

FIG. 1. Attenuation of sound in liquid helium. Solid curve, earlier results (reference 1); circles, present results (12.1 Mc/sec).

The circles represent the experimental points; the full curve indicates the results of earlier measurements.<sup>1</sup> The twin maxima in the attenuation in the neighborhood of 0.9°K are clearly resolved, and provide direct evidence for the existence of two distinct relaxation times in agreement with the prediction of Khalatnikov.<sup>2,3</sup> A full report will be published shortly.

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### Remark Concerning the Absolute Value of Avogadro's Number

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IN an earlier article<sup>1</sup> it was proposed to accept for x-ray work the value of

$$N_0 = 0.602567 \times 10^{24} \text{ (phys) or } 0.602403 \times 10^{24} \text{ (g mole)}^{-1} \text{ (chem)} \quad (1)$$

for Avogadro's number, for reasons explained in detail in the article.

DuMond and Cohen<sup>2</sup> have recommended the value

$$N_{\text{universal}} = (0.602472 \pm 0.000036) \times 10^{24} \text{ (g mole)}^{-1} \text{ (phys)} \quad (2)$$

for the same and other purposes. However they did not mention that their method of computation gave also a new conversion factor,<sup>3</sup>  $\lambda_g/\lambda_s = 1.002063$ , instead of the now generally accepted value 1.00202. If the new factor is used for the computation of  $N_0$  by the author's Eq. (4)<sup>1</sup> for calculation of  $N_0$  from  $N_s$  (Siegbahn's Avogadro number), the following value is obtained:

$$N_0' = (0.602489 \pm 0.000030) \times 10^{24} \text{ (g mole)}^{-1}, \quad (3)$$

which agrees completely with (2) within the error limits. The agreement between (2) and (3) shows that in both cases  $(\lambda_g/\lambda_s)^3 \times N$  is the same within the error limits, and that the x-ray crystal density method is by no means less accurate than other exact methods. Furthermore, if  $(\lambda_g/\lambda_s)^3$  and  $N$  are used simultaneously in one term, as for instance for the calculation of x-ray molecular weight, density, or the number of molecules per unit cell, both recommendations (1) and (2) are identical, and give the same result.

However, it is questionable whether the new conversion factor of 1.002063 will be accepted in x-ray spectroscopy and in precision determination of lattice parameters. It seems to the author that a new conversion factor will not be accepted until it is substantiated by new precision measurements of x-ray wavelengths by means of gratings. Until such time as a new conversion factor is generally accepted, to avoid confusion, it seems desirable to use the old conversion factor of 1.00202. By substituting this factor for  $\lambda_g/\lambda_s$  in Eq. (4),<sup>1</sup> the above-mentioned Avogadro number (1) is obtained (physical or chemical scale). This  $N_0$  therefore, was, and still is, recommended for x-ray work because it is in correct relationship with the accepted conversion factor of 1.00202 and Siegbahn's Avogadro number  $N_s$ , which was used for the computation of the fundamental value for the lattice spacing of calcite, and consequently for the determination of x-ray wavelengths.

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<sup>2</sup> J. W. M. DuMond and E. R. Cohen, Phys. Rev. **94**, 1790 (1954).

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### Fermi-Dirac Degeneracy in Liquid He<sup>3</sup> below 1°K\*

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THE temperature dependence of the nuclear magnetic susceptibility of liquid He<sup>3</sup> has been measured directly down to 0.23°K by observing the strength of the nuclear magnetic resonance absorption signal. In a previous communication<sup>1</sup> we reported measure-

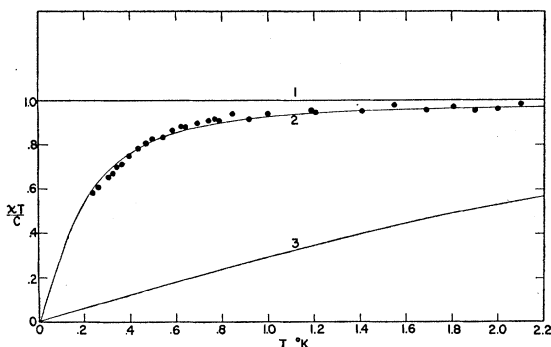


FIG. 1. Plot of  $\chi T/C$  vs  $T$ . ( $\chi$ =molar nuclear magnetic susceptibility of  $\text{He}^3$ ,  $T$ =absolute temperature,  $C$ =normalizing Curie constant.) Curve 1 represents the Curie law expected from Boltzmann statistics, curve 3 represents an ideal Fermi-Dirac gas with the same density and atomic mass as liquid  $\text{He}^3$  ( $T_0=5^\circ$ ), curve 2 represents an ideal Fermi-Dirac gas with a degeneracy temperature  $T_0=0.45^\circ\text{K}$ . The dots represent the experimental points.

ments in the gas at  $4.2^\circ\text{K}$  and in the liquid down to  $1.2^\circ\text{K}$ . These measurements give an answer to the much discussed<sup>2-12</sup> question of the extent to which liquid  $\text{He}^3$  behaves as an ideal Fermi-Dirac gas. At sufficiently low temperatures the spins of the particles of an ideal Fermi-Dirac gas would be expected to line up antiparallel and this would cause the spin magnetic susceptibility to deviate from the classical  $1/T$  Curie law and finally to become temperature independent.

