dependence of the modes arising from thermal expansion, depending on whether three-phonon processes due to cubic anharmonicity or four-phonon processes due to quartic anharmonicity give the overriding contribution to the self-energies. At 0°K only small residual self-energy contributions remain which amount to no more than 1% of the total LO phonon energies.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge valuable discussions with Professor D. H. Martin, Professor C. H. Perry, and Dr. J. F. Parrish. It is also a pleasure to acknowledge the valuable technical assistance given by J. Weston in the design and construction of the high-pressure infrared bomb at Queen Mary College, London.

PHYSICAL REVIEW B VOLUME 1, NUMBER 6 15 MARCH 1970

Measurement of $(\partial P/\partial T)_V$ and Related Properties in Solidified Gases. III. Solid D_2†

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(Received 27 October 1969)

Measurements in solid D_2 of pressure changes with temperature and para concentration are reported, and related thermodynamic properties are calculated. The study covers both the hcp and cubic phases in the temperature range $0.4 \leqslant T \leqslant 4.2$ K and para concentration range $0.02 \leqslant c \leqslant 0.90$. The measurements were carried out with a capacitance strain gauge capable of resolving pressure changes of 2×10^{-5} bar. Two types of study were made. (a) The pressure changes accompanying the phase transition were determined as a function of c, and the hysteresis was studied as a function of the number of cyclings through the transition. (b) The quantity $(\partial P/\partial T)_V$ was obtained in the cubic and hcp phases as a function of T and c. The results were analyzed in terms of separate contributions from the lattice and from the rotation of the paradeuterium molecules (p-D_2, lowest rotational level $J=1$). The molecular rotation was assumed to be quenched by the electric quadrupole-quadrupole (EQQ) interaction, and all other effects such as those due to crystalline field were neglected. The EQQ interaction parameter Γ was determined experimentally. The results from (a) extend the phase diagram to low para concentrations and show that the transition from the hcp to the cubic phase does not take place below $c=0.55$. The data from thermal cyclings, when analyzed in conjunction with corresponding data from x-ray diffraction, indicate that the changes in pressure (and in other thermodynamic properties) are due mainly to the order-disorder transition of the rotational motions and not to the crystalline phase change *per se*. The results from (b) give values of $\Gamma_{\text{eff (pair)}}/k_B = 1.05\pm0.07$ K and $\Gamma_{\text{eff }(c=1)}/k_B = 0.93\pm0.05$ K for low and high concentrations of p-D_2, respectively. For a rigid lattice, the theoretical value is $\Gamma_0/k_B = 1.20$ K. A comparison is made with values of Γ/k_B from a previous determination and with those predicted by the theory of Harris, which takes into account quantum effects in the solid. Anomalies in $(\partial P/\partial T)_V$ at very low p-D_2 concentrations are observed, but are not explained. The entropy of the rotational motion of the $J=1$ state is calculated above 0.4 K and is found to approach $R\ln3$ per mole of p-D_2 for $c \geqslant 0.6$.

I. INTRODUCTION

OVER the past five years, many theoretical and experimental papers have appeared which have advanced our understanding of the intriguing properties of solid H_2 and D_2. This work is fairly completely referenced in several recent publications.[1-5] Among the many interesting results are those obtained by x-ray diffraction[2] giving the relative stabilities of the crystalline phases both at 4 K and upon cycling through the phase transition, and those obtained by Raman spectroscopy[6] showing the rotational excitation states in orthohydrogen (o-H_2) and paradeuterium (p-D_2) that had been predicted by several authors.[3,7-10]

[†] Work supported by the National Science Foundation and the U. S. Army Research Office (Durham).

[*] Present address: Duke Medical Center, Durham, N. C.

[1] K. F. Mucker, P. M. Harris, D. White, and R. A. Erickson, J. Chem. Phys. **49**, 1922 (1968).

[2] A. F. Schuch, R. L. Mills, and D. A. Depatie, Phys. Rev. **165**, 1032 (1968).

[3] J. C. Raich and R. D. Etters, Phys. Rev. **168**, 425 (1968).

[4] J. F. Jarvis, H. Meyer, and D. Ramm, Phys. Rev. **178**, 1461 (1969).

[5] A. B. Harris, Int. J. Quantum Chem. **IIs**, 347 (1968); and (unpublished).

[6] W. Hardy, I. F. Silvera, and J. McTague, Phys. Rev. Letters **22**, 110 (1969).

[7] S. Homma, K. Okada, and H. Matsuda, Progr. Theoret. Phys. (Kyoto) **38**, 767 (1967).

