Nuclear Magnetic Resonance in Solid H₂ and D₂ under High Pressure*

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Nuclear magnetic resonance data are presented for solid H₂ and D₂ between 1.5 and 4.2°K and at pressures up to 5500 atm. For solid hydrogen, the ortho-para conversion, the transition temperature T_λ from the state of free rotation to that of a more ordered state, and the linewidth and second moment above T_λ have been measured as a function of density ρ and ortho concentration. The ortho-para conversion rate is approximately proportional to $\rho^{2.4}$ and the transition temperature T_λ for a given ortho concentration is roughly proportional to $\rho^{2.0}$. These results are compared with other experimental evidence and with theoretical expectations. The second moment for both H₂ and D₂ (the latter with an ortho concentration of 0.67) is compared to that calculated for the dipole-dipole interaction in a rigid lattice having the structure and dimensions determined from x-ray and neutron data. The experimental second moments are found to be larger than the calculated ones, and the discrepancy is discussed.

I. INTRODUCTION

BOTH solid H₂ and D₂ are interesting compounds to investigate by nuclear magnetic resonance (NMR) and such work has been reported in several papers.[1-7] Both solids are a mixture of two modifications, ortho and para, and can in principle be prepared with any ortho concentration[8] although this operation may be very difficult in some ranges of the ortho concentration. In H₂, the ortho molecule, in which both nuclear spins are parallel ($I=1$), will be the only one to give a nuclear resonance signal. In D₂, the part of the ortho modification with $I=2$ as well as the para state ($I=1$) will give a resonance signal. At low temperatures the para state is the stable one for H₂ as it has the lowest energy. For D₂ the ortho state is stable at low temperatures. Although for isolated molecules the selection rules prohibit transitions from one state to another, there is, in fact, a slow conversion when molecules interact. Such a conversion has been calculated for solid H₂ by Motizuki and Nagamiya.[9] The calculated values of the conversion rate dc/dt are in good agreement with the experimental ones,[5,7] about 1–2%/h for a 75% ortho composition. Since this conversion depends on the magnetic-dipole interaction, deuterium, which has a smaller dipole moment than hydrogen, has a conversion rate

from para to ortho which is calculated to be of the order of 0.03%/h for a 67% ortho mixture.[10] Recently this small conversion has been observed experimentally.[11]

At normal density, early NMR experiments on both isotopes showed three temperature regions to be considered:

(I) Above about 8°K, there is diffusion as well as free rotation in the solid. The line is narrow because of the molecular motion.

(II) In a certain temperature range below 8°K, the linewidth is practically constant and considerably broader than in region I. There is only rotation in the solid and the linewidth can be interpreted qualitatively in terms of the intermolecular dipole-dipole interaction.[1,2]

(III) Below a temperature T_λ there is a gradual alignment of the rotational angular momentum $\mathbf{J}$ in preferred directions and hence the intramolecular dipole-dipole interaction is no longer averaged out. The effect of the transition on the NMR spectrum has been analyzed quantitatively by Reif and Purcell.[2] Until recently, such a change in the line structure has been detected only for H₂, for which systematic investigations of the dependence of T_λ on the ortho concentration c at normal density have been carried out.[4,7] For D₂, evidence of a transition has recently been deduced from specific-heat[11] and NMR[12] data for low ortho concentrations.

A further step in the NMR study was to extend the measurements to high pressures. Both solids show a density increase of 60% for an applied pressure of about 6000 atm, and hence one expects to be able to observe the density dependence of many properties with relative ease. For instance the second moment M_2 of the resonance line above T_λ broadened by intermolecular dipole-dipole interaction is a strong function of intermolecular distance. The transition temperature T_λ of H₂ is also predicted to be a function of density as well as ortho

[1] J. Hatton and B. V. Rollin, Proc. Roy. Soc. (London) A199, 222 (1949).

[2] F. Reif and E. M. Purcell, Phys. Rev. 91, 631 (1953). F. Reif, thesis, Harvard University, 1953 (unpublished).

[3] B. V. Rollin and E. Watson, *Conference de Physique des Basses Temperatures*, Paris, 1955 (Simon et Cie., Paris 1955) No. 63, p. 474.

[4] T. Sugawara, Y. Masuda, T. Kanda, and E. Kanda, Sci. Rept. Res. Inst. Tohoku Univ. A-7, 67 (1955).

[5] T. Sugawara, Sci. Rept. Res. Inst. Tohku Univ. A-8, 95 (1956).

[6] G. W. Smith and C. F. Squire, Phys. Rev. 111, 188 (1958).

[7] G. W. Smith and R. M. Housley, Phys. Rev. 117, 732 (1960).

[8] C. M. Cunningham, D. Chapin, and H. L. Johnston, J. Am. Chem. Soc. 80, 2382 (1958).

[9] K. Motizuki and T. Nagamiya, J. Phys. Soc. Japan 11, 93 (1956).

[10] K. Motizuki, J. Phys. Soc. Japan 12, 153 (1957); 17, 1192 (1962).

[11] G. Grenier and D. White, J. Chem. Phys. 40, 3015 (1964).

[12] J. R. Gaines, E. M. de Castro, and D. White, Phys. Rev. Letters 13, 425 (1964).

TABLE I. Lattice constants, second moments and linewidths for H_2 and D_2 at zero pressure.

