magnetic shielding tensor. While  $CH_4$  is particularly suited to this technique, it can be applied to other tetrahedral molecules, such as  $CD_4$  and  $SiH_4$ , where  $60D_T \gg c_d$ .

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<sup>1</sup>G. Herzberg, <u>Infrared and Raman Spectra of Poly-</u> <u>atomic Molecules</u> (Van Nostrand, Princeton, N. J., 1945).

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<sup>5</sup>N. F. Ramsey, <u>Molecular Beams</u> (Oxford Univ., Oxford, England, 1956).

<sup>6</sup>For a review of these studies, see K. P. Wong,

J. D. Noble, M. Bloom, and S. Alexander, J. Mag. Res. <u>1</u>, 55 (1969).

<sup>7</sup>K. T. Hect, J. Mol. Spectry. <u>5</u>, 355, 390 (1960).

<sup>8</sup>Equation (1) omits the nuclear shielding terms, the scalar electron-coupled spin-spin interaction, and a rotational-distortion term which depends only on J. All three of these can be neglected here.

 ${}^{9}D_{T}O_{dist}$ <sup>(4)</sup> =  $W_{dist}$  of Ref. 3.  $O_{ss} = O_{ss}^{E} + O_{ss}^{T}$  of Ref. 4.

<sup>10</sup>J. Herranz and B. P. Stoicheff, J. Mol. Spectry. <u>10</u>, 448 (1963); R. S. McDowell, <u>ibid.</u> <u>21</u>, 280 (1966).  $D^{J}\tau/$ 10 (as defined in these two works) equals  $D_T$  (as defined in Ref. 7 and used here).

<sup>11</sup>I. Ozier, S. S. Lee, and N. F. Ramsey, to be published. The sign of  $g_J$  was determined in this work. <sup>12</sup>P. N. Yi, thesis, Harvard University, 1967 (unpublished).

<sup>13</sup>Since the entire discussion deals only with the J=2 rotational level, J is not explicitly included in the list of quantum numbers.

 $^{14}\text{Detailed}$  discussions of the  $\Gamma$  representation and the wave functions are given in Ref. 3 and in I. Ozier and K. Fox, to be published. However, both of these works state, incorrectly, that  $\rho$  is associated with the inversion of the space-fixed reference frame. In both cases,  $\rho$  should be associated with the inversion of the mole-cule-fixed reference frame, as is done here.

<sup>15</sup>It is assumed here that  $|D_U| < |D_T|$ . This was subsequently found to be the case experimentally.

<sup>16</sup>Notice that the values of  $m_I$  and  $m_J$  have been so specified that  $m \equiv m_I + m_J$  is conserved.

 $^{17}$ The sign of  $D_U$  is not significant here because the spectrum depends only on the magnitude of this constant.

<sup>18</sup>The apparatus used is described in M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, Phys. Rev. <u>121</u>, 807 (1961).

<sup>19</sup>Because an oscillating rf field was used rather than a rotating one, only the absolute value of the frequency observed is significant.

<sup>20</sup>A detailed description of the method used is given in I. Ozier, L. M. Crapo, and N. F. Ramsey, J. Chem. Phys. 49, 2314 (1968).

## LONG-WAVELENGTH PHONONS IN LIQUID HELIUM

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High-resolution neutron-scattering measurements have been made of long-wavelengthphonon energies  $\hbar\omega$  in liquid helium at 1.1°K as a function of wave vector Q. The results are approximately described by  $\omega = c Q (1 - \gamma \hbar^2 Q^2 - \delta \hbar^4 Q^4)$ , with  $\gamma$  very small ( $\langle 2 \times 10^{36} \text{ g}^{-2} \text{ cm}^{-2} \text{ sec}^2$ ) and  $\delta = (2.4 \pm 0.2) \times 10^{75} \text{ g}^{-4} \text{ cm}^{-4} \text{ sec}^4$ .