[8] H. Ueyama and T. Matsubara, Progr. Theoret. Phys. (Kyoto) **38**, 784 (1967).

[9] F. G. Mertens, W. Biem, and H. Hahn, Z. Physik **213**, 33 (1968).

[10] F. G. Mertens, W. Biem, and H. Hahn, Z. Physik **220**, 1 (1969).

The study of the rotational excitations by means of their influence on thermodynamic properties can serve as a valuable addition to the experiments mentioned above. In solid D_2, as opposed to H_2, such a study is relatively easy because the para-ortho self-conversion rate is quite slow.[11,12] The thermodynamic quantity $(\partial P/\partial T)_V$ was chosen for the present study because it is very simply related to the specific heat and can be measured with comparable accuracy. Also its measurement can be carried out for both cooling and warming the sample under controlled rates and, therefore, pressure-versus-temperature measurements of the hysteresis upon successive thermal cycling through the phase transition are complementary to the x-ray work.[2]

In two previous studies,[4,13] similar pressure measurements $P(T)$ at constant volume were made on solid H_2 and He^4. The first three sections of Ref. 4 constitute a review of some of the recent work on solid H_2 which is also pertinent to D_2. For solid D_2, the para and ortho molecules are in the $(J=1)$ and $(J=0)$ rotational states, respectively, and to be consistent with the hydrogen work, we define c as the concentration of $(J=1)$ molecules.

The first purpose of this paper is to present a detailed $P(T)$ study of the hcp-to-cubic and cubic-to-hcp transitions in D_2 which can be compared with that by x-ray diffraction.[2] A correlation of the data should allow us to draw conclusions about the rotational order-disorder transition in the cubic phase.

Our second purpose is to determine the electric quadrupole-quadrupole (EQQ) coupling parameter[14] Γ from measurements of $(\partial P/\partial T)_V$ in both the cubic phase at large c and in the hcp phase at small c. In cubic D_2, the determination relies on the theory of rotational excitations in the "ordered" phase,[7–10] whereas in hcp D_2 it is based on the properties of simple isolated configurations of the $(J=1)$ molecules interacting via the EQQ coupling mechanism. The results are compared with those predicted by a recent theory of Harris.[5]

Our third purpose is to present and discuss measurements of $(\partial P/\partial T)_V$ over a broad range of c in the hcp phase. The region of intermediate c is of particular interest because transitions from rotational order to rotational disorder may occur here.[15] The results are to be compared with recent ones for solid H_2 in the same $(J=1)$ concentration range.

Unlike H_2, solid D_2 of the $(J=1)$ species converts to $(J=0)$ sufficiently slowly to allow measurements of $(\partial P/\partial T)_V$ to be made at virtually constant c. This is of great advantage, especially in the cubic phase where $(\partial P/\partial T)_V$ is strongly dependent on c. Also unlike H_2, solid D_2 shows no evidence of molecular rearrangement[16] at low $(J=1)$ concentrations, and therefore its properties can be considered to be those of randomly distributed para and ortho molecules in a fixed lattice.

In Sec. II we present a short review of theory relevant to the analysis of our data. After a description of experimental methods in Sec. III, a study of the phase transition in D_2 is discussed in Sec. IV and is compared with a similar study in solid H_2. In Sec. V the measurements of $(\partial P/\partial T)_V$ in the hcp phase are presented and discussed. Section VII contains a tabulation and discussion of the rotational entropy of solid D_2.

II. THEORETICAL SURVEY

We make the same simplifying assumption as in Ref. 4 that the free energy is the sum of a lattice contribution F_L and a component describing the rotational motion F_{EQQ}. Furthermore, we assume that F_L is the same for all concentrations of $(J=1)$ molecules and for both hcp and cubic phases. We then assume that F_L can be represented by the Debye approximation, at least at temperatures below 4 K, and that F_{EQQ} depends only on the EQQ interaction parameter Γ, any effects from crystalline fields and other mechanisms being neglected. Here $\Gamma=6e^2Q^2/25r^5$, where eQ is the quadrupole moment for molecules with $(J=1)$ and r is the nearest-neighbor distance. For solid D_2, $Q=0.134\times10^{-16}$ cm^2,[17] $r=3.60\times10^{-8}$ cm[1,18,19] in both crystalline phases at zero pressure, and hence one calculates for a rigid lattice $\Gamma_0/k_B=1.20$ K.

