Nuclear Susceptibility of Solid Helium-3

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(Received 11 July 1963)

Measurements of the nuclear susceptibility of solid He³ in the α phase between 0.07 and 1.7°K are presented. The purity of this helium was better than 99.95%. All the results could be represented by a Curie-Weiss law $\chi = C(T+\theta)^{-1}$ indicating an antiferromagnetic exchange. While θ is smaller than about 10^{-2}°K at molar volumes larger than 22 cm³, it appears to increase systematically when the density increases further. The magnetic exchange between the nuclei, as deduced from our data, is fairly consistent at molar volumes above 22 cm³ with that obtained from specific heat and relaxation measurements. The higher density data, however, must be regarded as very tentative, in view of their disagreement with other data and theoretical expectations and are not presented in detail. Measurements of the longitudinal relaxation time were also carried out. In particular, for $V = 19.5$ cm³/mole, T_1 was found to increase approximately as $\exp(2/T)$ below 1°K, in contradiction with relaxation data of Reich, who found T_1 to be constant in this range. New susceptibility data are also presented for a solution of 99.0% He³ 1% He⁴ and a tentative explanation is given to account for the difference with the results on the "pure" He³. A method for measuring the pressure inside the solid He³ cavity is described. On the basis of these measurements, it is argued that the phase boundary in the V-T plane is unlikely to bend upwards at temperatures below 0.8°K, as deduced from Reich's relaxation measurements.

I. INTRODUCTION

IN the last few years, there have been several theoretical[1,2] and experimental attempts[3–10] to determine the magnetic exchange interaction between the nuclear spins in solid helium-3. Experimentally, the exchange interaction can be obtained in several different ways, namely, by specific heat, susceptibility measurements, and from relaxation measurements in nuclear magnetic resonance experiments. We shall discuss briefly these methods. Let us assume an isotropic exchange between two nuclei given by the Hamiltonian

$$\mathcal{3C} = -2J\mathbf{I}_1 \cdot \mathbf{I}_2, \qquad (1)$$

I is the nuclear spin, which for helium-3 is $\frac{1}{2}$. Then, in the specific heat there will be, in addition to the lattice

contribution, a term C_M due to exchange which, for $J/k \ll T$, will be equal to

$$C_M = \frac{z}{2} I(I+1)\left(\frac{J}{k}\right)^2 \frac{k}{T^2} = \frac{3}{8}z\left(\frac{J}{k}\right)^2 \frac{k}{T^2}, \qquad (2)$$

assuming the exchange to take place only between a central nucleus and its z nearest neighbors. If this term C_M can be isolated from the other contributions, the absolute value of J/k is determined. In magnetic susceptibility measurements, one will have for $J/k \ll T$ a Curie-Weiss law. For $I = \frac{1}{2}$, the susceptibility per atom will be given by the expression

$$\chi = \frac{\mu^2}{kT}\left[1 - \frac{z}{2}\left(\frac{J}{kT}\right) + O\left(\frac{J}{kT}\right)^2 + \cdots\right] \approx \frac{C}{T+\theta}, \qquad (3)$$

where μ is the nuclear moment of He³, $C = \mu^2/k$ is the Curie constant, and $\theta = (z/2)(J/k)$. Hence, from the susceptibility, one derives both the sign and magnitude of J/k. Provided that spins and lattice are in good thermal equilibrium during the measurements, specific heat and susceptibility data can be analyzed in a straightforward way without additional assumptions. If, for example, (J/k) is of the order of a few millidegrees or smaller, one has to carry out the measurements at temperatures lower than say 0.1°K in order to determine J with accuracy. There the lattice contribution to the specific heat becomes small and the departure from Curie's law becomes noticeable. Below temperatures of the order of 0.05°K, measurements may become rather arduous, because of the difficulty of attaining rapid thermal equilibrium between the thermometer and the sample and also because the specific heat of the thermometer, usually cerium magnesium nitrate, can become larger than that of the sample. Also, at these temperatures, there might be a contribution to the specific heat due to phase separation[4] for samples that have a

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[1] N. Bernardes and H. Primakoff, Phys. Rev. **119**, 968 (1960).

[2] E. M. Saunders, Phys. Rev. **126**, 1724 (1962).

[3] D. O. Edwards, J. L. Baum, D. F. Brewer, J. G. Daunt, and A. S. McWilliams, *Helium Three*, edited by J. G. Daunt (Ohio State University Press, 1960), p. 126.

[4] D. O. Edwards, A. S. McWilliams, and J. G. Daunt, Phys. Rev. Letters **9**, 195 (1962); Phys. Letters **1**, 218 (1962).

[5] G. Zimmerman, H. A. Fairbank, M. Strongin, and B. Bertman, Bull. Am. Phys. Soc. **8**, 91 (1963).

[6] H. A. Reich, Phys. Rev. **129**, 630 (1963). Due to a numerical error, all the values of J derived from T_2 data, have to be divided by 2π. Also, the factor 1.26 in his formula has to be substituted by 1.456. We are grateful to Dr. Reich for drawing our attention to these corrections.

[7] R. L. Garwin and A. Landesman, in *Proceedings of the Eighth International Congress on Low-Temperature Physics, London 1962* (unpublished).

[8] J. M. Goodkind and W. M. Fairbank, in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, 1960), p. 52.

[9] W. M. Fairbank and E. D. Adams, in *Proceedings of the Kamerlingh-Onnes Conference on Low Temperature Physics, Leiden, Holland, 1958*, Suppl. Physica **24**, 134 (1958).

[10] E. D. Adams, H. Meyer, and W. M. Fairbank, in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, 1960), p. 57.

purity of about 99.98%, which is the highest purity of He³ used recently.