The experimental results below  $2.1^\circ\text{K}$  are shown in Fig. 1. It is seen that the data fall between curve 1, the classical Curie curve, and curve 3, the curve for an ideal Fermi-Dirac<sup>3,13</sup> gas with a degeneracy temperature  $T_0=(\hbar^2/8mk)(3N/\pi V)^{2/3}=5^\circ\text{K}$ , calculated for an ideal Fermi-Dirac gas of the same density<sup>15</sup> and atomic mass as  $\text{He}^3$ . Curve 2 is the curve for a Fermi-Dirac gas with a degeneracy temperature of  $0.45^\circ\text{K}$ , arbitrarily selected to give the best fit of the data. It appears from this experiment that the nuclear spins of liquid  $\text{He}^3$  line up antiparallel as would be expected of a degenerate ideal Fermi-Dirac gas, but at temperatures an order of magnitude lower, the ordinate in Fig. 1 being a measure of the fraction of the  $\text{He}^3$  nuclear spins that have become saturated.

In order to normalize the susceptibility measurements we have made use of our previously published data<sup>1</sup> above  $1.2^\circ\text{K}$ . We reported that above  $1.2^\circ\text{K}$  the molar susceptibility, calculated from the measured volume susceptibility using the published density measurements<sup>14</sup> of 1949, seems to follow a  $1/T$  law indicating no apparent degeneracy. Kerr,<sup>15</sup> using the larger amounts of  $\text{He}^3$  now available at Los Alamos, has remeasured the density of liquid  $\text{He}^3$  to an estimated accuracy of  $\pm 0.3$  percent. When these latest values of the density are used to recalculate the data, a possible 4 percent deviation from Curie's law is indicated at  $1.2^\circ\text{K}$ . The data in Fig. 1 have been so normalized. However, this incipient degeneracy at

$1.2^\circ\text{K}$  is not outside possible experimental error which we estimate to be  $\pm 5$  percent for  $\chi T$ . In calculating the data of Fig. 1, the density of liquid  $\text{He}^3$  has been assumed to be constant below  $1^\circ\text{K}$ .

The nuclear resonance techniques used in this experiment and the method of calculating the susceptibility from these measurements have been discussed previously.<sup>1</sup> The  $\text{He}^3$  sample, 20 cc of  $\text{He}^3$  gas at STP, was obtained from the Stable Isotope Division of the Oak Ridge National Laboratory and was concentrated by us by fractional distillation to better than 99 percent purity. Temperatures below  $1^\circ\text{K}$  were obtained by adiabatic demagnetization of 25 grams of potassium chrome alum, pressed around a copper rod. This copper rod served as a thermal contact with the  $\text{He}^3$  cavity which was located six inches from the salt. The temperature was measured by means of a carbon resistor independently calibrated against the susceptibility of the paramagnetic salt as determined by ballistic measurements. An independent check of the temperature, within an accuracy of 10 percent, was made by placing a salt containing protons in direct contact with the  $\text{He}^3$  and measuring the strength of the nuclear magnetic resonance signal from the protons as a function of temperature.

The spin-lattice relaxation time  $T_1$  was found to be 30 seconds over the temperature range from  $0.23^\circ\text{K}$  to  $1.2^\circ\text{K}$ . In a previous experiment in which the only surfaces in contact with the  $\text{He}^3$  were the Pyrex walls of the container,<sup>1</sup>  $T_1$  was determined to be 200 sec at  $1.2^\circ\text{K}$ . We therefore conclude that the relaxation time in the present experiment was primarily determined by interaction with the surfaces in contact with the  $\text{He}^3$ , such as the copper walls, the coil, and the salt used for proton measurements, rather than by the spin-spin interaction of the  $\text{He}^3$  nuclei.

We are deeply indebted to Professor F. London for his intense interest in this experiment and for his frequent theoretical advice. His untimely death came just after the initial results below  $1^\circ\text{K}$  were obtained. We are also indebted to Professor Walter Gordy and Dr. H. Dehmelt who were co-workers with us in the early stages of this experiment. We wish to thank Mr. W. D. McCormick and Mr. E. J. Lynch for aid in taking the measurements and Mr. T. C. Chen for aid in the calculations.

