

tration of about 0.75. However, McCormick found that for a pressure of 2300 atm the transition had shifted from 1.6 to 3.1°K. Specific-heat measurements on H₂ under pressure also showed this shift.¹⁶

The same discussion will apply to D₂ where, however, the situation is reversed and the para molecules will be responsible for the transition.

C. The Resonance Line above T_λ

The crystalline dimensions will significantly affect the shape of the nuclear-resonance line. Above T_λ we assume isotropic random rotation of the molecules about their center of gravity. We then assume the line broadening to be caused only by the local fields due to the surrounding molecules. As the intermolecular distance is much larger than the distance between the nuclei of the same molecule, we consider both spins to be located at the center of gravity of the molecule.³² For a powdered sample with identical molecules having one nuclear species, the second moment for a rigid lattice is then given by³³

$$M_2 = \langle \Delta\nu^2 \rangle = (3/5h^2)g^4\beta^4 I(I+1) \sum_j R_{ij}^{-6} \text{ (sec}^{-2}\text{)}, \quad (3)$$

where I is the nuclear spin of the molecule, β is the nuclear magneton, g is the corresponding Lande factor, and R_{ij} is the distance between the molecules i and j . Let us further assume that the ortho and para molecules are distributed uniformly throughout the lattice. For a given ortho concentration c , and taking R_{ij0} and ρ_0 to be, respectively, the intermolecular distance and the density at zero pressure, the second moment for H₂ is

$$M_2 = (\rho/\rho_0)^2 c \times 1.73 \times 10^{-38} \sum_i R_{ij0}^{-6} \text{ (sec}^{-2}\text{)}. \quad (4)$$

As mentioned before, both ortho and para modification in D₂ give a nuclear signal. The Zeeman splittings for the nuclei in both molecules are the same. Therefore the secular part of the Hamiltonian in Van Vleck's treatment³³ expressed in terms of the total-nuclear-spin variable of the molecules has the same form as for identical spins [see Eq. (5) of Ref. 33]. Equation (3) then becomes

$$M_2 = \frac{3}{5h^2} g^4 \beta^4 \frac{\sum_{ij} R_{ij}^{-6} I_i(I_i+1) I_j(I_j+1)}{\sum_j I_j(I_j+1)}, \quad (5)$$

where I_i and I_j are the total nuclear spins of the molecules i and j . As a result, the second moment is the sum of the contributions of the paramolecules (concentration $1-c$) and the active ortho molecules (concentration $c \times 5/6$). Assuming a statistical equilibrium between the different types of ortho molecules, we find for D₂

$$M_2 = 4.78 \times 10^{-42} (\rho/\rho_0)^2 (2+3c) \sum_j R_{jk0}^{-6}. \quad (6)$$

³² This result has been proven theoretically, for several compounds with rotating groups, by: D. T. Kroon, Philips Res. Rept. 15, 501, 571 (1960); and experimentally by G. R. Miller and H. S. Gutowsky, J. Chem. Phys. 39, 1983 (1963).

³³ J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).

This expression gives a somewhat different result from that obtained by Reif who used Van Vleck's formula³³ for the second moment for two nonidentical nuclear species. Our calculations are presented in Table I for the different proposed lattices. It can be seen that the uncertainty in the lattice dimensions and the difference between x-ray and density results (see column 6) can introduce an uncertainty of about $\pm 3\%$ in the second moment calculated for the hcp structure. As can also be seen, the second moment is not very sensitive to the different structures that have been proposed. Harris³⁴ has calculated the effects of zero-point vibration and of spin-rotation on M_2 and has shown that they are small and at most of the order of 3% of the value of M_2 (rigid lattice).

So far the different experimenters^{1,2,4,6} have measured the linewidth in polycrystalline samples and related it to the square root of M_2 assuming a rigid hcp lattice and a Gaussian line shape. A rather important discrepancy between experiment and calculation was found for both H₂ and D₂ that has remained unexplained so far. We have therefore measured carefully the second moment which is then compared to theory. As will be seen below, there is an improvement in the agreement for H₂ between experiment and theory.

III. EXPERIMENTAL

A. The High-Pressure Apparatus

The high-pressure apparatus is essentially the same as that used by Stewart¹⁸ to measure the compressibility of solidified gases. The pressure is applied to the material as a uniaxial stress. Since solid hydrogen and deuterium are found to have a low shear strength and thus exhibit plastic flow, the uniaxial stress results in the material being subjected to a hydrostatic pressure, at least at pressures below, say, 8000 atm. Description of such a high-pressure apparatus is given in the papers by Stewart¹⁸ and in the review by Swenson.³⁵ Hence, only a short description is given here. The hydraulic pressure is applied by a hand pump to a pressure head at the top of the apparatus. It causes a compressional member to move downwards relative to a tensional member to which the high-pressure cavity is rigidly attached by a screw thread. The relative displacement is read to the thousandth of an inch on an Ames gauge.³⁶ The compressional member holds a piston with a potassium washer, which fits into the sample chamber and compresses the solid into the coil space. From the position of the piston tip in the cavity, the volume of the solid can be determined.

The arrangement of the resonance coil in the cavity is different from that of McCormick.¹⁵ In his experiments, the solid had to be squeezed into a coil of 2-mm diameter,

³⁴ A. B. Harris (to be published).

³⁵ C. A. Swenson, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1960), Vol. 11, p. 41.

³⁶ Ames dial gauge, Model 2822, Waltham, Mass.