We have

$$(F_L-F_{0,L})/k_BT=\phi(\Theta_D/T)\,, \tag{1a}$$

$$(F_{\mathrm{EQQ}}-F_{0,\mathrm{EQQ}})/k_BT=f(\Gamma/k_BT)\,, \tag{1b}$$

where $F_{0,L}$ and $F_{0,\mathrm{EQQ}}$ are the ground-state free energies. It then follows that

$$C_V=C_{V,L}+C_{V,\mathrm{EQQ}}\,, \tag{2a}$$

$$(\partial P/\partial T)_V=(\partial P/\partial T)_{V,L}+(\partial P/\partial T)_{V,\mathrm{EQQ}}\,, \tag{2b}$$

with

$$(\partial P/\partial T)_{V,L}=\gamma_LC_{V,L}/V\,, \tag{3a}$$

$$(\partial P/\partial T)_{V,\mathrm{EQQ}}=\gamma_{\mathrm{EQQ}}C_{V,\mathrm{EQQ}}/V\,, \tag{3b}$$

where

$$\gamma_L=-d\ln\Theta_D/d\ln V\,, \tag{4a}$$

$$\gamma_{\mathrm{EQQ}}=-d\ln\Gamma/d\ln V=5/3\,. \tag{4b}$$

For pure orthodeuterium (o-D_2) or parahydrogen (p-H_2) there is no quadrupole component, so that

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[11] K. Motizuki, J. Phys. Soc. Japan **12**, 163 (1957); **17**, 1192 (1962).

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

[13] J. F. Jarvis, D. Ramm, and H. Meyer, Phys. Rev. **170**, 320 (1968).

[14] T. Nakamura, Progr. Theoret. Phys. (Kyoto) **14**, 135 (1955).

[15] H. M. James, Phys. Rev. **167**, 862 (1968).

[16] L. I. Amstutz, J. R. Thompson, and H. Meyer, Phys. Rev. Letters **21**, 1175 (1968).

[17] G. Karl and J. D. Poll, J. Chem. Phys. **46**, 2944 (1967). We use their value of $Q=0.1368\times10^{-16}$ cm^2 for H_2, and an appropriate scaling of the mass to obtain the value for D_2.

[18] A. F. Schuch and R. L. Mills, Phys. Rev. Letters **16**, 616 (1966).

[19] K. F. Mucker, S. Talhouk, P. M. Harris, D. White, and R. A. Erickson, Phys. Rev. Letters **16**, 799 (1966).

$(\partial P/\partial T)_V = (\partial P/\partial T)_{V,L}$. This quantity can be subtracted from the measured one at a given concentration of $(J=1)$ molecules to obtain the contribution due to the rotational motion.

We now discuss the two simplest conditions under which the EQQ interaction parameter Γ can be determined. The first is that at low $(J=1)$ concentration where interaction is mostly between two nearest $(J=1)$ molecules, and the second is that for the pure $(J=1)$ solid. Before describing the method of experimental analysis, we should point out that a theory by Harris[20] takes into account the correlation effects of the nearest-neighbor motions and dielectric screening and shows that Γ must be renormalized so that it is expected to be smaller than that for a rigid lattice, Γ_0, calculated above. Furthermore, the effective parameter Γ_{eff} is different in the two limiting cases mentioned above for which we define $\Gamma_{\text{eff(pair)}}$ and $\Gamma_{\text{eff}(c=1)}$, respectively. These parameters will be seen to differ by about 10%. For intermediate concentrations c, we use the notation Γ_{eff}. This parameter presumably varies continuously between the two limiting values.

At low $(J=1)$ concentrations, $\Gamma_{\text{eff(pair)}}$ can be obtained by a fit of the experimental $(\partial P/\partial T)_{\text{V,EQQ}}$ data to those predicted theoretically, as already described.[4] At sufficiently small c, the $(J=1)$ molecules appear as isolated single molecules and in $(J=1)$ nearest-neighbor (nn) configurations of isolated pairs, triangles, etc. The EQQ interaction removes the degeneracy of the levels, the splitting being proportional to the effective EQQ pair-interaction parameter $\Gamma_{\text{eff(pair)}}$. The specific heat of the various configurations at low $(J=1)$ concentration has been tabulated by Harris[20] as a function of c and the reduced temperature $k_BT/\Gamma_{\text{eff(pair)}}$.

The computations for clusters with four or more $(J=1)$ molecules are quite complex and it has been assumed [20] that these have the same specific heat per $(J=1)$ molecule as the triangles. The reliability of the calculation improves as the concentration c diminishes because the contribution of these larger clusters vanishes faster than that of the triangles and pairs.

