ordering temperature and nuclear antiferromagnetic resonance experiments in the ordered state have revealed much about the spin interaction.<sup>1</sup> Corresponding knowledge on the interaction in the hcp solid has been quite limited because of the lower temperatures required. The only experiments have been the high-temperature NMR relaxation measurements<sup>2</sup> from which an effective exchange frequency has been obtained as a function of the molar volume. These experiments, however, have only yielded the magnitude of the interaction and not its sign, leaving unanswered the question of whether hcp solid  $^3\text{He}$  is a ferromagnet or an antiferromagnet in the ground state. Very recent calculations by Roger<sup>3</sup> have predicted that the hcp solid is ferromagnetic, which should be manifest in the magnetization as a positive Weiss temperature. In this Letter, we report magnetization measurements at temperatures low enough to resolve the Weiss temperature  $\Theta$ . The results show that the dominant interactions in the hcp solid are indeed ferromagnetic, in agreement with the theory.

The solid  $^3\text{He}$  samples were contained in the pores of a sintered-silver sponge and were cooled by nuclear demagnetization of PrNi<sub>5</sub> and copper in series.<sup>4</sup> The measurements were made for molar volumes ranging from 18.1 to 19.4 cm<sup>3</sup>/mol with  $^3\text{He}$  containing less than 3 ppm of  $^4\text{He}$  impurities. The sample cell design and the SQUID magnetometer technique have previously been described.<sup>5</sup> Briefly, silver powder<sup>6</sup> with a nominal particle size of 700 Å was sintered in two opposing cylindrical cavities machined in a single silver rod, the first serving as the  $^3\text{He}$  cell and the second as

a dummy for canceling the background magnetization of the silver. The volume available for  $^3\text{He}$  was 0.05 cm<sup>3</sup> and the surface area of the silver sponge was 1.4 m<sup>2</sup>, as obtained from an adsorption isotherm of nitrogen at liquid-nitrogen temperature. A NbTi wire of 80- $\mu\text{m}$  diameter, tightly wound around the cells in an astatic pair configuration, formed the input circuit of the SQUID. A magnetic field between 0.53 and 3.1 mT, depending on the molar volume, was trapped in a niobium cylinder slid over the cells. The cells were attached to a gold-plated copper platform welded to the copper refrigerant. The platform also held a pulsed platinum NMR thermometer, a 100- $\Omega$  Matsushita carbon resistor, a germanium resistance thermometer, and two heaters made from resistance wires. One of the heaters was located roughly at an equal distance from the cell and the NMR thermometer, and the other heater was wound around the base of the experimental platform near a weld to the copper refrigerant.

The strain-gauge capability of the SQUID magnetometer<sup>5</sup> and the germanium resistance thermometer allowed us to measure the  $^3\text{He}$  isopycnal and thus to determine the molar volume. When more than about 60% of  $^3\text{He}$  in the sample cell was solid, however, the apparent isopycnal deviated upward in pressure from the published melting curve<sup>7,8</sup> of solid  $^3\text{He}$ . This we interpreted as due to the presence of the solid making the sample cell stiffer and thereby reducing the gauge sensitivity. Therefore, the molar volume  $V$  was determined from the temperature, rather than the apparent pressure, at complete solidification. The uncertainty in the determination of  $V$  was  $\pm 0.05$  cm<sup>3</sup>/mol. Each  $^3\text{He}$  sample was annealed overnight at a temperature slightly below that of complete solidification. Any change in the strain gauge output, indicating annealing of the  $^3\text{He}$ , was completed during this period. When the molar volume was such that the isopycnal passed the bcc phase, the sample was again annealed overnight at a temperature slightly below that of the complete bcc-hcp transformation. The strain gauge was quite capable of detecting the pressure drop associated

with the bcc-hcp phase transformation, even though the absence of liquid  $^3\text{He}$  in the cell caused reduction in the gauge sensitivity.

