PHYSICAL REVIEW A VOLUME 4, NUMBER 4 OCTOBER 1971

Nuclear-Magnetic Susceptibility of Solid He^3: A Nuclear Antiferromagnet*

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(Received 26 April 1971)

Measurements of the nuclear susceptibility of pure solid He^3 from 0.4 to 0.04 °K are described. The He^4 content of the sample was less than 10 ppm. The susceptibility is shown to obey a Curie-Weiss law $\chi = c/(T-\Theta)$ with $\Theta = -1.5 \times 10^{-3}$ °K for a molar volume v of 23.3 cm^3/mole, $\Theta = -4 \times 10^{-3}$ °K for $v = 23.6$ cm^3/mole, and $\Theta = -5.4 \times 10^{-3}$ °K for $v = 24.2$ cm^3/mole. The negative values for Θ mean that solid He^3 nuclei should order antiferromagnetically at very low temperatures and low magnetic fields. The experimental data are compared with current theories and other experiments.

I. INTRODUCTION

Although the nuclear-magnetic properties of solid He^3 have been under intensive theoretical[1-11] and experimental[12-38] study for many years, it has only been quite recently that consistent results for the nuclear-spin-exchange energy J have been obtained experimentally.[20,26,31,32,33,35] The interest in solid He^3 is due to the fact that it is the only nuclear paramagnetic solid which should show appreciable nuclear-spin ordering at experimentally realizable temperatures. In most solids the dominant interaction between nuclear spins is the dipole-dipole interaction which should not produce nuclear ordering above temperatures of about 10^{-6} °K. However, in solid He^3 the large zero-point motion enhances the spin-exchange interaction such that the ordering temperature can be expected to be the order of 10^{-3} °K.[1-11]

The most straightforward method of obtaining both the sign and magnitude of J is by measurement of the nuclear susceptibility as a function of temperature. At temperatures well above the nuclear ordering temperature, the nuclear susceptibility is expected to follow a Curie-Weiss law,

$$\chi = C/(T-\Theta) , \tag{1}$$

where C is a constant and the Weiss constant Θ is related to J by

$$\Theta = \tfrac{1}{2} zJ/k , \tag{2}$$

z being the nearest-neighbor number and k the Boltzmann constant. The work described here was done on the bcc structure so that z is 8. A negative value of Θ (and hence J) would mean that the ordering will be antiferromagnetic and a positive value would mean it will be ferromagnetic.

Early nuclear susceptibility measurements[12,13,16,23] yielded various inconclusive results. Tendencies toward both antiferromagnetic and ferromagnetic behavior were seen with ordering temperatures as high as 0.2 °K.[2,10] It is now known that many of those early measurements were made on samples that contained considerable He^4 impurity. The effects of He^4 impurities on the exchange energy are very poorly understood and only recently have careful measurements of solid mixtures of He^3 and He^4 begun to clarify the situation.[10,11,21,22,27,28,34,37,38]

Values for the absolute value of J in solid He^3 have been derived from nuclear-spin-relaxation measurements[14,17,18] as well as from thermal-expansion coefficients.[20,29,36] These measurements predict ordering temperatures varying from a few tenths of a millidegree Kelvin up to a few millidegrees Kelvin, but are unable to give the sign of the exchange energy and hence the type of ordering.

With the preceding facts in mind, we have prepared a sample of He^3 with a He^4 impurity level no greater than 10 ppm and have used this sample for nuclear susceptibility measurements. The susceptibility was measured by NMR techniques in the temperature range 0.4–0.04 °K. We have been particularly careful to establish thermal equilibrium. Since theoretical calculations[1,2,7,8] predict the exchange energy to be largest at low densities, we have confined the measurements to the low-density region ($23.0 < v < 24.2$ cm^3/mole). The results of this work have been previously reported.[31]

II. EXPERIMENTAL

A. Purification of He^3 Sample

The He^3 sample was purified by fractional distillation at 1 °K. The apparatus used for the purification was constructed by Cohen according to the design of Sherman.[39] The initial purity of the He^3 gas before distillation was about 0.5% He^4. The He^4 content was reduced after one distillation to 3×10^{-4}. A second distillation reduced the He^4 impurity to 1×10^{-5}. Although purities as high as 5×10^{-7} have been achieved with this apparatus[21] we were unable to produce such a high purity.