Method	Structure	a (Å)	c (Å)	Volume per molecule (Å³)	M_2 (kc/sec)² (theor)	M_2 (kc/sec)² (exper)	Width (G)
				H_2			
Density[a]				37.5			
X rays[b]	hcp	3.75	6.12	37.2	67.6		
X rays[c]	hcp(?)	3.75	6.49	39.5	60.5(?)	75±1	6.0 ±0.2
X rays[c]	bct	4.57	3.75	39.2	62.2		
Neutrons[d]	bct	4.5	3.6	36.5	70.1		
X rays[e]	hcp	3.78	6.16	38.1	64.5		
				D_2			
Density[a]				32.5			
X rays[c]	bct	3.38	5.86	33.5	0.126	0.28±0.02	1.53±0.1
Neutrons[d]	bct	3.38	5.60	31.9	0.135		
X rays[e]	hcp	3.54	5.91	32.1	0.134		

[a] Reference 17.   [b] Reference 20.   [c] Reference 23.   [d] Reference 24.   [e] Reference 25.

concentration.[13,14] Since the ortho-para conversion depends on magnetic interactions, it is expected to increase strongly with density.

High-pressure experiments were initiated on H_2 by McCormick and Fairbank and preliminary results were reported.[15] In that work the expected effects mentioned above were essentially observed. After an interruption of two years, the work was started again by the present authors who used some of the high-pressure equipment designed and used by McCormick and Fairbank. The new results and their discussion form the subject of this paper.

Section 2 reviews some properties of solid H_2 and D_2. The proposed crystalline structures for both isotopes are described. The different theories for the occurrence of the transition point T_λ as a function of ortho concentration and structure are also reviewed. The theoretical second moment for both isotopes is calculated, assuming a rigid lattice. In Sec. 3 a description of the experimental arrangement is given. The method of measuring the ortho-para conversion rate in H_2 and the second moment for a given c and density ρ, and the technique for determining T_λ, are described. Finally, in Sec. 4 the results are presented and discussed for each isotope separately. The line shape in the region between 4.2 and T_λ is presented and the second moment is compared to theory. The data of T_λ versus density are compared with the recent specific heat data of Ahlers and Orttung.[16]

II. REVIEW OF SOME PROPERTIES OF SOLID H_2 AND D_2

A. The Crystalline Structure

Bulk measurements on solid H_2 and D_2 include the density data at 4°K by Megaw[17] for pressures up to

about 100 atm and the compressibility data of Stewart and Swenson[18,19] for pressures up to 10 000 atm. In Megaw's measurements the initial ortho concentration in H_2 was 0.55. Stewart and Swenson did not specify c but presumably it must have been between 0.50 and 0.75. Information on the crystalline structure of these isotopic solids has been gathered from several x-ray and neutron-diffraction experiments as well as from infrared data. Keesom, de Smedt, and Mooy[20] reported in 1931 the study of pure para hydrogen. Their results were interpreted as indicating a hexagonal close packed (hcp) structure. Their interpretation was substantiated by recent infrared data.[21,22]

There have been several x-ray investigations on H_2 and D_2 with $c=0.75$ and 0.67, respectively,[23] which seemed to indicate for both isotopes a body centered tetragonal (bct) structure and neutron-diffraction work confirmed this interpretation.[24] However, very recently, x-ray determinations by Kogan and co-workers[25] have again been analyzed in terms of a hcp lattice for both H_2 and D_2. Hence, this structure seems well established for both pure para and ortho-para mixtures. The lattice constants from all published sources are presented in the four first columns of Table I.

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[17] H. D. Megaw, Phil. Mag. 28, 129 (1939).

[18] J. W. Stewart, Phys. Rev. 97, 578 (1955); J. Phys. Chem. Solids 1, 146 (1956).
[19] J. W. Stewart and C. A. Swenson, Phys. Rev. 94, 772 1069 (1954).
[20] W. H. Keesom, J. de Smedt, and H. H. Mooy, Commun. Kamerlingh Onnes Lab. Univ. Leiden, 19, 35 (1931).
[21] H. P. Gush, W. F. J. Hare, E. J. Allin, and H. L. Welsh, Can. J. Phys. 38, 176 (1960).
[22] J. Van Kranendonk and H. P. Gush, Phys. Letters 1, 22 (1962).
[23] V. S. Kogan, B. G. Lazarev, and R. F. Bulatova, Zh. Eksperim. i Teor. Fiz. 37, 678 (1959) [English transl.: Soviet Phys.—JETP 10, 485 (1960)].
[24] V. S. Kogan, B. G. Lazarev, R. P. Ozerov, and G. S. Zadanov, Zh. Eksperim. i Teor. Fiz. 40, 1022 (1961) [English transl.: Soviet Phys.—JETP 13, 718 (1961)].
[25] V. S. Kogan, A. S. Bulatov, and L. F. Yakimenko, Zh. Eksperim. i Teor. Fiz. 46, 148 (1964) [English transl.: Soviet Phys.—JETP 19, 107 (1964)].

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B. The Rotational Ordering in Solid H_2

The rotational motion of the H_2 molecules in the solid has been investigated both experimentally and theoretically.[26,27] For the ortho molecules, the lowest rotational state is characterized by the quantum number $J=1$. The crystalline field removes the three-fold degeneracy of the m_J levels but the splitting is very small in comparison to the rotational energy $BJ(J+1)=2B \cong 120$ cm^{-1}. Above T_λ the separation between the m_J levels is smaller than kT and these levels will then be almost equally populated. As a result the ortho molecules will be essentially spherically symmetric and the dipole-dipole interactions between the two nuclei will be very small. For a large enough ortho concentration, a cooperative process of alignment of the angular momenta takes place below T_λ. This is evidenced by a sharp anomaly in the specific heat.[28,16] Tomita[13] has presented a phenomenological theory of this transition. He treated it as a cooperative phenomenon from a Bethe-Peierls short-range point of view. As the exact form of interaction between the molecules is not known, he only made general assumptions concerning its nature. From his theory he derived the dependence of T_λ on concentration c and on the number of nearest-neighboring molecules. He concluded that at absolute zero all the molecules are in the $m_J=0$ state. This is in qualitative agreement with the analysis of NMR data by Reif and Purcell[2] who proposed such a type of ordering.