Inelastic neutron-scattering measurements of the energies  $\hbar\omega$  of long-wavelength phonons in liquid helium at 1.1°K have been carried out for wave vectors  $Q \ge 0.2$  Å<sup>-1</sup> (phonon momentum  $p = \hbar Q$ ). The results show that the phonon velocity exhibits remarkably little dispersion for  $Q \le 0.5$  Å<sup>-1</sup>, that the term in  $Q^3$  in the expression for the phonon energies is very small, and that the term in  $Q^5$  represents a more accurate description of the observed dispersion. This result has important consequences for the calculation of other properties of liquid helium such as the ultrasonic attenuation at low temperatures. It may possibly help to resolve the present discrepancy between such calculations and the observed<sup>1</sup> attenuation. The intensities of the onephonon neutron groups are linear in Q and, within the limits of the experimental accuracy, exhaust the f sum rule<sup>2</sup> for  $Q \leq 0.3$  Å<sup>-1</sup>, but not for larger wave vectors.

If the long-wavelength-phonon energies are given by the expression

$$k_{\rm B} \epsilon \equiv \hbar \omega = c p \left( 1 - \gamma p^2 - \delta p^4 + \cdots \right)$$
$$= \hbar c Q \left( 1 - \gamma \hbar^2 Q^2 - \delta \hbar^4 Q^4 + \cdots \right),$$

where  $k_{\rm B}$  is the Boltzmann constant and c is the velocity of sound, the value of  $\gamma$  from these measurements has an upper limit of  $2 \times 10^{36} {\rm g}^{-2} {\rm cm}^{-2}$  sec<sup>2</sup> and may well be much lower. Estimates<sup>3,4</sup> of  $\gamma$  have ranged from  $\langle 2 \times 10^{35}$  to  $3 \times 10^{37}$  but no direct measurements of it have been reported previously. The value of  $\delta$  obtained from these measurements is  $(2.4 \pm 0.2) \times 10^{75} {\rm g}^{-4} {\rm cm}^{-4} {\rm sec}^4$ .

The measurements were carried out using a triple-axis crystal spectrometer<sup>5</sup> and a rotatingcrystal spectrometer<sup>5,6</sup> at Chalk River. The triple-axis spectrometer was operated in its constant  $|\vec{\mathbf{Q}}|$  mode of operation with variable incident energy. The (111) planes of germanium single crystals were used for both the monochromator and analyzer, with the analyzer set to reflect neutrons with a wavelength of 4.06 Å, so that higher-order contaminant neutrons could be suppressed by a beryllium filter. The half width at half-maximum height of the incoherent elastic scattering from vanadium corresponded to an energy of 0.75°K. The rotating-crystal spectrometer was used with the (111) planes of an aluminum monochromator to give an incident wavelength of 3.71 Å. In this case also, the half width of the vanadium peak was 0.75°K.

The results are shown in Fig. 1 where the phonon velocity  $(\omega/Q)$  is plotted against  $Q^2$  and  $Q^4$ . The results of the two sets of measurements are clearly in good agreement with one another. For values of  $Q^2$  up to 0.25 Å<sup>-2</sup>, the results show no dispersion within the experimental uncertainty in the measurements. In this region there is a tendency for the results to lie above the velocity given by conventional velocity of sound measurements<sup>7</sup> but we do not believe that this difference is significant. A very small difference,  $\ll 1\%$ , is expected because the ultrasonic measurements are made in the collision-dominated or  $\omega \tau \ll 1$  regime ( $\tau$  is the relaxation time of a thermal phonon), while the neutron-scattering measurements are made in the collisionless or  $\omega \tau \gg 1$  regime.

The principal source of systematic errors in the measurements arises from the finite resolution of the spectrometers which increases the effective value of the momentum transfer for the smallest wave vectors above that determined by the mean values of the angular settings. Corrections based on the calculated size of this effect were made in plotting the points shown in Fig. 1. A few measurements were also made with the vertical divergence of the triple-axis crystal spectrometer reduced from  $3^{\circ}$  to  $1.5^{\circ}$  and these



FIG. 1. Measurements of the velocity of phonons in liquid helium as a function of  $Q^2$  (upper figure) and  $Q^4$ (lower figure) at 1.1°K. The results obtained with the triple-axis spectrometer are shown by solid circles and have smaller errors than those obtained with the rotating-crystal spectrometer shown by open circles. The ultrasonic measurements (Ref. 7) are shown by a filled square.

supported our calculations of the size of this effect. Despite these precautions a large part of the uncertainty in the velocity arises from uncertainty in this correction. The errors assigned to the rotating-crystal spectrometer measurements are twice as large as those of the triple-axis crystal spectrometer measurements at low momentum largely because the vertical divergence in these measurements was 6°.