The He^4 impurity of the sample was measured using a specially modified CVC 24-210B mass-spectrometer leak detector. This leak detector

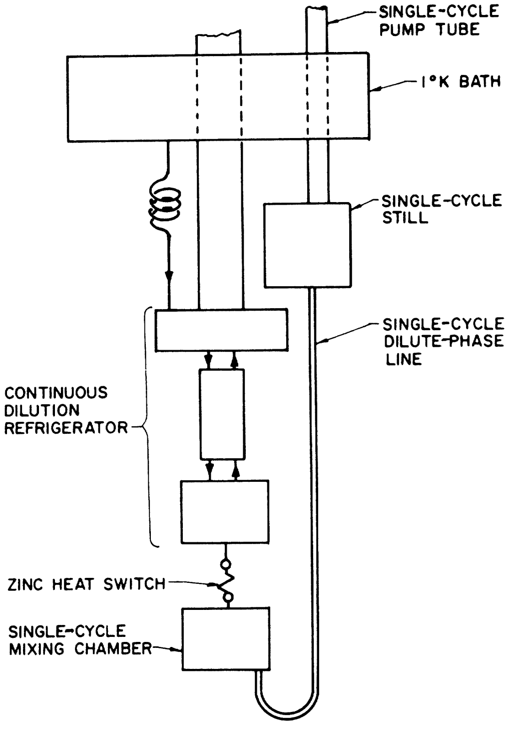

FIG. 1. Schematic of two-stage dilution refrigerator.

had been extensively checked for linearity with respect to total and partial pressures. The purity of the sample gas was measured both before and after the experimental runs.

B. He^3-He^4 Dilution Refrigerator

The apparatus upon which the experimental measurements were made consisted of a two-stage He^3-He^4 dilution refrigeration system. A schematic of the refrigeration system is shown in Fig. 1. At the time these measurements were made, the single-cycle refrigerator was only in the early experimental stage and, hence, was not used. Only the continuous-dilution refrigerator was used so that the heat switch between the mixing chambers was always kept in the normal state during the measurements. We shall limit the description to the continuous-dilution refrigerator.

Since the principles of dilution refrigeration have been adequately covered in the literature (see, for example, Wheatley, Vilches, and Abel[40]), we shall just give the general characteristics of our refrigerator. The refrigerator is described in detail elsewhere.[41]

The pumping system for the refrigerator consists of an NRC-B4 diffusion pump backed by a Welch 1397B forepump. The only modification of the forepump which was necessary in order to make it leak-free was the replacement of the paper gasket on the rear oil casing by a neoprene gasket. The factory shaft seal is completely adequate. This pumping system, together with the pumping lines, allowed a maximum circulation rate of about 10^{-4} mole/sec. The optimum circulation rate was found empirically to be 2×10^{-5} mole/sec.

An assembly diagram of the continuous refrigerator is shown in Fig. 2. The configuration shown was used during tests of the refrigerator in which a cerium magnesium nitrate (CMN) magnetic thermometer was used. The still has a volume of 85 cm^3 and a diameter-to-height ratio of 4. A 1.6-mm orifice is machined in the top of the still to limit the superfluid film flow into the pump tube. The heater for the still is a 200-Ω $\frac{1}{2}$-W Speer grade 1002 carbon resistor which is glued with GE 7031 varnish to the outside surface. The temperature of the still is monitored with another similar resistor. When the refrigerator is running, the typical He^4 concentration in the circulated gas is about 4%.

The heat exchanger is a modular-type exchanger with sintered copper as the contact medium. There are four identical heat exchangers which are sealed to the refrigerator by means of indium O rings. It might be remarked here that the refrigerator is completely demountable, each component being sealed by means of flanges and indium O rings. This allows continuing improvement of the refrigerator as well as easy adaptation to different experiments.