More recently the problem of the transition has been considered by Bell and Fairbairn[14] who disagree with Tomita's treatment and results. These authors find that for cubic structures no cooperative transition should be observed. For a hexagonal close packed structure, a special ordering in alternating layers of molecules in the state ($m_J=\pm 1$ and $m_J=0$, respectively) is achieved below a temperature T_λ. Hence, the $m_J=\pm 1$ states will not be depopulated as the temperature falls, in apparent contradiction to Reif's results. Assuming electric quadrupole-quadrupole interaction to be responsible for the transition, a zero-order treatment gives $T_\lambda=5.8°K$ for $c=1.0$. The dependence of T_λ on c has not yet been evaluated because of the mathematical complexities.

For solid H_2 there have been several experimental studies on the ortho-concentration dependence of T_λ at normal density. The results from NMR and specific-heat experiments are presented in Fig. 1. For c larger than about 0.65, the transition temperature as derived from the peak of the specific heat is systematically higher than that derived from the disappearance of the side peaks in the NMR spectrum. A convenient fit for NMR data at normal density ρ_0 below $c=0.77$ combined with specific-heat data below $c=0.65$ is given by a straight
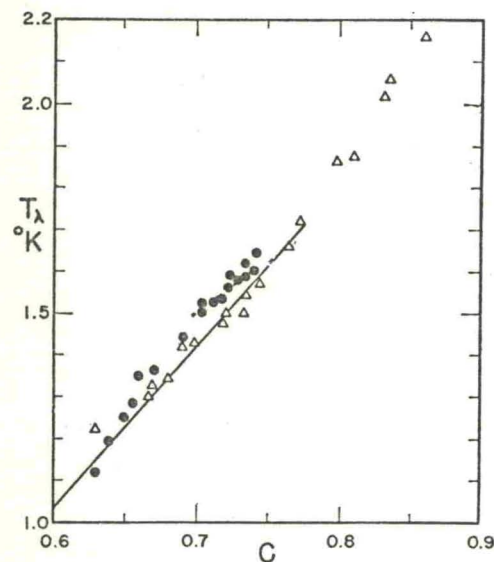

FIG. 1. The transition temperature versus concentration c. △ nuclear-resonance data (Refs. 4, 7) ● specific-heat data (Refs. 16, 28).

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$$T_\lambda(\rho_0,c) = -1.23+3.78c. \qquad (1)$$

This expression will be of use later in connection with our own data.

So far only results at normal densities have been mentioned. At high densities London[29] has predicted that the decrease of molecular volume could result in the anisotropy of the Van der Waals repulsion between molecules becoming the major factor in determining their orientation. One would eventually obtain an oscillatory rather than a rotational type of motion.

From simple theoretical considerations for a cooperative transition[30] it is apparent that the transition temperature T_λ is proportional to the interaction energy between the molecules and also depends on the structure. This can be written as

$$T_\lambda(\rho,c) = V(\rho)\varphi(c), \qquad (2)$$

where V is the interaction, which depends on density, and φ is a function of ortho concentration and the number of nearest neighbors and depends on the structure. At normal density, according to Nakamura,[31] the electric quadrupole interaction is mainly responsible for the lifting of the degeneracy of the lowest rotational level. The Van der Waals interaction and the valence forces contribute in a minor way to this anisotropic potential. Hence this potential V and therefore T_λ would be expected to vary approximately as $\rho^{5/3}$. Smith and Squire[6] reported no change in T_λ when the pressure was increased to 216 atm for H_2 with an ortho concen-

[26] L. Pauling, Phys. Rev. 36, 430 (1930).
[27] J. Van Kranendonk, Physica 25, 1080 (1959).
[28] R. W. Hill and B. W. A. Ricketson, Phil. Mag. 45, 277 (1954). R. W. Hill, B. W. A. Ricketson, and F. Simon, Conférence de Physique des Basses Températures, Paris, 1955 (Simon et Cie., Paris, 1955), No. 76, p. 317.

[29] F. London, Phys. Rev. 102, 168 (1956).
[30] See for instance J. Slater, Introduction to Chemical Physics (McGraw-Hill Book Company, Inc., New York, 1939).
[31] T. Nakamura, Progr. Theoret. Phys. (Kyoto) 14, 135 (1955).

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 H_2 under pressure also showed this shift.[16]

The same discussion will apply to D_2 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 by[33]

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

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 H_2 is

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

As mentioned before, both ortho and para modification in D_2 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 treatment[33] 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 D_2

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

This expression gives a somewhat different result from that obtained by Reif who used Van Vleck's formula[33] 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 ±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. Harris[34] 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 H_2 and D_2 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 H_2 between experiment and theory.

III. EXPERIMENTAL

A. The High-Pressure Apparatus

The high-pressure apparatus is essentially the same as that used by Stewart[18] 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 Stewart[18] 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,

[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).

[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.

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and was hence forced through a constriction. This geometry might have been unfavorable because of the internal friction in the solidified gas. It might have been responsible for some of the pressure hysteresis observed by McCormick. In the present arrangement, the coil is supported only by a base, as shown in Fig. 2. In this construction, the compressed solid can flow outside as well as inside the coil. The coil assembly can be readily inserted and taken out of the high-pressure cavity. The coil is a single layer of #30 Nyclad copper wire with a 1-μH inductance. It is held together and connected to a brass ring with a small amount of Armstrong adhesive A-12. One end of the coil is soldered to the ring which in turn is in electrical contact with the surface of the cavity. The other coil lead is soldered to a metal rod that passes through the middle of a Teflon insulator and is attached to the top of a sealing cone. This cone is insulated from the cavity by a conical seal of pipestone. The sealing cone narrows to a bolt which extends beyond the bottom of the cavity and is held there by a Teflon washer and a nut. The end of the bolt is soldered to a rigid coaxial transmission line which is connected to the oscillator on top of the cryostat. A Speer carbon resistor, thermally grounded to the high-pressure cavity, is used to monitor the temperature.