It should be mentioned that the calculations neglect EQQ interactions between $(J=1)$ next-nearest neighbors (nnn), so that a $(J=1)$ molecule surrounded by all twelve $(J=0)$ nearest neighbors has zero specific heat. In reality the EQQ interaction between two nnn $(J=1)$ molecules separated by $\sqrt{2}r$ will contribute a splitting of the energy levels of $2^{5/2}=5.6$ times smaller than that between nn molecules. The splitting may be reduced further through dielectric screening by the intermediate $(J=0)$ molecules. Hence, the corresponding Schottky anomaly in the specific heat should become relatively important only at $T<1$ K.

The second situation for which Γ can be determined is that where $c=1$. For the ordered cubic phase, there exist several theories[3,7–10] that are based on a model of rotational excitations. In these theories the dispersion curves of the rotational excitation waves (librons) in k space have been calculated. Qualitatively the theories agree in that they all show eight excitation modes with an average energy

$$\Delta_{\text{BZ}(c=1)} = 19\Gamma_{\text{eff}(c=1)} \tag{5}$$

over $\mathbf{k}$ space in the Brillouin zone (BZ) neglecting zero-point effects.[3] However, the densities of states obtained[7,8,10] from the dispersion curves have different energy-band widths, depending on the approximation used. For convenience to the reader, values of the density of states at $T=0$ K are reproduced in Fig. 1 as a function of the reduced energy $\epsilon = E/\Delta_{\text{BZ}(c=1)}$.

In the past, theories[3,7–10] were based on EQQ interaction between nn molecules only. Recently, Berlinsky, Harris, and Coll[21] calculated the effect of interactions between nnn molecules on the rotational energy modes. At $k=0$, the effect is to shift the eight modes to energies that are higher by an average of about 20%. Hence the center of gravity for p-D_2 in the cubic phase is given by

$$\Delta_{(\mathbf{k}=0,c=1)} \cong 23\Gamma_{\text{eff}(c=1)}\,. \tag{6}$$

Furthermore, from the work of Refs. 3 and 22, it can be seen that the average energy throughout the BZ is very much the same as the molecular field energy gap. When the effect of nnn interactions is included, one has[21]

$$\Delta_{\text{BZ}(c=1)} = 21.2\Gamma_{\text{eff}(c=1)}\,. \tag{7}$$

For simplicity, let us denote by Δ the center of gravity of the libron energy band throughout the BZ at a given concentration c. Then, at sufficiently low temperatures, where $k_BT \ll \Delta$, we have to a very good approximation

$$\left(\frac{\partial P}{\partial T}\right)_{\text{V,EQQ}} = \frac{\gamma_{\text{EQQ}} C_{\text{V,EQQ}}}{V} = \frac{\gamma_{\text{EQQ}}\, c}{V} \times\left(\frac{\sum 2(\epsilon\Delta/k_BT)^2\,\{\exp-(\epsilon\Delta\,|\,k_BT)\}n(\epsilon)d\epsilon}{\sum_{\text{BZ}} n(\epsilon)d\epsilon}\right), \tag{8}$$

where the quantity in large parentheses is the average specific heat for systems with energy states $J_z=0$, $J_z=\pm1$ using the density of states $n(\epsilon)$.

We calculated the specific heat for the three published densities of state in Fig. 1 and then produced by computer a tabulation in small increments of (k_BT/Δ) for use in analyzing the data. The splitting Δ was obtained from a fit of the experimental $(\partial P/\partial T)_{\text{V,EQQ}}$ to Eq. (8). A low temperatures, $(\partial P/\partial T)_V$ and C_V afford a particularly sensitive method of determining Δ because of their exponential dependence on this quantity. For $k_BT/\Delta < 0.1$, an uncertainty in C_V of 10% gives an uncertainty in Δ of less than 2%.

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[20] A. B. Harris (unpublished).

[21] A. J. Berlinsky, A. B. Harris, and C. Coll, Solid State Commun. **7**, 297 (1969).

[22] H. M. James and J. C. Raich, Phys. Rev. **162**, 649 (1967).