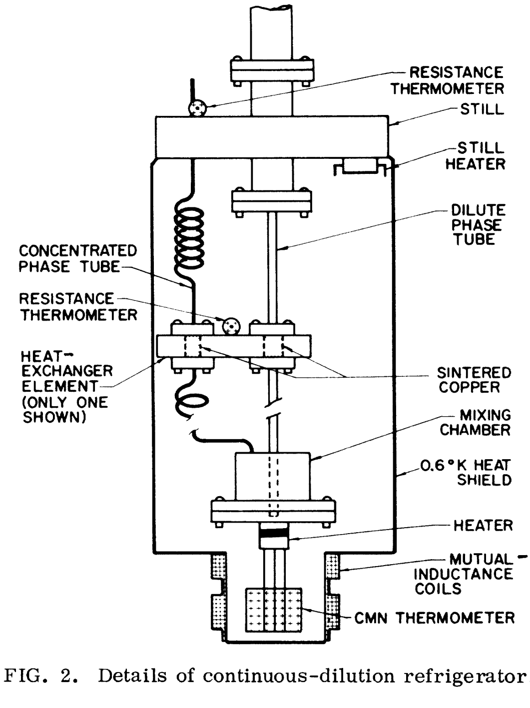

FIG. 2. Details of continuous-dilution refrigerator.

The mixing chamber is made of oxygen-free high-conductivity (OFHC) copper, has a volume of 12 cm^3, and has copper powder sintered into it for thermal contact to the liquid. The bottom of the mixing chamber is removable to facilitate the mounting of experimental samples.

A typical operating characteristic of the refrigerator is shown in Fig. 3. The temperatures are measured on the outside of the mixing chamber. The minimum temperature obtained in continuous operation is 0.025 °K and a temperature of 0.020 °K can be maintained for short periods in transient operation. The temperatures reached during the measurements on solid He^3 were limited to about 0.040 °K by the complications caused by the presence of the second-stage dilution refrigerator mixing chamber.

C. Sample

The apparatus in the region of the sample chamber is shown in Fig. 4. It was necessary to separate the sample chamber from the single-cycle mixing chamber so that the magnetic fields used for the NMR would not interfere with the operation of the superconducting zinc heat switch. The rather complicated offset of the sample chamber is necessitated by the magnetic field configuration. The sample chamber fitting (see Fig. 4) contains 0.5 g of sintered copper sponge for the thermal contact to the sample. This sponge has a surface area of about 100 cm^2. The filling capillary is mounted so that the sample must flow through the sintered copper sponge upon entering the sample chamber.

The sample chamber itself is made of nylon and screws directly onto the sample chamber fitting, the high-pressure seal being made by differential thermal contraction of the sample chamber and the fitting. It has a volume of about 2×10^{-2} cm^3. The rf coil for the nuclear resonance on the He^3 is wound directly onto a coil form machined into the outside of the chamber.

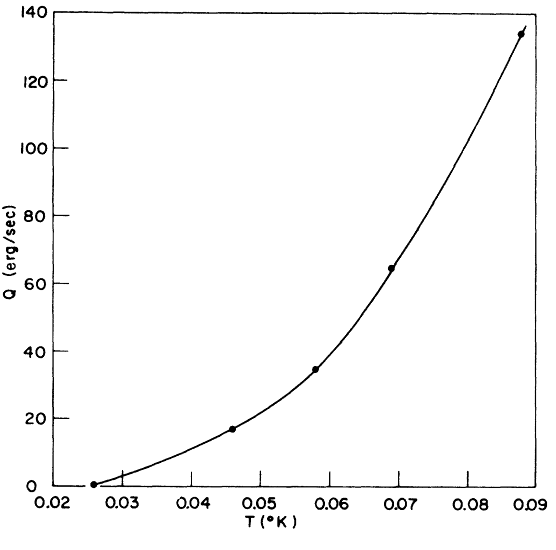

FIG. 3. Heat extraction capability of the continuous-dilution refrigerator as a function of the mixing chamber temperature.