Before each new experiment, the piston is kept outside the cavity. The cavity is sealed by a thin foil of copper pressed over the bore with a hollow plug. An indium O-ring insures leak tightness. After the apparatus has been cooled to 77°K, it is cooled very slowly to 4.2°K. Electrolytic H_2 or D_2 with a purity of about 99.6% is condensed slowly into the cavity via a stainless capillary which is heated over its whole length so as to prevent blocking during this process. We assumed that the slow cooling along the thin capillary would get rid of the remaining small O_2 impurity in the gas by adsorption on the walls. Once the cavity is filled with solid, the foil is pierced by the piston and the potassium gasket is made tight by a quick compression to about 1000 atm. During the various pressure cycles, the coil is subjected to repeated strains and usually only lasts for about three experiments.

B. Electronics

The nuclear resonance signal is detected by a low-level Robinson oscillator[37] followed by a phase sensitive detector. The operating frequency is about 14 Mc/sec for H_2 and 5 Mc/sec for D_2 and is measured by a Hewlett-Packard electronic counter. The magnetic field is modulated by an audio field of about 0.5 G for H_2 and 0.2 G for D_2. The applied field from a 12-in. Varian magnet is kept constant and the frequency of the oscillator is swept slowly. The derivative of the absorption line is traced on a chart recorder and frequency markers are inserted at regular intervals. The use of low rf levels is

[37] F. N. H. Robinson, J. Sci. Instr. 36, 481 (1959).

A HOLLOW PLUG
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C POTASSIUM
D COPPER FOIL
E CAPILLARY
F COIL
G BRASS RING
H TEFLON SPACER
I PIPESTONE CONE
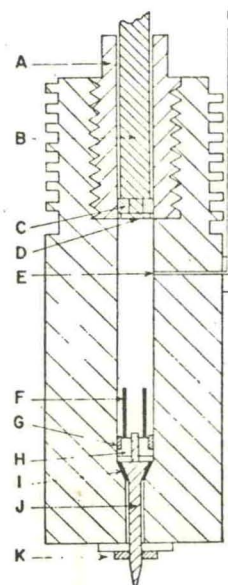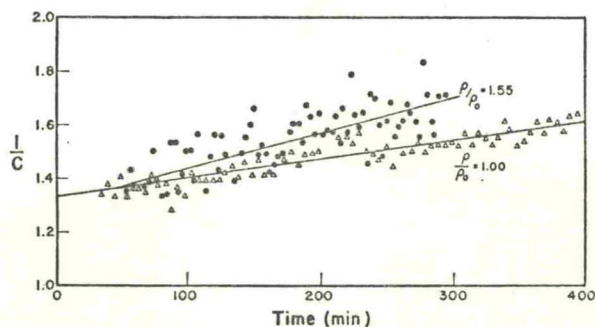J SEALING CONE
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FIG. 2. The high-pressure cavity with piston and rf coil.

necessary to avoid saturation and the resulting distortion of the line. Sugawara's extensive study[5] indicated that an undistorted line is observed with an H_{rf} of less than 10^{-2} G. In the present experiment, the level is kept at about 6×10^{-3} G, corresponding to an rf level of about 12 mV rms across the coil.

C. Procedure During an Experiment

A crucial part of the experiment was the determination of the density. As it was not possible to completely fill the sample chamber with the solidified gas, it was necessary to cycle the pressure up and down from zero to the maximum pressure to be reached. After about three such cycles, the solid was packed uniformly and the piston-displacement reading became reproducible. The determination of the density was then made from the piston position x. For this it was necessary to find the piston position x_0 for zero pressure. However, due to friction in the solid and between the piston, the washer and the inner wall of the sample chamber, the pressure P inside the solid never returned to zero after a cycle. This friction caused the x versus the exterior applied pressure P_{app} to form a hysteresis loop. But it was empirically found that a plot of the slope of the displacement $\Delta x/\Delta P$ as a function of the increasing applied pressure gave a straight line above 500 atm. By extrapolating this relation to lower pressures, one could obtain an approximate value for x_0. The error in relative density was estimated to be about 0.01. This is the combined error in the x versus P_{app} extrapolation and the uncertainty in the measurement of the piston-tip position relative to the bottom of the cavity. Cycles of P_{app} versus the volume V of H_2 in the cavity gave a P-V relation in agreement with that of Stewart and Swenson.[18,19]

FIG. 3. The ortho concentration plotted as $1/c$ versus the time after cooling to $4.2°K$ for relative densities of 1.00 and 1.55. The relative density $\rho/\rho_0 = 1.55$ was produced 50 min after the cryostat had reached $4.2°K$.

An experiment was always started with the room-temperature ortho concentration in each gas. During the experiment there was, as mentioned before, a sizable ortho-para conversion for H_2 and it was important to know the concentration at any moment. The first concern was therefore to obtain a reliable determination of the conversion rate. A measurement of the ortho concentration by the thermal-conductivity method[38] before and after an experiment could not be carried out because the potassium washer on the piston was not tight to gas and after warming up the cavity above $4°K$ the gas could not be recovered. The conversion rate was found by measuring the area under the resonance curve as a function of time for various densities. This area is known to be proportional to the ortho concentration. For this purpose, the derivative of the line had to be twice integrated graphically. At the same time this experiment could give a determination of the linewidth and second moment for various ortho concentrations at a given density. All the linewidth measurements were made at $4.2°K$ as this temperature was found to be

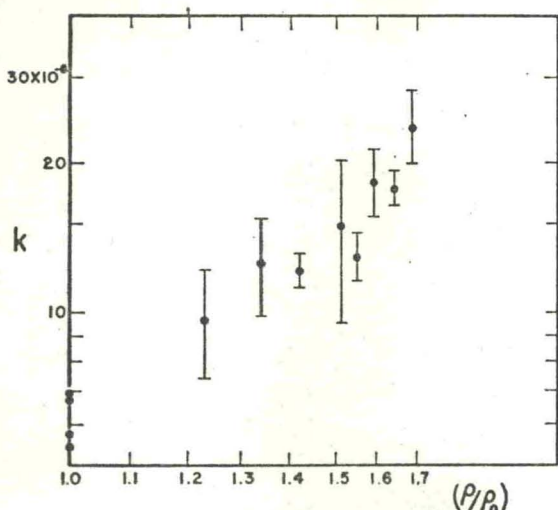FIG. 4. The ortho-para conversion constant k in $(\%/min)^{-1}$ versus the relative density.