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## Spin-Orbit Interaction and the Effective Masses of Holes in Germanium\*

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WE reported<sup>1</sup> earlier the observation of cyclotron resonance of electrons and holes in germanium crystals; in particular, we reported the observation of two approximately isotropic effective masses for holes,  $m^*/m=0.04$  and  $0.3$ . The association of these masses with the motion of holes has been confirmed by experiments at  $K$  band with circularly polarized radiation, which also reveal a structure to the  $m^*=0.3m$  resonance. These experiments, which will be published shortly, determine the sign of the charge carrier. The questions which arise are: (1) Why are there two masses? (2) Why can the masses be resolved, in view of the warped nature of energy surfaces<sup>2</sup> near degenerate points? (3) Why are the masses so light? We consider these questions below.

(1) Herman and Callaway<sup>3</sup> have carried out calculations suggesting that the top of the valence band in germanium occurs at the center of the Brillouin zone and is threefold degenerate, corresponding to  $p$  bonding orbitals on the Ge atoms. We suggest that spin-orbit interaction<sup>4</sup> is responsible for the observation of essentially two, rather than three, masses. The top of the valence band has point group symmetry properties related to atomic  $p_{3/2}$  states and is quadruply degenerate, but in crystals with a center of symmetry the contact is that of two double-degenerate bands. There is therefore a possibility of two different masses. The band arising from atomic  $p_{3/2}$  states is lower (for holes) by perhaps 500 to 2000  $\text{cm}^{-1}$ , as estimated from atomic spectra and by a suggested interpretation of the infrared absorption<sup>5</sup> of  $p$ -Ge.

(2) We have carried out for this proposed level scheme a general second-order perturbation determination of the energy surfaces near  $\mathbf{k}=0$ , following the method of Shockley.<sup>2</sup> The calculation hinges largely on symmetry properties of the bands and is *not* based on a strong-binding model. The perturbation is

$$H' = \hbar \mathbf{k} \cdot [(\mathbf{p}/m) + \zeta(\mathbf{S} \times \mathbf{r})], \quad (1)$$

where the spin-orbit term is not important; its inclusion however does not alter the general form of the result. Here  $\mathbf{k}$  is the wave vector and  $\mathbf{p}$  the momentum operator. We paid special attention to tracing the origin of spherical and nonspherical (warping) contributions to the energy surface. The symmetry properties and representations of the bands as given by Elliott are useful in this connection. The most general form of the energy to second order may be written as

$$E(k) = Ak^2 \pm [B^2k^4 + C^2(k_x^2k_y^2 + k_y^2k_z^2 + k_z^2k_x^2)]^{1/2}, \quad (2)$$

where  $A, B, C$ , are constants derived from the matrix elements of  $H'$  connecting the valence band edge (representation  $\Gamma_{8g}$ ) with other states. It turns out that the principal nonspherical perturbation (which enters through  $C$ ) arises from the perturbation by a state with antibonding  $s$  character ( $\Gamma_{7u}$ ) which is separated<sup>6</sup> from  $\Gamma_{8g}$  by some 6 ev. The spherical perturbations  $A, B$  arise principally from the antibonding  $p_{3/2}$  and  $p_{1/2}$  states ( $\Gamma_{6u}, \Gamma_{8u}$ ) which are separated from  $\Gamma_{8g}$  by 0.7-0.8 ev. The perturbations involve the usual energy denominator, so that the spherical terms could be larger than the nonspherical, but other arguments suggest that the differences may not be great.

Nonspherical energy surfaces give cyclotron resonance if the tube mass<sup>6</sup> on a plane in  $\mathbf{k}$  space perpendicular to the magnetic field is independent of the energy. Otherwise, an accelerated electron will enter a tube of different period, and the phase will be destroyed. With the nonspherical term, it is possible to define for certain field directions two sets of tubes for which cyclotron resonance is possible. With the field parallel to the  $[100]$  axis, and  $C^2 \ll 4B^2$ , the two resonances on a single energy surface are separated by

$$\Delta\omega \approx \omega_0 \frac{C^2}{16B} \left( \frac{2m}{\hbar^2} \right) \frac{m^*}{m}, \quad (3)$$

to first order. For strong warping only one of the lines will be strong.

Our preliminary measurements with  $H$  in the  $[100]$  direction indicate that there are actually two peaks near  $m^*/m=0.3$ , with a separation  $\Delta\omega/\omega_0 \approx 0.2$ , which leads to the rough estimate  $B^2/C^2 \approx 1$ . For the  $0.04m$  effective mass we would then estimate  $\Delta\omega/\omega_0 \approx 0.03$ , which cannot be resolved at present. The  $0.3m$  structure should be somewhat anisotropic.

(3) The spherical terms in the energy are quite large, as the perturbing levels are unusually close. It is quite reasonable that the masses should be light: the coefficients  $A, B$  will be  $\gg \hbar^2/2m$ .

It appears that it is possible to account for the features of the hole resonances, as observed up to the present. The effect of spin-orbit interaction on the electron cyclotron resonance is to lift the degeneracy of the antibonding  $p$  band so that the  $p_{3/2}$  band is lowest. The ellipsoid model proposed for  $n$ -Ge by Meiboom and