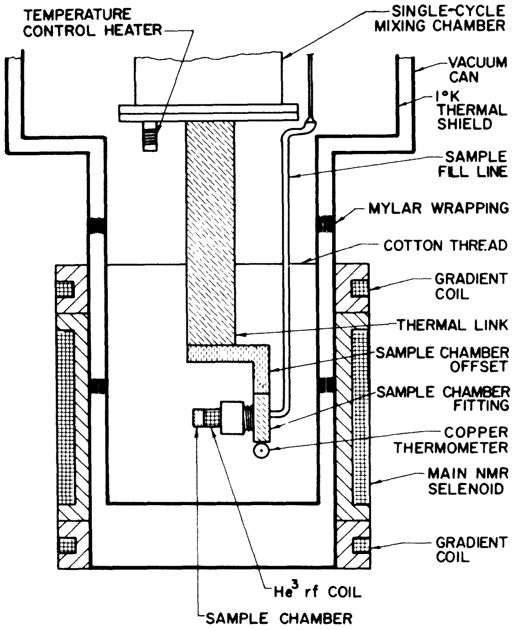

FIG. 4. Details of the sample region.

Thermometry is accomplished in this experiment by measuring the nuclear susceptibility of a small bundle of No. 56 B & S gauge copper wires which are soldered with pure zinc to the sample fitting. Since zinc is normal in the 1000-G field of the NMR solenoid, the thermometer is in good contact with the sample. The copper thermometer is calibrated at 0.4 °K against a previously calibrated carbon resistor. The rf coil for the nuclear resonance on the copper is wound on a nylon former which is pushed over the bundle of wires.

The main NMR solenoid is a sixth-order corrected solenoid[42] producing a 1000-G field in which both the He^3 NMR and the thermometry are done. This solenoid is operated in the persistent mode and has a provision for sweeping the field over a range of about 10 G. At each end of the main NMR solenoid is one member of a gradient coil pair. This gradient pair is superconducting and also operated in the persistent mode. It produces a field gradient of about 150 mG/mm A at the center of the main solenoid. The purpose of the gradient pair is to control the linewidth of the He^3 absorption signal to avoid large radiation damping corrections.[43] If V_0 is the rf carrier voltage and ΔV

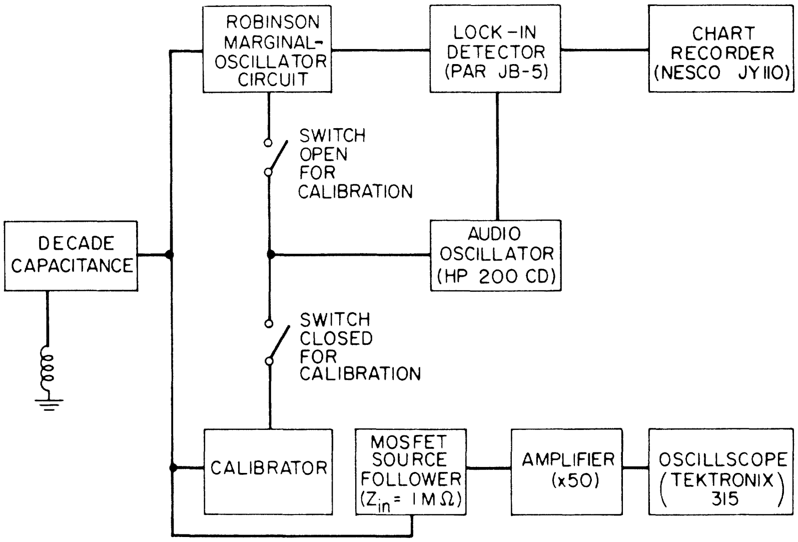

FIG. 5. Block diagram of the electronics for measuring the nuclear-magnetic susceptibility of the copper thermometer.

is the height of the He^3 absorption signal, then the radiation damping correction to the nuclear susceptibility is $(1-\Delta V/V_0)^{-1}$. $\Delta V/V_0$ was kept below 0.1 in all the experiments.

D. Electronics

A block diagram of the electronics used to measure the nuclear susceptibility of the copper thermometer is shown in Fig. 5. The output of a frequency-modulated Robinson[44] oscillator operating at a center frequency of about 1 MHz is fed into a lock-in detector which is referenced at the modulation frequency of 400 Hz. The amplitude of the frequency modulation is slightly more than the NMR linewidth for copper. The calibrator is used to accurately change the level of oscillation; this level is also monitored on an oscilloscope. The output of the lock-in detector is recorded on a chart recorder. The height of the recorded absorption signal is proportional to the nuclear susceptibility and hence inversely proportional to the absolute temperature. The constancy of the linewidth was carefully checked.