[38] E. R. Grilly, Rev. Sci. Instr. 24, 72 (1952).

above T_λ for all the densities used. For D_2, where the conversion rate is negligible, the recordings of the derivative were taken as a function of density by increasing the pressure step by step at constant temperature between 1.6 and $4.2°K$.

For determinations of the T_λ in H_2, the initial pressure-cycling procedure was done as before at $4.2°K$. The pressure was then set to a certain value and the temperature of the helium bath was slowly reduced. Eventually the transition temperature was passed. As it was difficult to see the satellites appear at T_λ, the method used by McCormick[15] was adopted. This technique consisted of taking tracings of the line at different temperatures below T_λ. Then a plot of the ratio of the satellite height to that of the central line was made versus temperature.[39] A straight line was fitted to these points and the temperature of zero intercept was taken as T_λ. Ten lines were taken on the average for each transition point. As the lines were covered in about 30 min, the change in ortho concentration would not seriously affect the results. The lines were taken over a spread of about $1°K$. This gave a good range in the value of the ratio and made the T_λ determination reasonably accurate. About 30 points were taken at various densities and ortho concentrations.

IV. RESULTS AND DISCUSSION

A. Hydrogen

(a) Ortho-Para Conversion

The ortho-para conversion was measured at $4.2°K$, as this is the most convenient temperature. The ortho concentration was measured in arbitrary units as described before and was normalized to 75% at the beginning of the experiment $(t=0)$. As expected, c was found to decrease faster with time as the density was higher. (See Fig. 3.) The increased scatter at high densities is due to the difficulty in doubly integrating the broadened line. The location of the line extremities becomes more uncertain at high densities. The expected functional relationship between c and t comes from an integration of the relation given by Cremer and Polyani,[40]

$$dc/dt = -kc^2, \qquad (7)$$

where k is the reaction constant, assumed to be independent of c. If there is a possibility of a small O_2 impurity, there is an additional conversion rate[9] equal to Kc. The constant K is a function of the distance from the O_2 to the nearest ortho molecules. When H_2 is solidified, there is initially a rapid conversion of the ortho molecules around the impurity.[9] After some time, of the order of 30 min, the conversion is calculated to

[39] For a typical line derivative below T_λ see for instance Fig. 7 in Ref. 6. The "satellite" lines there are labeled $H_s{}^1$ and $H_s{}^{11}$.

[40] E. Cremer and M. Polanyi, Z. Physik. Chem. B21, 459 (1936); E. Cremer, ibid. B29, 445 (1938).

proceed more slowly because the remaining ortho molecules are far away from the impurity. We have not been able to observe such a rapid initial conversion for the normal density, where the scatter in c is smallest. The concentration as a function of time could always be expressed by integration of Eq. (7) and hence is plotted as $1/c$ versus time in Fig. 3. At normal density several experiments give $k = 6 \times 10^{-6}$ (% per min)$^{-1}$. This is about twice the rate found by several previous experimenters,[7,40,41] although Sugawara and co-workers[4] also report approximately the same conversion rate. The reason for this result, which was reproducible, is unclear at present.

The dependence of k on density can be predicted in principle from Motizuki and Nagamiya's paper[9] and is rather complicated. This is partly because such quantities as the sound velocity and the Debye temperature (Θ_D) occurring in Motizuki and Nagamiya's expression
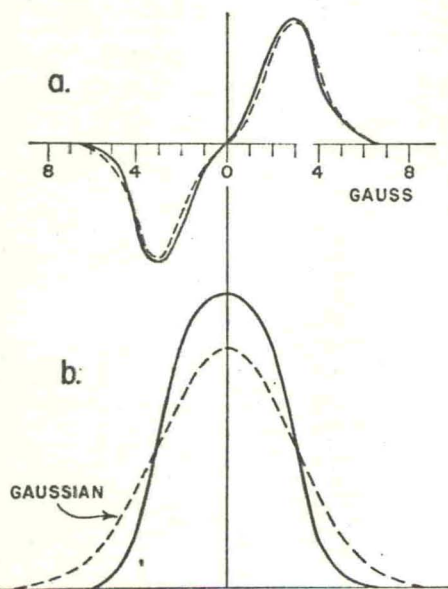
FIG. 5. (a) Derivative of an H₂ line at 4.2°K for $c = 0.71$ and normal density compared to a line of the same ortho concentration recorded by Sugawara,[5] dashed curve. (b) The same line integrated and compared to a Gaussian line of approximately the same area.

are also dependent on density. The assumption of a Debye solid may not be justified for solid H₂, and so far no experimental determinations of these quantities as a function of density have been made.