In nuclear magnetic relaxation measurements, on the other hand, one can derive the exchange integral from the values of the longitudinal and transversal relaxation times T_1 and T_2 at more easily attainable temperatures. Assuming that one can treat solid He³ as a rigid lattice of point ions (an assumption that becomes more valid as the density increases) one can determine J from the exchange narrowing of the nuclear-resonance line, provided that no other effect contributes to this narrowing. The theory of exchange narrowing from electron-spin resonance was developed by Anderson and Weiss[11] using the second and fourth moments calculated by Van Vleck.[12] It was first applied to nuclear magnetic resonance (NMR) results by Goodkind and Fairbank,[8] and later by Reich,[6] for the analysis of line narrowing. One obtains[6]

$$J = \frac{h(T_2)_{\text{obs}}}{2\pi \times 1.456(T_2')^2_{\text{calc}}} \text{ ergs},\qquad(4)$$

where $(T_2')_{\text{calc}}$ is that calculated for dipole-dipole interaction for a rigid lattice. According to Reich's calculations,

$$T_2' = 2.102 \times 10^{-6} \, V \quad (\text{sec}) \quad \text{bcc phase},$$
$$T_2' = 2.980 \times 10^{-6} \, V \quad (\text{sec}) \quad \text{hcp phase}.$$

If $J > \mu H_0$ where H_0 is the applied magnetic field, the values of J/k obtained from Eq. (4) may have to be multiplied[11] by a factor 10/3. On the other hand, from the magnetic field dependence of the longitudinal relaxation time T_1, when T_1 is temperature-independent, Reich[6] finds for small enough fields

$$T_1 \propto \exp[(\mu H_0)^2/2J^2],\qquad(5)$$

from which J is derived. Using a more complete calculation due to Hartman,[13] which gives the exchange J as a function of T_1, Reich claims a reasonable consistency between the values of J as obtained, respectively, from T_1 and T_2. These results will be discussed later together with those obtained from the other methods.

The first susceptibility measurements in solid He³ down to 0.15°K were reported by Fairbank and Walters.[14] These authors used a Rollin type circuit and the susceptibility was obtained from the height of the NMR absorption at a frequency of 30 Mc/sec, in the same way as for the liquid.[15] The curve shown in their publication showed a departure from Curie's law. However, there were other unpublished curves obtained by these authors, and also by Adams and Fairbank[9] that showed

the susceptibility to have a value sometimes above, sometimes below that of Curie's law. These data were not found to be reproducible. In a few instances, Curie's law was obtained over the whole temperature range. After some improvements in the cryostat and a change of the resonance frequency from 30 to 3 Mc/sec, the susceptibility was measured at several densities down to about 0.07°K by Adams, Meyer and Fairbank.[10] While Curie's law was approximately followed for molar volumes above about 23 cm³, the deviation from this law became very noticeable at smaller molar volumes. When helium-3 was solidified from a starting pressure of 68 atm, the susceptibility was even found to pass over a maximum at about 0.1°K. At higher densities, it took about one hour after adiabatic demagnetization before the susceptibility reached a constant value and there were indications that a rather long period was needed to cool the sample. Therefore, measurements were not carried out at molar volumes smaller than 20.5 cm³. The observed effects were at that time thought to be due to a possible antiferromagnetic alignment of the spins, although the susceptibility at higher temperatures did not follow Eq. (3) and several other aspects were unclear. On the other hand, the specific heat measurements of Edwards et al.[4] indicated that $|J/k|$ was smaller than 2.10^{-3} °K. Also, the relaxation measurements of Goodkind and Fairbank[8] showed that J/k for a molar volume of about 20 cm³ was less than 10^{-4} to 10^{-5} °K. This estimate was later confirmed by the measurements of Reich.[6] Hence, while there was fair agreement between the experiments at low densities, the susceptibility results[10] were clearly inconsistent with the other results at molar volumes smaller than 23 cm³/mole. At the time when the susceptibility experiments were carried out, the purity of the helium-3 was checked simply by measuring the saturated vapor pressure of the liquid at several temperatures. It was concluded that the He³ was, at any rate, pure to within 99%. Also at that time, a slight amount of the diamagnetic He⁴ was not expected to affect the susceptibility results appreciably. A later mass spectrometric analysis showed that the He³ with which the measurements had been carried out contained 1% of He⁴. Hence, it appeared possible that the discrepancies between specific heat and susceptibility could be traced back to differences in sample purity, especially as recent calorimetric work on dilute solutions of He⁴ in He³ showed a phase separation in the solid rendered visible by a specific heat[4] maximum. The previous interpretation of the susceptibility results obtained before[10] is hence doubtful.

In this paper we present new susceptibility measurements in solid helium with a purity of better than 99.95%.[16] The measurements were carried out between

[11] P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1953).

[12] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

[13] S. R. Hartman (to be published) and private communication.

[14] G. K. Walters and W. M. Fairbank, in *Symposium on Solid and Liquid Helium-3, Columbus, 1957* (Ohio State University Press, Columbus, Ohio, 1958), p. 99.

[15] W. M. Fairbank and K. G. Walters, in *Symposium on Solid and Liquid Helium-3, Columbus, 1957* (Ohio State University Press, Columbus, Ohio, 1958), p. 205.

[16] The helium-3 was supplied by Monsanto Chemical Company. Their mass spectrometric analysis, as well as ours on a Consolidated Nier spectrometer did not show any trace of He⁴. Hence, we estimate the purity of our He³ to be better than 99.95%.

FIG. 1. The nylon and copper cavities with the manganin pressure gauge.

COPPER CAVITY   NYLON CAVITY
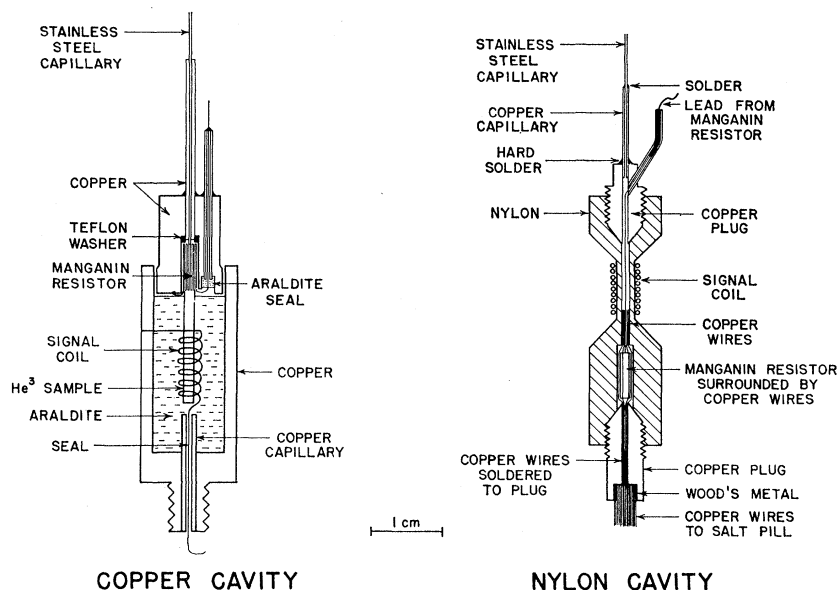
about 0.07°K and 1.5°K in the α phase and between 0.4°K and 2°K for one density in the β phase. It is clear that measurements at still lower temperatures will give a more accurate value of the exchange interaction which, for low densities, is of the order of a few milli-degrees or less. On the other hand, results near and in the β phase show already an apparent departure from Curie's law at temperatures of the order of 0.5°K, and some difficulties with the measurements occur there as mentioned later.