The nuclear absorption signal for the solid He^3 sample is detected with a modified Rollin circuit[45] operating at 3 MHz. A block diagram of this circuit is shown in Fig. 6. The constant-current generator (oscillator, attenuator, and a 100-kΩ thin-film resistor) feeds the He^3 rf circuit at its resonant frequency. The rf voltage across the He^3 coil is amplified by a high-impedance preamplifier and fed into a short-wave receiver. The receiver has been modified so that the output of the audio detector can be filtered and displayed on an oscilloscope with the carrier suppressed by a dc bias. In addition, the output of the receiver is monitored with a differential voltmeter so that the gain of the amplifier system can be kept constant to within $\pm\frac{1}{2}\%$.

As the magnetic field is swept slowly through the He^3 resonance signal, the NMR absorption signal appears on the oscilloscope and is photographed.

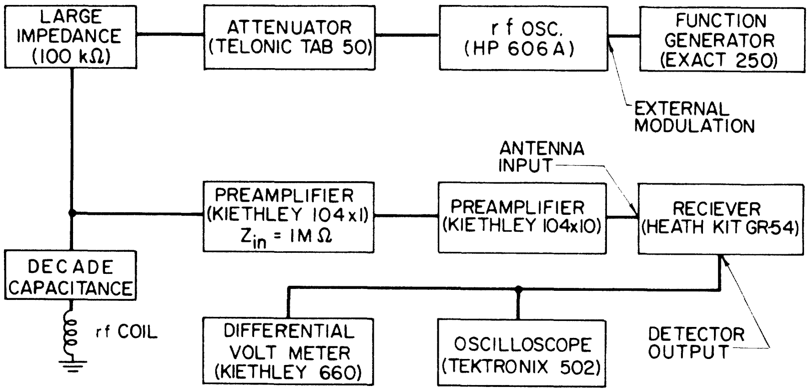

FIG. 6. Block diagram of the electronics for measuring the nuclear-magnetic susceptibility of the solid He^3.

The height of the signal is measured with vernier calipers and from this the relative nuclear susceptibility of the sample can be calculated.

To assure that the differential gain as well as the total gain of the system remains constant, a calibration system has been devised. The rf carrier can be modulated with a one-cycle sine-wave pulse from a function generator. The result of this after being detected is photographed along with the input pulse. The ratio of the heights of the output to the input pulse provides a differential gain calibration for the system.

E. Procedure

After the apparatus has reached 4.2 °K, the sample He^3 is introduced to the sample chamber and pressurized to the desired pressure. This pressure is determined approximately by the molar volume desired in the solid. The main NMR solenoid is turned on and the absorption signal in high-density He^3 fluid is observed. Cooling down to 1.5 °K is accomplished by introducing the He^3 – He^4 mixture to the continuous-dilution refrigerator to act as exchange gas between the 1 °K bath and the sample.

When the apparatus has come to equilibrium at 1.5 °K, very slow circulation of the continuous refrigerator is commenced. During the slow cool down from 1.5 °K the molar volume of the solid He^3 sample is measured. This is done as follows: The spin-lattice relaxation time for the high-density fluid is much longer than for the solid; thus, the nuclear resonance signal for the fluid is much more easily saturated than for the solid. Empirically it has been found that a level of 2 mV across the He^3 coil is sufficient to easily saturate the fluid signal, but not the solid signal. About 20% liquid in the solid can be detected this way. Thus, during the cooling, the level across the He^3 coil is set at 2 mV and the temperature at which no saturation can be observed is noted. This temperature is measured using a carbon resistor on the single-cycle mixing chamber. This resistor has been previously calibrated between 4.2 and 0.3 °K against He vapor pressures. Once the freezing temperature of the sample is known the molar volume of the sample can be determined from the works of