Figure 4 gives the data for k plotted versus (ρ/ρ_0) on a logarithmic scale, and it is seen from the slope that k is approximately proportional to (ρ/ρ_0).[2,4] The values from this figure were used to compute c in the rest of the experiments where c enters as a parameter of the quantities being measured. The error in c is about 2%. We found that the conversion rate for $(\rho/\rho_0) = 1.65$ (which corresponds to a pressure of about 4800 atm)
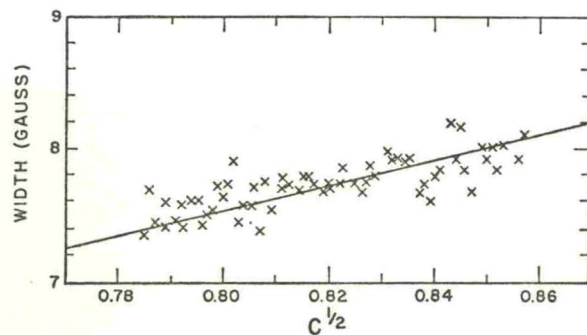
[41] G. Ahlers, J. Chem. Phys. 40, 3123 (1964).

FIG. 6. Linewidth for H₂ at 4.2°K with $(\rho/\rho_0) = 1.34$ plotted versus $c^{1/2}$. The straight line is the best fit consistent with the condition that $\Delta H = 0$ for $c = 0$. Each width is measured to ± 0.4 G.

is 6.7%/h. This compares with 7.5%/h found by McCormick[15] at this same density. Considering the errors involved, the agreement is satisfactory.

It is interesting to note that while the absolute value of the conversion rate is higher than that of Ahlers,[41] the density dependence we find is approximately the same as that obtained by Ahlers, who finds $k \propto (\rho/\rho_0)^{8/3}$ and who gives a detailed discussion of the expected density dependence.

(b) The Shape of the Unsplit Line

The parameter usually reported in previous work has been the linewidth ΔH, which is the distance, in G, between two points of maximum slope. It has usually been tacitly assumed that the line was Gaussian. Figure 5 shows the derivative for a typical line at 4.2°K compared to a nearly identical line at the same concentration presented by Sugawara.[5] The integrated curve is compared to a Gaussian one of the same area and same width. It is seen that the experimental curve is narrower, perhaps because of exchange, and drops to noise level within 7 G from the center. For this particular density and concentration we believe that the wings are so
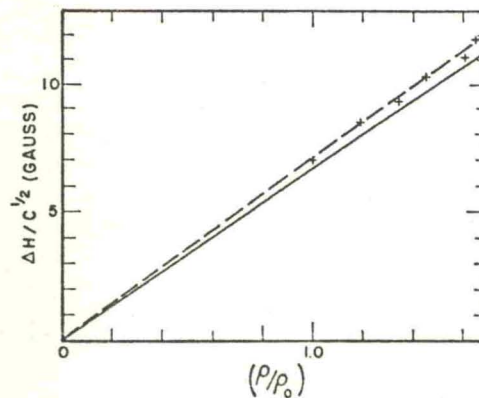
FIG. 7. Plot of the ratio of $\Delta H/c^{1/2}$ versus relative density for H₂ at 4.2°K. The solid line is that calculated for hcp lattice (Ref. 25) according to the theory of second moments and the empirical relation 8.
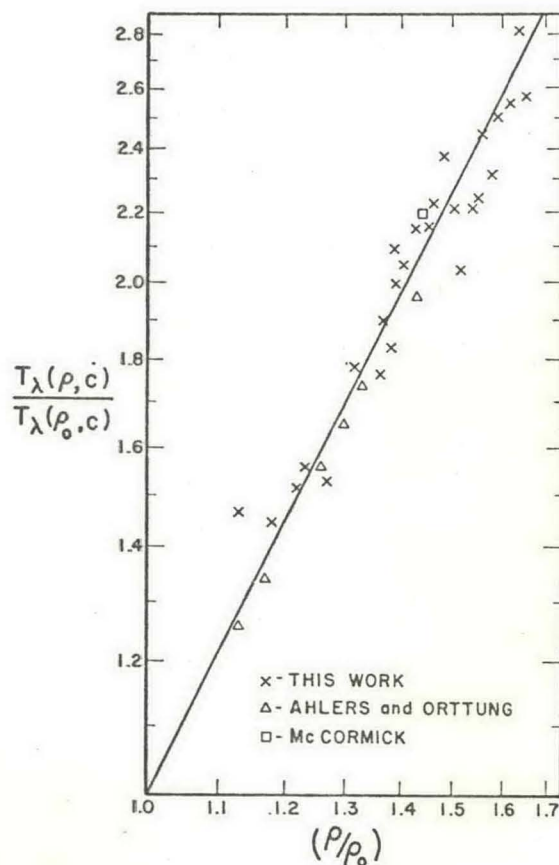
FIG. 8. Plot of the ratio of $T_\lambda (\rho,c)/T_\lambda(\rho_0,c)$ versus relative density. The solid line has a slope of 2.0. The points from specific-heat measurements are deduced from Fig. 8 of Ref. 14.

small that they cannot be measured beyond this distance. An empirical relation was obtained between ΔH and the second moment M_2 for selected samples of lines at different densities and ortho concentration (Table II). It was found quite generally that

$$\Delta H = (2.95 \pm 0.15)M_2^{1/2}(h/g\beta)\ (G).\qquad (8)$$

This ratio of 2.95 is to be compared with the value of 2.0 for a Gaussian line. In order to compare our results with those of previous workers, we will present them in terms of the linewidth as well as the root of the 2nd moment. Comparison with the theory for a rigid lattice [Eq. (4)] can then be made with help of Eq. (8). From theory one expects ΔH to be proportional to $c^{1/2}$ and to the relative density (ρ/ρ_0). That this is so is shown in Fig. 6 and Fig. 7. The line $\Delta H/c^{1/2} = 7.1(\rho/\rho_0)$ G fits the points well within error. It should be noted that all these data were taken with c between 0.75 and 0.55. McCormick measured the linewidth versus relative density but with c undetermined. He found approximately $\Delta H = 5.8(\rho/\rho_0)$ G. Our results would give this relation for 68% ortho. As this might have been the median value of the concentration in his work, there is no great discrepancy between his result and ours.