In addition, new results on the 1% He^4–He^3 solution are presented and a tentative explanation is given for their large discrepancy from those on pure He^3.

II. EXPERIMENTAL

A. The Cryostat

The cryostat with which the measurements were carried out is approximately the same as that described in previous communications.[10,17] He^3 is solidified in a cavity capable of withstanding a pressure of 2500 lb. The cavities used were of two different types, respectively of nylon and of copper, as shown in Fig. 1. Nylon cavities have been used successfully by Goodkind, Adams, Fairbank, and Cohen[18,19] for experiments on liquid He^3 and by Reich,[6] Garwin and Landesman[7] for measurements up to 500 atm. In our cavity, two copper plugs were screwed into the nylon, one plug being electrically grounded to the cryostat and connected to one end of a 10 000 Ω manganin resistance wire, the pressure gauge which will be described below.

[17] A. L. Thomson, H. Meyer, and E. D. Adams, Phys. Rev. 128, 509 (1962).
[18] J. M. Goodkind, E. D. Adams, D. Cohen, and W. M. Fairbank, in *Proceedings of the Eighth International Congress on Low-Temperature Physics, London, 1962* (to be published).
[19] E. D. Adams and J. M. Goodkind, Cryogenics 3, 83 (1963).

The other plug was used to bring out of the cavity the other end of the manganin wire. Copper wires (30 SWG) not shown on the Figure, were cemented with araldite to the lower plug and soldered to the upper one, hence establishing thermal contact between the upper and the lower plug. A bundle of 47 SWG copper wires extended within the cavity to bring the helium-3 into good thermal equilibrium with the paramagnetic salt. This nylon cavity worked satisfactorily during several experiments, but after a number of cooling cycles it cracked. It was finally decided to use a copper cavity as previously described by Adams, Meyer, and Fairbank,[10] but having a copper cap large enough for inserting the pressure gauge. One lead of this gauge was grounded to the cap, the other left the cap through an araldite seal. The cap was soldered to the body of the cavity with 99.9% pure indium. Since indium is in its normal state in a field of 1000 G (gauss), as used for the nuclear resonance, a broadening of the line through an inhomogeneous field brought about by induced currents was avoided. Usually indium is taken as being a very plastic metal. However, at liquid helium temperatures, this seal was able to withstand pressures at least up to 170 atm over a surface of about 0.7 cm^2 without breaking. The nuclear susceptibility was again measured from the nuclear resonance absorption at 3.3 Mc/sec using the same circuit as before. It was noticed, however, in contrast to liquid helium-3, that at sufficiently high pressures and at temperatures below about 0.3°K, some broadening of the absorption line could occur. Therefore, as a measure of precaution, the susceptibility was determined both from the absorption height and from the area under the resonance absorption curve. Just as for the determinations from the absorption height, the nuclear susceptibility is not exactly proportional to the area, because of the damping of the resonant tank circuit. By carrying out a

calculation similar to that of Bruce, Norberg, and Pake,[20] we find that the susceptibility is given by

$$\chi \propto S(1 + (S/2\pi V_0 \Delta t) + \cdots), \quad (6)$$

where S is the area under the absorption curve, V_0 is the rf level and Δt is the time needed to sweep over the width of the line. The detailed calculation is presented in Appendix A. When the susceptibility is measured from the maximum absorption height, one has, for the Rollin-type circuit, the relation[20]

$$\chi \propto \Delta V/V_0[1 - (\Delta V/V_0)] \quad (7)$$

where ΔV is the maximum voltage drop during absorption. Because the susceptibility of solid He[3] follows approximately Curie's law, the absorption becomes large enough that with our tank circuit of $Q=16$ and the filling factor $\sim\frac{1}{3}$, the term $\Delta V/V_0$ can become 0.25 at 0.06°. To reduce this term, the inhomogeneity of the applied magnetic field was increased artificially so as to broaden the absorption line. The term $\Delta V/V_0$ was thus kept below 0.15 and the term $S/(2\pi V_0 \Delta t)$ below about 0.04 at the lowest temperatures. Because of the small relaxation time T_1 in the α phase, the rf level used there was often approximately 3 mV peak to peak and, hence, the signal-to-noise ratio was better than in the liquid where only 1 mV was used. However, for the measurements near the β-phase boundary and in the β phase, the relaxation time was found to be so long that rf levels of 1 mV and less had to be used. For every density, a check for saturation was carried out by measuring the absorption height as a function of the rf level. If the height was proportional to V_0 within say 1%, saturation was assumed to be negligible. The rf level at which the final data were taken was always half or less of that at which a just perceptible deviation from the straight line occurred. While the susceptibility measurements obtained from the maximum absorption height had a possible systematic error of about 3% or less, the area data are somewhat less reliable and showed more scatter, because of a slight drift of the dc magnetic field. This drift, due to shortcomings in the regulation of the power supply, could vary from one experiment to another. However, the susceptibility from both height and area was found to agree within the experimental scatter except at high densities and low temperatures when line broadening occurred.