The results of Fig. 1 give a value of  $\gamma = (0 \pm 2) \times 10^{36} \text{ g}^{-2} \text{ cm}^{-2} \sec^2$ . The curve of  $\omega/Q$  vs  $Q^4$ , on the other hand, is nearly linear over a wide range of  $Q^4$  and yields a value of  $\delta = (2.4 \pm 0.2) \times 10^{75} \text{ g}^{-4} \text{ cm}^{-4} \sec^4$ . This result is significant because of its implication for calculations of phonon-phonon interactions and hence the transport properties which depend crucially on these interactions, such as the propagation of sound, thermal conductivity, viscosity, etc., particularly at low temperatures. For example, the ultrasonic attenuation at frequency  $\omega$  is given by<sup>8</sup>

$$\alpha(\omega) = AT^{4}[\tan^{-1}(\omega\tau) - \tan^{-1}(\beta\omega)],$$

where A is a constant. If  $\gamma = 0$  and the quintic term dominates the dispersion, then  $\tau$  is propor-



FIG. 2. Measurements of the contribution of the onephonon scattering to the structure factor S(Q) at 1.1°K. The results obtained with the triple-axis spectrometer are shown by solid circles and have smaller errors than those obtained with the rotating-crystal spectrometer shown by open circles. The solid line at low Qis the theoretical limit for S(Q) at 0°K.

tional to  $T^{-5}$  rather than to the  $T^{-7}$  found<sup>3</sup> for a finite  $\gamma$ . Similarly  $\beta = \frac{5}{2} \delta (\hbar \overline{\omega} / c)^4 \tau$  instead of  $\frac{3}{2}\gamma(\hbar\overline{\omega}/c)^2\tau$ , where  $\hbar\overline{\omega}=3k_{\rm B}T$ . In the absence of the cubic term,  $\beta$  is inversely proportional to temperature in agreement with the findings of Abraham et al.<sup>1</sup> although its magnitude is too small by a factor  $\sim 50$ . The agreement with the temperature dependence does, however, show that these results may be an aid to understanding at least some of the previously unexplained results on the ultrasonic properties of liquid helium.

The integrated intensities of the one-phonon neutron groups are shown in Fig. 2. The absolute intensity of the scattering was deduced from measurements at large momentum transfers where the total scattering function S(Q) is unity. The straight line through the origin is the theoretical limit of S(Q) as  $Q \rightarrow 0$ . This line and the more accurate triple-axis measurements agree for  $Q \leq 0.3$  Å<sup>-1</sup>. The first moment of the scattering function  $S(Q, \omega)$  is given by<sup>2</sup>

$$\int \omega S(Q, \omega) d\omega = \hbar Q^2 / 2M,$$

where *M* is the mass of the helium atom. If the velocity of the phonons is a constant (which is approximately the case for  $Q < 0.5 \text{ Å}^{-1}$ ), then departures from linearity in Q for the one-phonon neutron cross section must be accompanied by additional scattering. This additional scattering has been observed and the results are in good agreement with the above predictions as we plan to describe in detail in a more comprehensive paper on neutron scattering from liquid helium.

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## EXISTENCE OF ION MOBILITY DISCONTINUITIES IN SUPERFLUID HELIUM\*

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Previous investigators have reported the existence, at certain values of the drift velocity, of discontinuities in the mobility of positive and negative ions in superfluid helium. A different experimental technique gives results which seem to indicate that such discontinuities are probably spurious.

The study of positive and negative ion complexes in superfluid helium has over the last decade yielded a variety of interesting results. Perhaps the simplest thing one can do in this area is to measure the equilibrium drift velocity  $v_D$  of such

ions under the action of a uniform electric field E. Such experiments have given a great deal of information on the nature of the ion complexes and on their interaction with the normal-fluid excitations.

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