TABLE II. Experimental moments of H_2 lines at 4.2°K for several densities and ortho concentrations.

ρ/ρ_0	c	ΔH (in kc)	M_2 [$(kc)^2$]	M_4 [$(kc)^4$] ($\times 10^{-4}$)	$\dfrac{M_4}{M_2^2}$	$\dfrac{\Delta H}{M_2^{1/2}} \dfrac{g\beta}{h}$
1.00	0.743	25.3	75.4	1.346	2.36	3.02
1.00	0.646	25.5	70.8	1.18	2.36	3.04
1.19	0.648	31.0	101.8	2.44	2.36	3.08
1.34	0.622	31.6	124.3	3.76	2.42	2.80
1.45	0.72	37.8	151.7	5.53	2.40	3.07
1.60	0.579	37.1	167.9	6.85	2.43	2.86
				average	2.39	2.95

With the empirical ratio [Eq. (6)] the theory of the second moment would predict the linewidth to be about 6.5 $(\rho/\rho_0)c^{1/2}$ for both the hcp and bct lattices. The agreement between theory and experiment is just within the combined error. It could perhaps be further improved if the following possibilities were considered:

(1) Clustering of ortho molecules or at any rate some sort of correlation between their respective positions and rotations.
(2) A larger influence of the zero point motion and rotation than theoretically expected.[34]

These possibilities cannot presently be discussed in more detail because of the lack of more extensive data on the dynamical behavior of solid H_2.

TABLE III. The transition temperature T_λ as a function of density and ortho concentration. (Experimental data.)

ρ/ρ_0	$P \times 10^2$ (atm)	Ortho concentration c	T_λ (°K)
1.13	4	0.69±0.01	2.05±0.06
1.18	6	0.71	2.10
1.22	8	0.69	2.10
1.23	8	0.73	2.41
1.27	11	0.71	2.23
1.32	14	0.73	2.74
1.36	17	0.73	2.70
1.37	17	0.71	2.79
1.38	18	0.73	2.79
1.39	19	0.69	2.92
1.39	19	0.73	3.06
1.40	20	0.72	2.99±0.08
1.40	20	0.70	2.92
1.43	22	0.73	3.31
1.45	24	0.68	2.91
1.46	25	0.68	3.02
1.47	26	0.715	3.23
1.48	27	0.715	3.53
1.50	29	0.685	3.01
1.51	30	0.69	3.03
1.52	31	0.69	2.77
1.54	33	0.68	3.02
1.56	36	0.71	3.21
1.58	38	0.66	2.89
1.59	40	0.725	3.81±0.10
1.62	44	0.72	3.81
1.63	46	0.71	3.65
1.65	49	0.725	3.87
1.66	50	0.72	4.16
1.68	53	0.695	3.59

at 4.2°K
tions.

M_4	ΔH	$g\beta$
$M_2{}^2$	$M_2{}^{1/2}$	h
.36	3.02	
.36	3.04	
.36	3.08	
.42	2.80	
.40	3.07	
.43	2.86	
.39	2.95	

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| 99±0.08 |
| 92 |
| 31 |
| 91 |
| 02 |
| 23 |
| 53 |
| 01 |
| 03 |
| 77 |
| 02 |
| 21 |
| 89 |
| 31±0.10 |
| 31 |
| 55 |
| 57 |
| 16 |
| 59 |

(c) The Transition Temperature T_λ

The data on 30 points are given in Table III. The determination of the relative density and pressure has been described above and the concentration was determined by the summation of the various conversion rates over the time periods of the different pressures. The concentration c given is the combined error of the conversion rate and the spread of the concentration over the lines taken. The error is an increasing function of pressure due to the increase in the conversion rate with higher pressure. The temperature T_λ is the intercept mentioned above. There is appreciably more scatter in the determination of T_λ by the techniques mentioned above than by specific heat data,[25,16] because in NMR data T_λ is obtained by extrapolation while in specific heat experiments it is directly seen by a maximum in C_p.

Using the empirical relation between T_λ and c at one atmosphere [Eq. (1)] and the functional dependence on the density [Eq. (2)] it is possible to determine the value of the ratio $V(\rho)/V(\rho_0)$ for a given density. This ratio is plotted on a logarithmic scale (Fig. 8) and it is found that one has approximately

$$\frac{T_\lambda(\rho,c)}{T_\lambda(\rho_0,c)}=\frac{V(\rho)}{V(\rho_0)}=\left(\frac{\rho}{\rho_0}\right)^{2.0}. \qquad (9)$$

Hence the empirical relation between T_λ, ortho concentration and relative density is given by

$$T_\lambda=(\rho/\rho_0)^{2.0}[-1.23+3.78c] \quad \text{for} \quad 0.6\leqslant c\leqslant 0.75. \quad (10)$$