B. The Strain Gauge

Solid He[3] was produced by having the liquid He[3] in the cavity solidify when the melting curve was reached. If the capillary leading to the cavity blocked immediately when the melting curve was reached, the density in the cavity stayed constant. From experiments with liquid He[3] above the minimum of the melting pressure curve, it was concluded, however, that some slippage of of the solid plug could occur in a certain pressure region.[17] In order to be certain about the quantity of He[3] present in the cavity, a pressure gauge was mounted inside the He sample container a few millimeters above the resonance coil. It consisted of a 0.03 cm diam enamel-insulated manganin wire of about 30 m length having a resistance of 10 000 Ω at temperatures below 4°K. The wire was folded many times until it formed a loose bundle of about 1 cm length and a diameter of 3 mm. The bundle, wrapped in a very thin sheet of mylar, was fitted loosely into the cavity, as shown in Fig. 1. Another manganin resistance wire, the dummy, matched to the first one within 20 Ω, was placed in a small copper container filled with Apiezon oil J and in good thermal contact with the cavity. The manganin resistance brought outside the cryostat via manganin leads constituted the two arms of a Wheatstone bridge operated at about 100 cps. The signal of unbalance was amplified by a turnable narrow-band amplifier and, after passing through a phase-sensitive detector, it was displayed on a chart recorder. The pressure coefficient of manganin was found to be $-1/R(dR/dP)=2.76 \times 10^{-6}$ atm^{-1} at 4°K and below, and with a power input of 20 ergs/min pressure changes of 0.5 atm could be detected with the external magnetic field turned off. When the field was on, a spurious noise was introduced that limited the accuracy to ± 1 atm. Higher resolution should be achieved with a better amplifier; however, this was not considered necessary in view of the uncertainties in other parts of our experiments. By doubling the voltage across the bridge, the resolution was of course increased by 2 but it was then found that some drifts occurred at temperatures below say 0.2°K. After the cavity had been heated in that temperature region, the pressure in the cavity had apparently changed and did not return to its original value. Such effects were absent at higher temperatures and were not found for heat inputs of 20 ergs/min, which were then always used below 0.5°K. The method of measuring the pressure by the piezoresistance of manganin has been standard at high pressures for a long time.[21] It is less sensitive than the elegant strain-gauge type measurements first used at these low temperatures by Edwards et al.[3] for their determination of the melting curve of He[3]. On the other hand, it can extend over a much larger pressure range since it is independent of the thickness of the cavity wall. Several other alloys and also a carbon resistor were tested at room temperature for their suitability as pressure gauges, and the results are given in Appendix B. None of these resistances were found to be as useful as manganin, although the coefficient $(1/R)(dR/dP)$ of the carbon resistor is far greater than that of manganin.

[20] C. R. Bruce, R. E. Norberg, and G. E. Pake, Phys. Rev. 104, 419 (1956).

[21] P. W. Bridgman, The Physics of High Pressure (G. Bell and Sons, London, 1949).

C. Performance of an Experiment

Once the whole cryostat was cooled to 4.2°K, the helium exchange gas in the space surrounding the cavity and the paramagnetic salt was pumped away for about one hour. The outer He⁴ bath was then cooled to a temperature below about 2°K, and the cavity was cooled to this temperature by condensing He³ into a small pot thermally connected to the cavity. From then on, exchange gas was not used again during the whole duration of the experiment, as thermal contact between the large He⁴ bath and the cavity was readily achieved by reflux of the liquid He³ into the small pot. When this liquid was completely pumped away, the thermal insulation of the sample from the bath was very satisfactory.

The manganin pressure gauge was then calibrated against an external Ashcroft test gauge over a certain pressure range in the liquid phase after cycling the pressure several times. The pressure was then held constant at a certain value P_0 and the cavity cooled until the melting curve for He³ was reached. As the cavity cooled further, the pressure inside the cavity was found to drop until a constant pressure P_1 was reached, which signified that there was only solid He³ in the cavity. Assuming that the capillary to the cavity blocked immediately when the melting curve was reached from the high-temperature side, the expected pressure in the cavity could be calculated from the known melting curve and the molar volumes in the liquid and solid phases.[22] This pressure was, in most cases, found to be equal to the measured P_1 within 0.5 atm. However, at pressures below about 45 atm P_1 was sometimes higher, indicating a slippage of the plug of solid helium in the capillary. From the measured P_1 the density of solid He³ was deduced using the PVT diagram of Mills and Grilly[23] along the melting curve. As the thermal expansion of He³ is very small, P_1 stayed practically constant within a given phase over the whole temperature range.

After demagnetization from 0.4°K, a final temperature of about 0.05°K was usually reached. The nuclear susceptibility of the solid helium-3 was then observed and was found to increase for about 10 min and finally tended to a constant value. In order to assure that the solid He³ had cooled to the temperature of the paramagnetic salt, data were only taken half an hour later and at temperatures above about 0.065°K. The cavity and the salt were heated from one temperature to the next by a small resistance wire wrapped around the salt pill. When the heat was switched on, the resonance-absorption height decreased immediately. After switching off the heat, it reached a steady value within five minutes, showing that there was good contact between the nuclear spins and the cavity. At temperatures above about 0.3°K the resistance of the manganin wire was

measured continuously, and a check calibration of the gauge was carried out after all the He³ in the cavity had been melted. Usually the pressure in the cavity read before and after the demagnetization agreed within experimental error.

In order to check if the nuclear susceptibility was proportional to the density at temperatures above 0.5°K, the susceptibility was measured for several densities during the same run between 1.5 and 0.5°K. This experiment is of course not as conveniently done as in the liquid, because for each new density, the cryostat has to be warmed to a temperature beyond the melting curve and cooled again. A heating wire for unblocking the capillary and squeezing more solid He³ into the cavity was not used, as it was feared that the crystallization under these conditions would not be as regular as under a slow cooling along the melting curve.