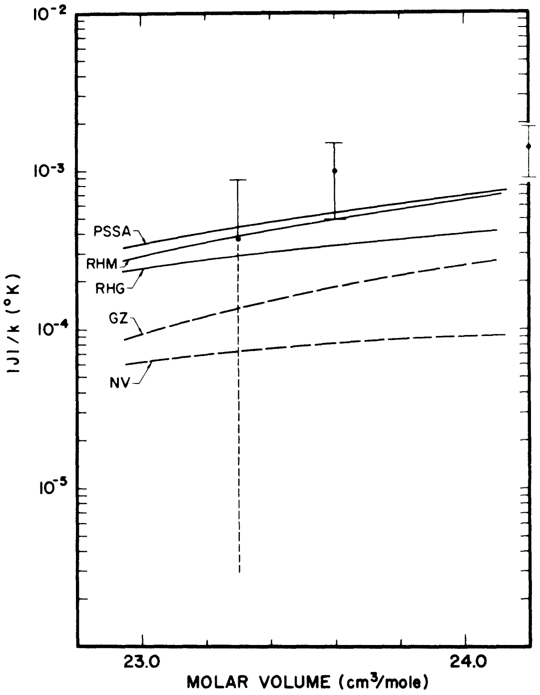

FIG. 8. Exchange parameter $|J|/k$ of solid He^3 vs molar volume. The solid curves are the experimental work of Panczyk *et al.* (Ref. 20) (PSSA), R. C. Richardson *et al.* (Ref. 17), and M. G. Richardson *et al.* (Ref. 18) (RHG). The dashed curves are the theoretical work of Guyer and Zane (Ref. 18) (GZ) and Nosanow and Varma (Ref. 7) (NV).

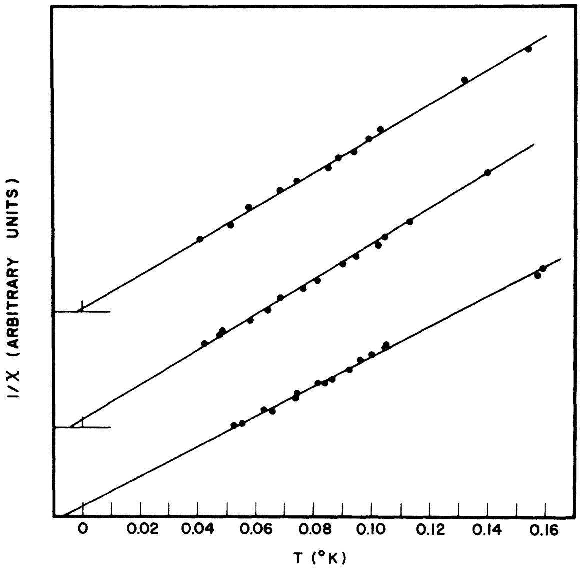

FIG. 7. Inverse susceptibility of solid He^3 vs temperature at molar volumes of 23.3, 23.6, and 24.2 cm^3/mole, reading from top to bottom.

TABLE I. The Weiss Θ's and exchange parameters J/k derived from least-squares fits to the data shown in Fig. 7.

Molar volume (cm^3/mole)	Weiss Θ (10^{-3} °K)	J/k (°K)
23.3 ± 0.2	-1.5 ± 2	$(-3.8 \pm 5) \times 10^{-4}$
23.6 ± 0.2	-4.0 ± 2	$(-1.0 \pm 0.5) \times 10^{-3}$
24.2 ± 0.2	-5.4 ± 2	$(-1.4 \pm 0.5) \times 10^{-3}$

Grilly and Mills[46] and Sydoriak, Mills, and Grilly.[47]

The susceptibility has been measured for three molar volumes, 23.3, 23.6, and 24.2 cm^3/mole. The lowest of these is the most accurate since the sample was formed at constant volume by the blocked capillary method.[14] The two larger molar volumes probably represent lower bounds on the molar volumes because of the difficulty in estimating the freezing temperatures by the above method.

Once the molar volume of the sample has been measured, the level across the He^3 coil is reduced to 0.25 mV, the sample is cooled to 0.4 °K, and the temperature is stabilized there using the electrical heater on the single-cycle mixing chamber. The copper nuclear resonance circuits are tuned so that the copper signal is in the magnet sweep and 20 copper signals are taken. This is the calibration of the copper thermometer.

The sample is the cooled to 0.1 °K in steps of 0.05 °K. At each temperature the sample is allowed to come to equilibrium for 20 or 30 min and then data are taken. The data consist of 20 copper signals and nine He^3 pictures as well as level calibrations at each temperature.