Empirically speaking, the exponent 2.0 indicates a composite dependence of the potential on distance as R^{-6}. This is in rough agreement with interactions due to quadrupole and Van der Waals forces. In Fig. 8 we also give the ratio $T_\lambda(\rho,c)/T_\lambda(\rho_0,c)$ determined from the specific heat data of Ahlers and Orttung.[16] Their data
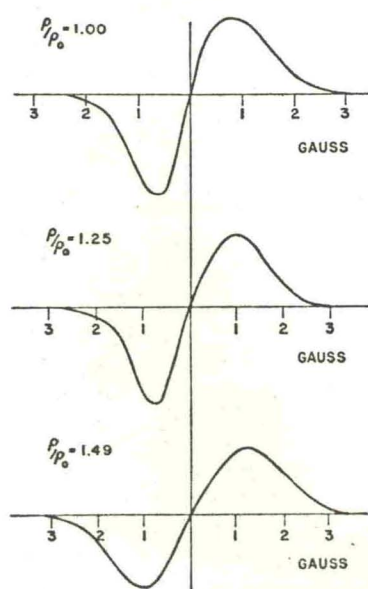
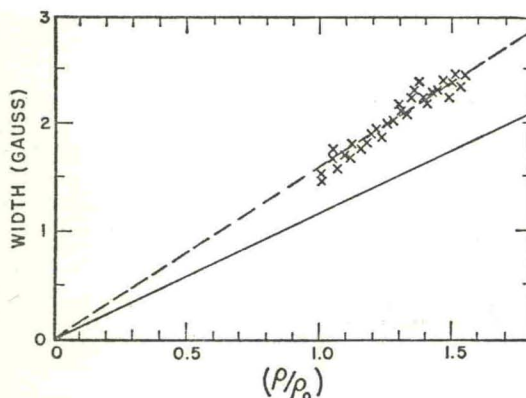FIG. 9. Derivatives of the D₂ line as a function of relative density at 4.2°K.

FIG. 10. Linewidth of D₂ as a function of relative density at 4.2°K. The solid line is that calculated for the hcp lattice (Ref. 25) according to the theory of second moments and the empirical relation (11).

are consistent with ours within the combined experimental error. McCormick[15] reported one transition point, 3.1°K at 2300 atm, without indicating the concentration. According to Eq. (10), one estimates $c=0.71$ for this pressure. Depending on the time elapsed at one atmosphere and at 2300 atm, this would be possible if the data were taken between one and two hours after cooling the H₂ to 4.2°K. This point is thus compatible with the results of our work. As mentioned before, Smith and Squire[6] reported no change in a transition temperature of 1.57°K from zero to 216 atm. However, if the data were taken in steps with increasing pressure over a period of time, the ever present conversion would change the concentration c and thus the expected transition temperature. Hence the effect of the increased density would be partly compensated for by the decreased concentration. This may account for their failure to observe a change in T_λ.

B. Deuterium

The derivative of the deuterium line is shown in Fig. 9. There is a slight departure from antisymmetry about the center which is not due to any saturation. This effect tends to disappear at high densities as shown in this figure. The integrated D₂ lines have a shape much closer to Gaussian than to those of H₂. Evaluation of the second moment and the linewidth for several densities gives the empirical relation

$$\Delta H = (2.0\pm0.1)M_2{}^{1/2}(h/g\beta) \text{ (G)}. \qquad (11)$$

The linewidth was found to be independent of temperature below 4.2°K at all densities. A plot of ΔH versus relative density is given in Fig. 10. While the scatter is relatively large compared to the change observed, the data roughly follow the straight line:

$$\Delta H = 1.6(\rho/\rho_0) \text{ (G)}. \qquad (12)$$

Hence the data would extrapolate to approximately zero linewidth for zero density. This shows that, according to

this large extrapolation, there would be no density-independent contribution to the width due to intramolecular interactions. Our data at normal density are in reasonable agreement with those of Sugawara[5] who reports a width of 1.4 G. There is again qualitative confirmation of the expected dependence between linewidth and density [Eq. (7)]. But as seen in Table I, the discrepancy between the experimental and the theoretical second moment is more serious than for H_2. This disagreement was already found by Sugawara et al.[4] who suggested that the large linewidth is due to the effect of intermolecular quadrupole broadening. If the broadening were due to zero-point vibration and rotation, one would expect it to be even larger for H_2, which is contrary to experiment. So far the reasons for this discrepancy remain unexplained. The reasons for the slight line asymmetry at low densities are also not understood.

In addition to a study of linewidth, a search was made for a possible transition and splitting of the para-deuterium signal. No such phenomenon was observed at temperatures down to 1.5°K and pressures up to 5400 atm. Even if the transition had been in the range of temperatures and pressure covered, it would have been located with difficulty since only the para D_2 will show a line structure and its signal is only one fifth of that of the ortho molecules at the normal concentration.

V. CONCLUSION

In summary, our measurements on the ortho-para conversion, the transition temperature T_λ, and on the second moment in H_2 have confirmed qualitatively theoretical expectations and are in agreement with the data of McCormick and the specific-heat results. In D_2, there are significant discrepancies between the calculated and the experimental second moment which still are not explained.

Experiments are in progress[42] for a systematic investigation of the transition temperature and the line shape

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[42] See note added in proof.

for H_2 at normal densities and temperatures between 4.2 and 0.3°K. We also intend to carry out such measurements on D_2 for various ortho concentrations and on D_2 diluted in para hydrogen. This would correspond effectively to a relative deuterium concentration of less than unity. With a systematic approach along these lines we hope to come nearer to an explanation for several unsolved questions in these solids.

Note added in proof. D. C. Rorer and one of the authors (H.M.) have carried out a careful study of the line shape for normal H_2 and D_2 between 1.25 and 4.2°K at normal density. From the derivative of the lines the second and fourth moments were computed. It was possible to express the second moments roughly as

$$M_2(nD_2)=0.29+0.115T^{-2} \text{ (kc/sec)}^2 \quad 1.25<T<4°K,$$

$$M_2(nH_2)=60+300T^{-2} \text{ (kc/sec)}^2 \quad 1.7<T<4.2°K.$$

The constant term is attributed to the intermolecular dipole-dipole interactions, and the temperature-dependent one to intramolecular dipole-dipole interaction, as predicted by recent calculations of A. B. Harris (to be published). The agreement of the so-obtained constant terms with the calculated on from Eq. (4) is better than before for solid H_2. However, a serious discrepancy still remains for D_2.

We also obtained for the same temperature range the approximate relations

$$M_4(nD_2)=0.26+0.25T^{-2} \text{ (kc/sec)}^4,$$

$$M_4(nH_2)=(2+26T^{-2})\times10^4 \text{ (kc/sec)}^4.$$