III. RESULTS

A. Pressure Measurements Near the α–β Phase Boundary

The phase boundary between the α and β phases has been measured accurately by Mills and Grilly[22] down to 1.8°K. Under the assumption that nothing anomalous happens at lower temperatures, one finds by extrapolation that, at temperatures below 0.5°K, the pressure at which the phase change occurs is constant and approximately 105 atm. If the boundary is crossed at higher temperatures while the density is kept constant, a change of pressure inside the cavity will be noticed. For instance, if the crossing takes place at a temperature of about 0.6°K, the pressure drop at constant volume in passing from the α into the β phase should be of the order of 1-2 atm, an amount our manganin pressure gauge will still detect. Should an anomalous bend occur in the transition curve, there would be the possibility of a substantially larger pressure drop. We have carried out pressure measurements at a molar volume of 20.2 cm³ ($P=97.5$ atm, α phase) and at 19.5 cm³ (110.8 atm, β phase below about 1.9°K) to see if by any chance the α-β phase boundary was crossed. From the difference in T_1 data (which will be described later) it was apparent that He³ at these two densities was indeed in two different phases. The measurements extended from 0.3°K upwards and showed no change of pressure within 1 atm until a temperature of about 2°K. There, for the molar volume of 19.5 cm³, the phase boundary was reached, as expected from Mills and Grilly's data.

Hence, we conclude that the α-β transition curve becomes horizontal in the P-T plane, the pressure below 0.5°K being between 98 and 110 atm. Recently, Heltemes and Swenson[23] reported specific heat measurements in solid α and β He³. Some measurements were taken at densities very near the phase-transition boundary. Had the boundary been crossed, a latent heat would have been observed. Also a change of the specific heat would have been noticed, because of the change

[22] E. R. Mills and R. L. Grilly, Ann. Phys. (N. Y.) **8**, 1 (1959).
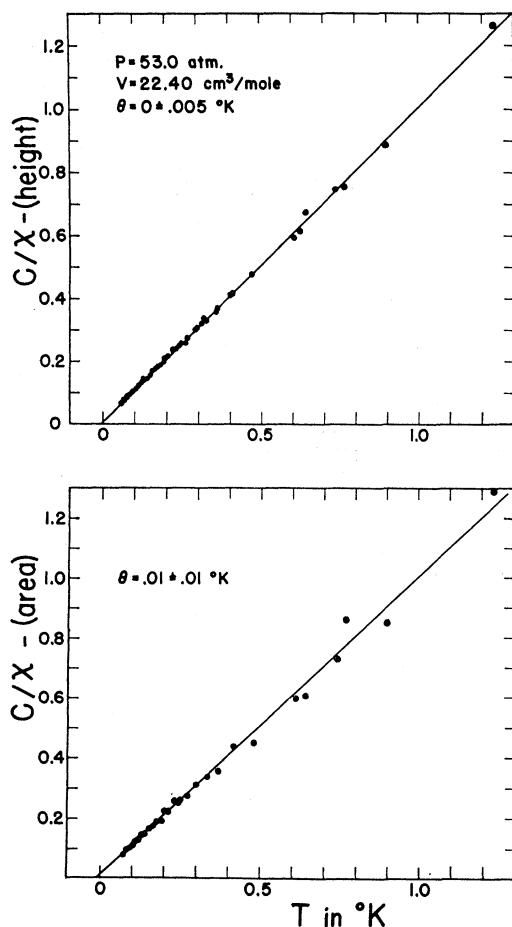[23] E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

FIG. 2. The susceptibility of solid helium-3 plotted as C/χ for $V=22.40$ cm³/mole as measured from the height and from the area under the absorption curve.

of the Debye Θ_D from one phase to the other. This was not the case and Heltemes and Swenson were able to determine the limiting pressure of the α-β curve at the low temperature end to be about 110 atm. While we could not determine this pressure as accurately, our conclusions are qualitatively the same. On the other hand, Reich[6] has deduced from his relaxation time measurements in solid He³ that the α-β phase boundary in the V-T plane bends sharply upward at temperatures
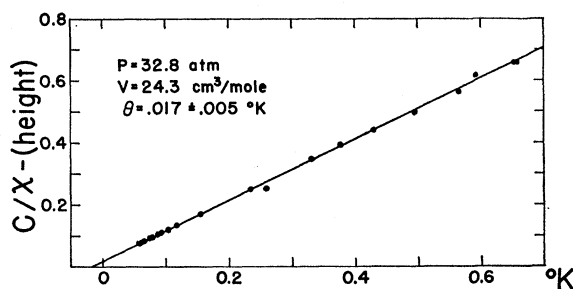
FIG. 3. The susceptibility of solid helium-3 plotted as C/χ for $V=24.3$ cm³/mole as measured from the height of absorption.

below about 0.7°K. This corresponds to a bending downwards of the phase boundary in the P-T plane in such a way that at 0.7°K and at 0.6°K the melting pressure is, respectively, 100 and 90 atm. This is inconsistent with specific heat measurements and with our own pressure data.

B. Susceptibility Measurements in "Pure" He³

It should be remembered that in our present measurements in solid He³ as well as in the previous experiments in liquid He³, [17,18] the susceptibility was obtained in arbitrary units. In the liquid, where the density could be varied very quickly by increasing the pressure at constant temperature, the susceptibility per mole above 1°K was found to be independent of the density and followed Curie's law. Hence, the ratio χ/C, where C is the Curie constant per atom was normalized to unity at 1.00°K. As mentioned before, the check to see if the susceptibility per mole of the solid is also independent of the density at a given temperature is less straightforward. Perhaps, because of this, there was some scatter in the results, but data taken for molar volumes of 23.7, 22.9, 21.8, 21.2 cm³ between 0.5 and 1.2°K showed that within about 5%, the susceptibility per mole was independent of the density. Hence, for the solid, the same normalization has been used for these densities.