The platinum NMR thermometer was operated at 125 kHz and was calibrated at temperatures between 15 and 50 mK against the Matsushita carbon resistor, which had been calibrated previously and had proven to be reproducible.<sup>4</sup> To further test the reproducibility of the carbon resistor, after the present set of measurements it was again calibrated against a U.S. National Bureau of Standards superconducting fixed point device (SRM 768) and against a  $^3\text{He}$ -melting-curve thermometer,<sup>9</sup> each in a separate run. The former calibration agreed within 3% with the present one, and the latter did so within 5%.

The magnetization data were taken by raising the sample  $^3\text{He}$  temperature in steps from the lowest temperature after the demagnetization of the copper refrigerant. For most of the data points, we applied heat for a short period to the experimental platform using one of the two heaters and waited until the  $^3\text{He}$  magnetization and the platinum NMR absorption fully recovered to new values. However, this method was impractical at temperatures below 70  $\mu\text{K}$  because the time constant of the recovery was extremely long as a result of the nuclear heat capacity of the copper refrigerant and the thermal resistance between the experimental platform and the copper refrigerant. In this temperature region, we took advantage of the large time constant and raised only the temperature of the platform, leaving the copper refrigerant essentially at a constant temperature. An electric current, which was initially several times its final value, was first applied to the heater to speed up the warming of the  $^3\text{He}$ , and was then decreased to its final value. During the course of our experiment the thermal time constant  $\tau_3$  of the  $^3\text{He}$  was measured in the temperature range between 60 and 250  $\mu\text{K}$  by observation of the relaxation of the  $^3\text{He}$  magnetization when the platform temperature was raised stepwise.  $\tau_3$  was roughly proportional<sup>10</sup> to  $T^{-3}$ , and was 300 and 6 min, respectively, at 60 and 250  $\mu\text{K}$  for 19.4  $\text{cm}^3/\text{mol}$ . Care was taken during the magnetization measurements to achieve a thermal equilibrium between the  $^3\text{He}$  and the platinum NMR thermometer by waiting at least for a period equal to  $\tau_3$  of the  $^3\text{He}$  after the  $^3\text{He}$  magnetization assumed a constant value while the heater current was held constant. We also examined a possible temperature gradient between the  $^3\text{He}$  and the thermometer by using each of the two heaters on the platform. The magnetization data showed no dependence on the location of the heater, lending support to the existence of a thermal equilibrium between the  $^3\text{He}$  and the thermometer.

Figure 1 shows the magnetization of solid  $^3\text{He}$  as a function of inverse temperature. A plot such as this

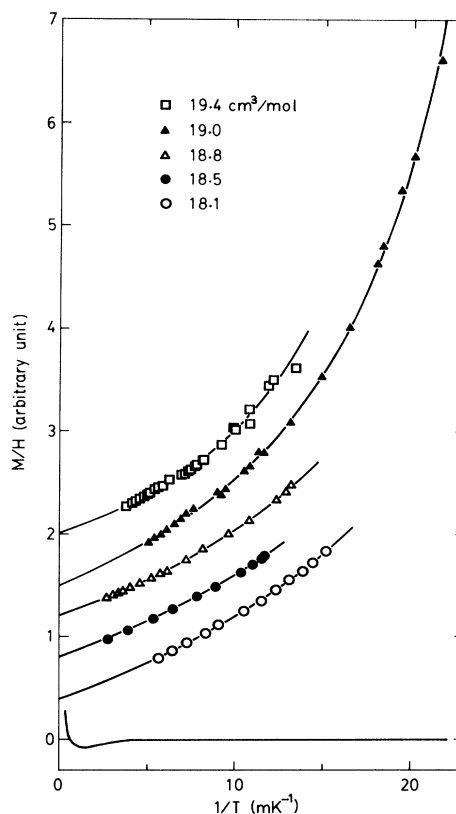


FIG. 1. Magnetization of hcp  $^3\text{He}$  at several molar volumes. The lines through the data points are least-squares fits as discussed in the text. The solid curve at the bottom is the background, which has been subtracted from the data. The zeros of both the  $^3\text{He}$  data and the background are arbitrary.

will be a straight line if the  $^3\text{He}$  magnetization obeys Curie's law. Deviation downward from the straight line at low temperatures will be an indication of antiferromagnetic interactions being predominant, and deviation upward at low temperatures will be an indication of ferromagnetic interactions. The data show clearly that the dominant interactions in hcp  $^3\text{He}$  are ferromagnetic for the range of molar volumes studied.