At a temperature of 0.1 °K, the gradient coils are turned on to reduce the size of the He^3 signal and, hence, the radiation damping correction. Data are taken both before and after turning on the gradient coils.

The procedure below 0.1 °K is the same as before except the temperature steps are reduced to 0.01 °K. The rf levels on the He^3 and the copper thermometer coils are periodically varied over a factor of 4 to assure that the nuclear resonance signals are not being saturated. At some temperatures data are taken at widely separated times to check thermal equilibrium.

The procedure on the warm-up cycle is essentially the same as the above. An attempt is made to place the data points on the warm-up portion of the cycle between the cool-down points.

III. RESULTS AND DISCUSSION

The nuclear-magnetic susceptibility of solid He^3 has been measured at three different densities, corresponding to molar volumes of 23.3, 23.6, and 24.2 cm^3/mole. The precision of these values has been discussed above. The susceptibility measurements extend from 0.4 to 0.04 °K. Since it is expected that the nuclear susceptibility should follow a Curie-Weiss law, Eq. (1) is this temperature region, we should have

$$c/\chi = T - \Theta \quad . \tag{3}$$

Hence, by plotting $1/\chi$ vs T and drawing the best straight line through the points, the intercept on the T axis should give us the value of the Weiss Θ.

The data for the three molar volumes are shown in Fig. 7. Only the data below 0.2 °K are shown because this is the temperature region in which the signal-to-noise ratio for the copper thermometer is best and in which most of the data were taken. The data do fall on straight lines and, hence, within experimental scatter, solid He^3 does obey the Curie-Weiss law in this molar volume and temperature region.

The values for the Weiss Θ's, obtained from least-squares fits to the data and the corresponding values for the exchange parameter J/k, calculated from Eq. (2), are shown in Table I. The errors on the Weiss Θ's shown in Table I were obtained by determining the maximum- and minimum-sloped lines that could reasonably fit the data. This, we believe, gives quite generous values for the error limits.

The data agree qualitatively with theoretical predictions. J is negative and, hence, the ordering in the solid at very low temperatures should be antiferromagnetic. Also the tendency for $|J|$ to increase with increasing molar volume is evident. The comparison of the values of $|J|/k$ from this experiment and from other experimental and theoretical work is shown in Fig. 8.

The measurements reported here, combined with other recently reported susceptibility measurements,[32,33,35] form a compelling argument that at low magnetic fields, solid He^3 is a spin-$\frac{1}{2}$ Heisenberg antiferromagnet at very low temperatures. However, recent measurements in high magnetic fields[48] have shown that the thermodynamic properties of solid He^3 at very low temperatures are anomalous. Hence, it appears that the status of our understanding of solid He^3 is far from complete.

ACKNOWLEDGMENTS

The authors would like to express their appreciation for the technical assistance of Gilbert Hawkins, Larry A. Dietz, and Gerhard K. Sander. Numerous discussions with Dr. W. O. Hamilton were very helpful.

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[*] Research supported in part by the Army Research Office, Durham, the Center for Materials Research, Stanford University, and the National Science Foundation.

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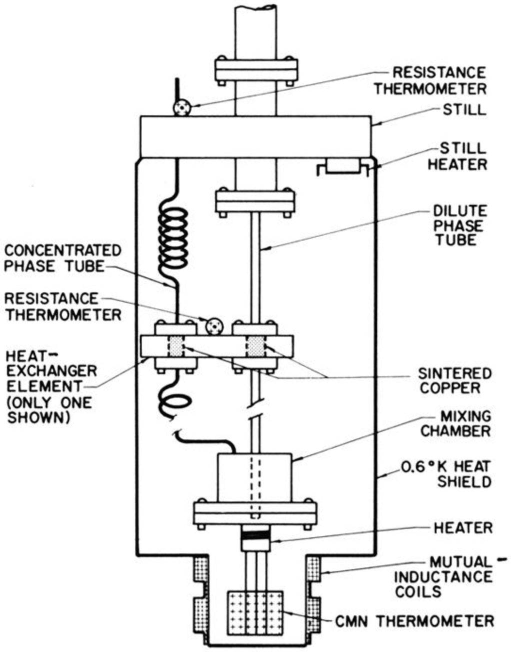

FIG. 2. Details of continuous-dilution refrigerator.