In Figs. 2 and 3, we present some of the susceptibility curves taken at constant density as a function of T. Some of the low-density curves were taken with the nylon cavity, the others with the copper cavity. In Fig. 2, the susceptibility is plotted as C/χ against T for $V=22.4$ cm³/mole and one can see that within
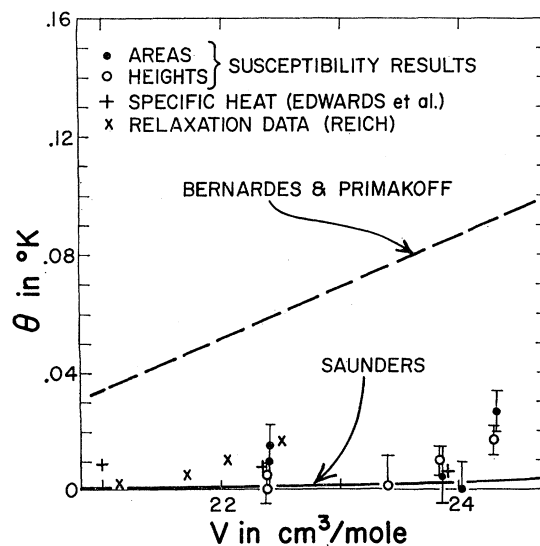

FIG. 4. The Weiss constant $\theta=zJ/2k$ plotted against molar volume and compared to other data. The points obtained from specific heat data. (Edwards et al. Ref. 4) are the upper limit for θ consistent with their measurements. Reich's values for θ were taken from his Table 2.

FIG. 5. Some of the susceptibility curves, plotted as C/χ for a 1% He⁴ solution in solid He³. Notice the maximum for a molar volume of 22.1 cm³. Such a maximum was found in a previous series of measurements (Ref. 10) for 22.5 cm³. The susceptibility for 24.6 cm³ seems not affected by the isotopic phase separation.
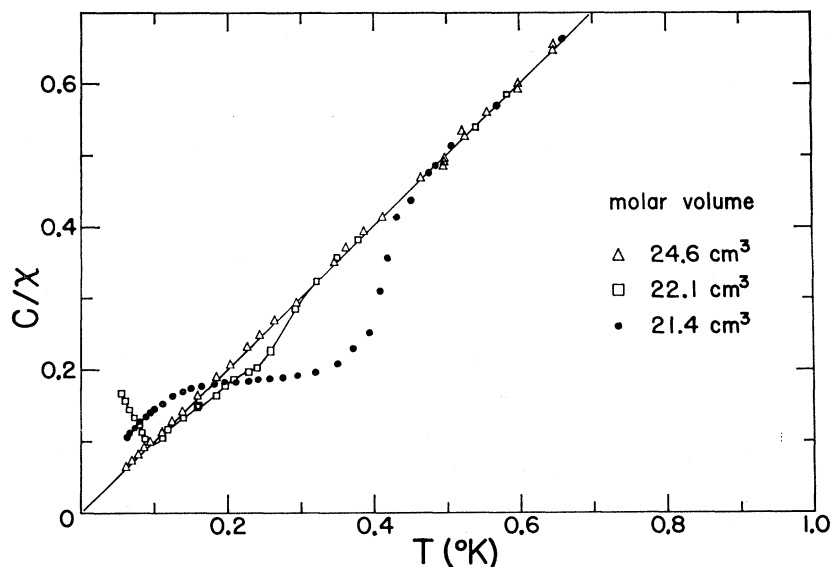
experimental error, Curie's law is followed. The same behavior was found for $V=23.85$ cm³/mole. At several densities, the susceptibility was found to be systematically lower than that according to Curie's law. Since there was a possibility that this departure is due to magnetic exchange interaction, as given in Eq. (3), the inverse C/χ was again plotted against T. Hence, the intercept of the curve will give the Weiss constant $\theta=z/2(J/k)$. It was found that the susceptibility indeed always followed a Curie-Weiss law and below 22 cm³/mole the apparent θ was found to increase systematically with density to a value of about 0.1°K at 19.5 cm³/mole. From the experiments it was concluded that there was good thermal contact between spins and the lattice at all temperatures and all densities, although it took about 5 min for this equilibrium to be reached at temperatures below 0.08°K. In Fig. 5 the Weiss constants derived from our susceptibility data for molar volumes larger than about 22 cm³ are compared to those derived from other experiments and those predicted theoretically. Data are also presented in Table I.

Measurements of the longitudinal relaxation time T_1 were carried out by the saturation technique.[15] With this method, relaxation times longer than about three seconds could be measured. In the α phase, T_1 was found to be smaller than this value except for $V=20.5$

cm³/mole at temperatures below 0.08°K where we found $T_1=150$ secs. Above 0.1°K, T_1 was smaller than 3 secs. Relaxation measurements below 0.1°K are not as conclusive as those at higher temperatures, because of the poorer thermal contact between the lattice and the heat sink, represented by the Chrome alum. The best relaxation measurements were those carried out between 0.4 and 1°K where the thermal contact between the heat sink and the lattice was still good and where the temperature could be kept constant over a long time. It was found that in the β phase for $V=19.5$ cm³/mole, T_1 increased rapidly with falling temperature its value being ~150 sec at 0.4°K. The results are summarized in Table II. Because of this strong increase varying very roughly as $\exp(2/T)$, it was feared that at still lower temperatures, T_1 would be so large as to saturate the resonance even at small rf powers. For this reason, no susceptibility data in the β phase were taken below 0.4°K. As T_1 is a strong function of the frequency at which resonance occurs,[6] future susceptibility experiments at high densities will have to be carried out at an appreciably lower frequency.

DISCUSSION

Bernardes and Primakoff[1] were the first to calculate the exchange integral in solid He³. They predicted that the exchange would be antiferromagnetic in the α

TABLE I. Values of the Curie-Weiss θ for solid He³ (determined mostly from the maximum height of the absorption curve).

Pressure inside cavity	Molar volume	θ
32.8 atm	24.3 cm³	0.017±0.005 °K
35.0	24.1	0.00 ±0.01
36.7	23.9	0.007±0.005
41.8	23.4	0.00 ±0.01
53.0	22.4	0.00 ±0.01
53.0	22.4	0.005±0.005

TABLE II. Value of T_1 for a pressure of 110.8 atm ($V=19.5$ cm³/mole).