The solid curve shown at the bottom of the figure is the background of the empty sample cell due to incomplete cancellation by the astatic pair coils. This background has been subtracted from the data. Since the SQUID magnetometer only measures the temperature dependence of the magnetization, one is only concerned with the subtraction of the temperature-dependent part of the background, whose zero is again arbitrary. Note that the background correction has been necessary only for a few data points above 250  $\mu\text{K}$  ( $1/T < 4 \text{ mK}^{-1}$ ), the small region where the background was temperature dependent. Even without the background correction, the deviation of

the data from a straight line is evident.

A more conventional presentation of the data is given in Fig. 2, in which the inverse magnetization of solid  $^3\text{He}$  has been plotted against temperature. In order to present the data in this manner, the arbitrary zero  $B$  in the background-corrected data was determined by least-squares fitting of the data with a Curie-Weiss form

$$A/(T - \Theta) + B, \quad (1)$$

which contained three fitting parameters,  $A$ ,  $\Theta$ , and  $B$ . Then  $B$  was subtracted from the data. It was not possible to determine the zero with a reasonable accuracy by simple measurements at high temperatures where the  $^3\text{He}$  magnetization was negligible, because the background magnetization was strongly temperature dependent at these temperatures. For instance, in a magnetic field of 0.91 mT, the background correction was as large as the  $^3\text{He}$  magnetization already at 1 mK.

The data presented in this way show that the magnetization follows very well the Curie-Weiss law, straight lines through the data points intercepting the temperature axis at positive Weiss temperatures  $\Theta$ . The positive sign of  $\Theta$  means, in terms of the multiple-exchange model,<sup>1</sup> that the dominant processes are exchanges involving an odd number of atoms,<sup>11</sup> most likely the exchanges among three nearest-neighbor atoms. Roger<sup>3</sup> has recently calculated multiple-atom exchange frequencies for hcp  $^3\text{He}$  and has found two kinds of dominant three-atom exchange among the nearest neighbors, one within the

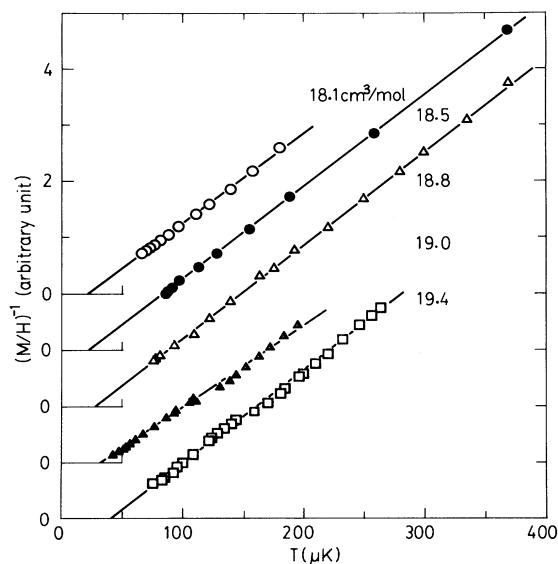


FIG. 2. Temperature dependence of the inverse magnetization of hcp  $^3\text{He}$  at several molar volumes. The straight lines represent least-squares fits to the data as discussed in the text.

basal plane of the hcp lattice and the other out of the plane. His prediction is in qualitative agreement with our observation.