T (°K)	T_1 (sec)
0.385	140
0.400	150, 130
0.59	52
0.68	28
1.20	≲3

phase, its absolute value decreasing with increasing density. Finally, at sufficiently high densities, the exchange would become ferromagnetic. For a molar volume of 24 cm³ they found $J/k=0.02°$K. In their calculations they assumed the lattice to have face-centered cubic structure. Bernardes and Primakoff's calculations were criticized by Nosanow and Shaw[24] who argued that single-particle wave functions were not acceptable for calculations dealing with both helium isotopes. Also, the expression for the exchange integral they used is different from that derived later by Herring[25] for a coupling between two spins. A more recent theoretical approach was made by Saunders[2] who calculated the exchange in the α phase taking correctly the structure to be body-centered cubic. Like Bernardes and Primakoff he used spherically symmetrical wave functions for the He³ nuclei. His results are also plotted in Fig. 4. He did not, however, carry out the calculations for the β phase where the crystalline structure is hcp. Some of his approximations in the use of an effective Hamiltonian were not rigorously justified and, hence, it is not easy to estimate the error in his calculation.

Edwards et al.[4] found from specific heat data that the exchange integral for all densities in the α phase was smaller than about $2\times10^{-3}°$K. It was also found that in the β phase ($V=19.45$ cm³/mole) J/k was smaller than about 0.7×10^{-3} °K. These results are consistent with those by Zimmerman, Fairbank, Strongin, and Bertman[5] who, in addition, made measurements in a field of 550 G. As mentioned before, relaxation measurements by Goodkind and Fairbank[8] also showed that J/k must be smaller than 10^{-4} to 10^{-5} °K at 20 cm³/mole. Anderson, Reese, and Wheatley[26] measured the susceptibility by spin-echo techniques at a pressure of 35 atm corresponding to 24 cm³/mole and found that Curie's law was obeyed within experimental error down to about $0.035°$K. The results obtained by Reich[6] from T_2 and the field dependence of T_1 show a steady decrease of J with increasing density. It should be remarked here that the J tabulated by Reich for the region when $J/k\gg\mu H_0/k=0.2\times10^{-3}$ °K should probably be multiplied by a factor of 10/3. Hence, we have plotted, in Fig. 5, Reich's values multiplied by this factor for molar volumes greater than 21 cm³. For molar volumes larger than 22.5 cm³, his exchange tends to values larger than that obtained by all the other experimenters. In this region especially, zero-point vibration is very large and, hence, the narrowing of the line from which the exchange was derived might be due to a certain extent to motional narrowing. In this case, the assumption of a rigid lattice of point ions on which the theory is based does not seem justified, but holds probably much better at high densities.

[24] L. R. Nosanow and G. L. Shaw, Phys. Rev. 128, 546 (1962).
[25] C. Herring, Rev. Mod. Phys. 34, 631 (1962).
[26] A. C. Anderson, W. Reese, and J. C. Wheatley, Phys. Rev. Letters 7, 366 (1961).

As far as our own results are concerned, they are reasonably consistent with the specific heat data and with Saunders theoretical prediction for molar volumes larger than 22 cm³. However, at higher densities, our apparent antiferromagnetic interaction increases rather strongly, while all the other experimental evidence and the theoretical predictions show that it should decrease. From the purely experimental point of view, the measurements at these higher densities seem to be just as reliable as those at the lower densities, because no noticeable time lags in the response of the nuclear resonance signal were encountered. Also, care was taken to avoid saturation as was mentioned before. However, as will be shown later, there is evidence from susceptibility data on samples containing 1% He⁴, that the apparent susceptibility is strongly affected at high densities by the phase separation. Therefore, it is conceivable that the high-density data for our "pure" sample are still influenced by a very small He⁴ amount, due perhaps to a slow process of isotopic separation. Hence, our data at molar volumes smaller than 22 cm³, reproducible as they are, have not been presented and this subject will hopefully be clarified by further investigations in this laboratory.

Our relaxation data at 19.5 cm³/mole can be compared to those of Reich at 19.47 and 19.32 cm³/mole taken at a frequency of 5.2 Mc/sec. According to Reich, T_1 is independent of the temperature below about $1.4°$K while our data, on the contrary, show that there is roughly an exponential variation with T^{-1} in the range between 1 and $0.4°$K. Our data would hence indicate some relaxation by some type of diffusion, the energy W for this diffusion being, however, only of the order of a few degrees K. This result is consistent with our data in the α phase and also with unpublished ones of Goodkind where it was found that T_1 at high densities in the α phase becomes large (of the order of 150 secs) at temperatures of about $0.1°$K.

Garwin and Landesman[7] report that at a molar volume of 18.7 cm³/mole the time needed to bring the spins in thermal equilibrium with the lattice, became very large as the temperature decreased, reaching a value of the order of 2000 min at $0.4°$K. This large time constant would be explained by an exchange interaction much larger than that derived from T_2 measurements. Such long relaxation times between lattice and spins were, however, not reported in Reich's experiments. Clearly, more work is needed to clarify the behavior of the longitudinal relaxation time.

Measurements on a Solid Solution 99% He³ – 1% He⁴

As mentioned in the Introduction, the susceptibility data reported earlier[10] were actually carried out on a 99% He³—1% He⁴ solid solution. These results showed some rather striking features and it was decided to repeat them. In the present experiments, the suscepti-

bility qualitatively reproduces the behavior shown before and it is drastically different from that for much purer He³. For comparison's sake, the susceptibility in Fig. 5 is plotted the same way as in the previous figures.

The explanation for this discrepancy may lie in the phase separation of solid solutions in He⁴ in He³ which was discovered recently by Edwards, McWilliams, and Daunt[4] from specific heat measurements and confirmed by Zimmerman, Fairbank, Strongin, and Bertman.[5] Edwards et al.[4] were able to analyze their data in terms of a phase separation similar to an order-disorder transformation with a sharp specific heat maximum. They were only able to obtain results at molar volumes larger than 24 cm³ since, at higher densities, it became very difficult to obtain reliable drift rates for their measurements, which were hence not analyzed. Also, the cooling rate of the sample after adiabatic demagnetization was rather peculiar.[27] These difficulties may be linked to those encountered by susceptibility measurements. It is possible that the heat to be removed from the sample at high densities to give the phase separation is appreciably larger than that found at densities near the minimum of the melting curve, which could explain the indication of a large specific heat as reported by Adams et al.[10] Also, the phase separation may proceed more slowly at high densities, so that disequilibrium effects become apparent. At molar volumes larger than 23 cm³/mole these effects are small in susceptibility measurements but already visible. Effects of phase separation at $V=21.4$ cm³/mole seem to extend up to 0.3°K, while according to Edwards et al., the phase separation takes place, at ~0.18°K for 1% He⁴ at a molar volume of about 24 cm³. Hence, there is probably a shift of this phenomenon towards higher temperatures when the density is increased, as suggested by recent specific heat measurements.[5] At any rate, the susceptibility measurements at molar volumes below 23 cm³ are not representative of the behavior of pure He³ and could be attributed to disequilibrium effects between the thermometer and the spins, although during our measurements a state of quasiequilibrium seemed always reached. A detailed analysis of the curves presented previously[10] and here (Fig. 5) cannot be made because the kinetics of the phase separation is not known. Arguments that the previously reported susceptibility data were in error because of disequilibrium have already been made by Garwin and Landesman[7] and by Reich,[6] who attributed them to thermal lags between the spins and the lattice of He³, but who were unaware of phase separation effects.