The Weiss temperatures  $\Theta$  obtained by the fitting with the Curie-Weiss form of Eq. (1) are summarized in Fig. 3. Comparison of our results with the effective exchange parameters  $J_{\text{eff}}$  obtained from the NMR relaxation measurements at much higher temperatures is complicated by the possibility that the ferromagnetic interactions in hcp  $^3\text{He}$  are anisotropic, as Roger's calculation has indicated. If, for instance, the anisotropy is such that the Heisenberg nearest-neighbor spin-exchange frequency  $J'_1$  for a pair of spins out of the Basal plane of the hcp lattice is different from  $J_1$  for a pair within the plane, then the Weiss temperature is  $\Theta = 3(J_1 + J'_1)$  but not  $\Theta = 6J_{\text{eff}}$ . This is because<sup>12</sup> the simple average  $J_{\text{eff}} = (J_1 + J'_1)/2$  holds only when  $J'_1 = J_1$ . Nevertheless, we naively assume that  $\Theta = 6J_{\text{eff}}$ , and compare the NMR data with our values for  $\Theta$ . The result is represented in the figure by a solid curve, calculated from a smoothed line through the  $T_2$  data<sup>13</sup> drawn by Guyer, Richardson, and Zane.<sup>2</sup> We find reasonable agreement in the qualitative molar-volume dependence and in the order of magnitude, the results from the  $T_2$  data lying somewhat lower than our data, particularly at lower molar volumes. The agreement is satisfactory, in view of the possible anisotropy in the interaction and also in view of the uncertainty in the shape of the correlation function

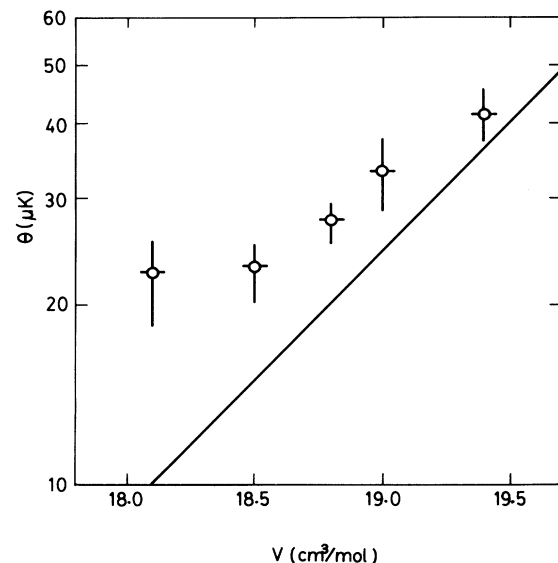


FIG. 3. Molar volume dependence of the ferromagnetic Weiss temperature  $\Theta$  of hcp solid  $^3\text{He}$ . The solid curve is a representation of the NMR  $T_2$  data compiled and smoothed by Guyer, Richardson, and Zane (Ref. 2) and has been calculated with the assumption  $\Theta = 6J_{\text{eff}}$  (see text).

that enters the analysis of the NMR data.

It is also interesting to compare our  $\Theta$  with Roger's calculation<sup>3</sup> on the molar-volume dependence of the three-atom exchange frequencies. Because of the uncertainty in the prefactors in his results, it is convenient to compare the molar-volume derivatives  $d \ln \Theta / d \ln V$ . The theory gives values for the derivative ranging from 19.5 to 22.2 for the molar volumes of our experiment, whereas the experimental value<sup>14</sup> is  $11.1 \pm 1.0$ . The theory seems to overestimate the molar-volume dependence of  $\Theta$  by roughly a factor of 2.

In Fig. 2 we cannot resolve within our accuracy a deviation from the Curie-Weiss law as the temperature approaches  $\Theta$ , a deviation indicative of antiferromagnetic interactions in competition with the dominant ferromagnetic interactions or of a higher-order term in the high-temperature expansion of the ferromagnetic Heisenberg Hamiltonian. In an attempt to resolve such a deviation and possibly to observe a ferromagnetic ordering in hcp <sup>3</sup>He, we also studied samples with higher molar volumes than shown in Fig. 1. We made three solids in the range between 19.6 and 19.7 cm<sup>3</sup>/mol, close to the maximum molar volume for the hcp solid. Contrary to our expectation,  $\Theta$  values for these samples were not only smaller than for those in Fig. 1 but essentially zero within the uncertainty of the least-squares fitting. This we believe was due to poor sample quality, because the apparent pressure changes in these three samples at the bcc-hcp transformation were at best 0.12 bar, only 6.5% of the change seen in the 19.4-cm<sup>3</sup>/mol sample. In a bulk geometry, Straty and Adams<sup>7</sup> have observed large amounts of supercooling of the bcc solid into the hcp phase region when the sample molar volumes were close to the maximum for the hcp phase. Supercooling of the bcc solid probably occurs much more easily in the confined geometry of our silver sponge. It is likely that, in those three samples that we made, the major portion of the bcc solid supercooled even to the lowest temperatures, so that there was very little, if any, hcp solid.

In summary, hcp solid <sup>3</sup>He is ferromagnetic in a marked contrast with the bcc solid. The values of the Weiss temperature  $\Theta$  are in reasonable agreement with the effective exchange frequencies obtained from previous high-temperature NMR relaxation measurements.

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<sup>1</sup>For review from a theoretical standpoint, see M. Roger, J. H. Hetherington, and J. M. Delrieu, *Rev. Mod. Phys.* **55**, 1 (1983).

<sup>2</sup>See a review by R. A. Guyer, R. C. Richardson, and L. I. Zane, *Rev. Mod. Phys.* **43**, 532 (1972).

<sup>3</sup>M. Roger, *Phys. Rev. B* **30**, 6432 (1984).

<sup>4</sup>H. Ishimoto, N. Nishida, T. Furubayashi, M. Shinohara, Y. Takano, Y. Miura, and K. Ôno, *J. Low Temp. Phys.* **55**, 17 (1984).

<sup>5</sup>T. Hata, S. Yamasaki, M. Taneda, T. Kodama, and T. Shigi, *Phys. Rev. Lett.* **51**, 1573 (1983).

<sup>6</sup>Vacuum Metallurgical Co., Kyobashi 1-11-2, Chuo-ku, Tokyo 104, Japan.

<sup>7</sup>G. C. Straty and E. D. Adams, *Phys. Rev.* **150**, 123 (1966).

<sup>8</sup>E. R. Grilly and R. L. Mills, *Ann. Phys. (N.Y.)* **8**, 1 (1959).

<sup>9</sup>We have used the melting-curve temperature scale of D. S. Greywall, *Phys. Rev. B* **31**, 2675 (1985).

<sup>10</sup>The  $T^{-3}$  dependence of the thermal time constant  $\tau_3$  of <sup>3</sup>He indicated that the thermal boundary resistance between the solid <sup>3</sup>He and the silver sponge was proportional to  $T^{-1}$ , since the exchange heat capacity of solid <sup>3</sup>He is proportional to  $T^{-2}$  to the lowest order. The time constant  $\tau_3$  was independent of the magnetic field  $H$  on the sample for  $H = 1.4$  and 3.1 mT, since for these low magnetic fields the exchange heat capacity, which is magnetic-field independent, dominated over the nuclear Zeeman heat capacity.

<sup>11</sup>D. J. Thouless, *Proc. Phys. Soc., London* **86**, 893 (1965).

<sup>12</sup>W. J. Mullin, private communication.

<sup>13</sup>The  $T_1$  data, which will yield the Weiss temperatures lying somewhat *higher* than our data, are not chosen for comparison, because they are more susceptible to the choice of the correlation function than the  $T_2$  data. See Ref. 2.

<sup>14</sup>This value is obtained by fitting the data with a power law  $\Theta \propto V^n$ , for which  $d \ln \Theta / d \ln V = n$ . The experimental value, when evaluated around the midpoint of the molar volumes of our experiment, is of course insensitive to the choice of the fitting function. A fitting function  $\Theta \propto V^{-19/6} \times \exp(-bV^{-5/3})$  similar to Roger's theoretical expression would yield  $10.9 \pm 2.4$  for 18.8 cm<sup>3</sup>/mol, roughly the midpoint of all the data points shown in Fig. 3. Even a simple linear function would give  $10.3 \pm 2.9$  for the same molar volume.