CONCLUSION

For solid He³ purer than 99.95%, nuclear susceptibility results are reasonably consistent with specific heat measurements and relaxation data for molar volumes larger than 22 cm³. At these low densities, they also agree with data on a 1% He⁴ solution as presented previously[10] and in this paper. At higher densities there appears a systematic discrepancy which might possibly be due to the presence of some He⁴ impurities. Hence, at the present time, these high-density data appear unconvincing and will have to await further confirmation. Clearly, a sizeable amount of work remains to be done to clarify the magnetic properties of solid He³. Research is in progress for the study of susceptibility and the relaxation time T_1 of pure He³ at pressures up to 1200 atm and at various frequencies between 0.06 and 4°K. More measurements with dilute solutions of He³ and He⁴ will also be carried out.

APPENDIX A

Calculation of the Experimental Susceptibility from the Area under the Absorption Curve

By making the external impedance large enough, care is taken that the rf current through the tank circuit in the Rollin detection system[28] is practically constant whether there is absorption or not. It can then be shown that the voltage across the tank circuit is[21]

$$V = V_0(1+4\pi fQ\chi''+i4\pi fQ\chi')^{-1}, \quad (A1)$$

where V_0 is the voltage when there is no absorption, f the filling factor of the coil, Q the quality factor, χ' and χ'', respectively, the real and imagninary parts of the nuclear magnetic susceptibility/cm³. This equation assumes that during resonance, the charge ΔL of the inductance of the tank circuit is much smaller than L, which is satisfied in our experiments. If one takes for χ' and χ'' the Bloch susceptibilities,[28] one obtains

$$V = V_0\left(1+\frac{a}{(1+y^2)}+\frac{iay}{(1+y^2)}+\cdots\right), \quad (A2)$$

where $a=2\pi fQ\omega_0T_2\chi$ and $y=(\omega-\omega_0)T_2$; $\omega/2\pi=$ frequency at the center of the absorption curve, and χ static nuclear susceptibility per cm³. In our circuit, the rf voltage V, after amplification in the i.f. strip, is rectified by a simple diode detector which registers the

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[27] D. O. Edwards (private communication).

[28] See, for instance, E. R. Andrew, in Nuclear Magnetic Resonance (Cambridge University Press, Cambridge, 1958).

magnitude of the signal, not its phase. Therefore, the observed height of the resonance curve at any time is $V_0 - |V|$. Using Eq. (A2), this is given to a good approximation by

$$V_0 - |V| = \frac{a(2+a)}{2(1+y^2)} - \frac{3}{8}\left[\frac{a(2+a)}{(1+y^2)}\right]^2 + \cdots. \quad (A3)$$

In order to observe resonance, the magnetic field is swept linearly with time. The area under the resonance curve, as observed on the oscilloscope is hence

$$S = \int_{-\infty}^{+\infty} (V_0 - |V|)d(t - t_0), \quad (A4)$$

where t_0 is the time when the absorption is at its maximum. This change in magnetic field with time has the same effect as a linear change in rf frequency with time. Therefore, we can put

$$S = K\int_{-\infty}^{+\infty} (V_0 - |V|)d(\omega - \omega_0), \quad (A5)$$

where K is a proportionality constant. Integration gives to a good approximation

$$S = (KaV\pi/T_2)(1 - a/4 + \cdots). \quad (A6)$$

Solving for the susceptibility χ and remembering that $T_2 = (|\omega_{\frac{1}{2}} - \omega_0|)^{-1}$ where $\omega_{\frac{1}{2}}$ is the frequency at which χ'' has half the maximum value one finds

$$\chi \propto S\left(1 + \frac{S}{2\pi V_0 \Delta t} + \cdots\right), \quad (A7)$$

where Δt is the time taken to sweep from one-half

maximum absorption to the other one. The second term in the brackets is kept small and is only of the order of about 0.04 at the lowest temperatures. A similar calculation has been carried out by Norberg, Bruce, and Pake[20] for a rf bridge detection system, where the voltage V_θ is approximately compensated. Under these conditions, the susceptibility is shown to be exactly proportional to the area, subject to the assumptions made previously.

APPENDIX B

Piezoresistance of Some Materials

Several alloys and one carbon resistor were tested for their suitability as a pressure sensitive resistor. The alloys, Formvar or enamel insulated, were kindly supplied free of charge by Driver Harris Company, Bridgeport, Connecticut. Although manganin wire has been used for a long time as a pressure gauge, its relative resistance change with pressure is rather low and it was hoped to find among new alloys one with a higher sensitivity. Cupron, the 240 Ω Speer carbon resistor and of course manganin showed over the whole pressure range (0-170 atm) a linear decrease of R with increasing P, $1/R\, dR/dP$ being respectively -1.9×10^{-7}, -1.33×10^{-4} and -2.54×10^{-6} at room temperature. At 77°K and at temperatures below 4°K, this coefficient for manganin was, respectively, -2.60×10^{-6} and -2.75×10^{-6}. Tophet A, Evanohm, and Karma did not have a linear pressure variation, Tophet A being practically unaffected by pressure. Karma, however, had a relative resistance change of about 3×10^{-5} and might possibly be of use as a pressure gauge if suitably calibrated. The carbon resistor, although very sensitive to pressure changes, is not suitable at low temperatures because of the large temperature dependence of the resistance.