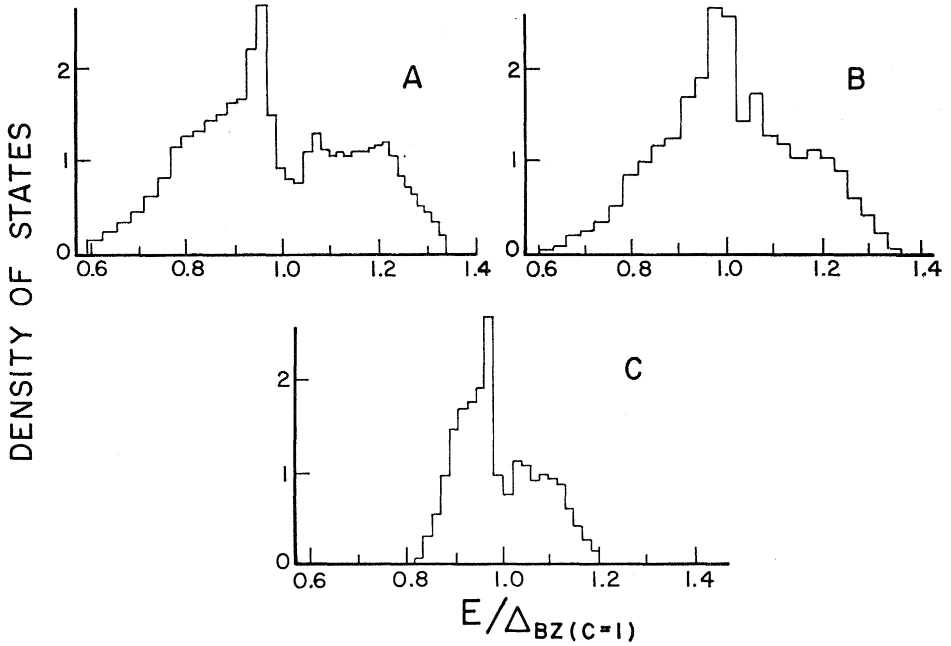

FIG. 1. Densities of states for rotational excitations in the $(J=1)$ manifold. Densities are plotted against reduced energy $E/\Delta_{BZ(c=1)}$, the center of gravity of which is $\Delta/\Gamma=19$. Curves have been normalized to give the same maximum height. Histogram A, Mertens, Biem, and Hahn (Ref. 9); histogram B, Ueyama and Matsubara (Ref. 8); histogram C, Homma, Okada, and Matsuda (Ref. 7).

Clearly the Δ so obtained will depend on the theoretical densities of state used in fitting the data.

It is difficult, if not impossible, to prepare specimens of pure p-D_2 or o-H_2, and experiments at various high concentrations of $(J=1)$ molecules must be carried out and the results extrapolated to $c=1$. In our analysis we assume that the distribution of the excited states is the same as that for pure $(J=1)$ solid, but that Δ is a function of c.

In solid D_2 one has the opportunity of studying the rotational ordering wholely within the cubic phase, since this phase can be stabilized at temperatures well above the transition temperature by repeated thermal cycling.[2] Extrapolation of the experimental results to the limiting case of pure p-D_2 then affords a comparison with theoretical predictions. James and Raich[22] used a self-consistent molecular field approximation to obtain a corresponding set of wave functions. Using a truncated Hamiltonian (Ising model) they obtained exact solutions for the energy eigenvalues. They showed that a first-order transition should occur at a temperature $T^*=6.86\Gamma/k_B$. The Ising-model approximation together with a statistical treatment based on Bethe's method[23] does not predict a sharp transition, but rather a maximum in the specific heat at a temperature T^* very close to that predicted by the molecular field approximation. Calculation of the temperature of the maximum in C_V shows it to be closely proportional to c, an effect that is anticipated also for the molecular field approximation.

Harris[24] discussed the exact partition function for the particular truncated Hamiltonian[22] and showed that it did not have the nonanalytic behavior of the partition function derived from the molecular field approximation. He finds a region $5.81<T<6.86$ where the ordering parameter $\langle 3J_Z^2-2\rangle_T$ varies rapidly with T. Furthermore, Harris[5] points out that, since the models used to calculate T^* overestimate the temperatures by about 20–25%, we might expect for pure p-D_2 in the cubic phase,

$$k_BT^*/\Gamma\approx 6\times\tfrac{3}{4}=4.5. \qquad (9)$$

Recently, Raich and Etters[25] used a cluster-variation treatment to study the orientational transition and calculate the ordering parameter as a function of progressive truncation of $\mathcal{H}_{EQQ}$. They found the transition temperature to be substantially lower than that from previous treatments of this system.

Turning now to the hcp phase, we find that molecular field theories[15,26] of rotational ordering predict a first-order transition at $T^*=6.4\Gamma/k_B$ for pure p-D_2. Here again, one might expect the transition temperature to be approximately proportional to c. In D_2 the hcp structure is stable at all temperatures in the solid region for $c\lesssim 0.52$.

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[23] J. C. Raich and R. D. Etters, J. Phys. Chem. Solids 29, 1561 (1968).

[24] A. B. Harris, Solid State Commun. 6, 149 (1968).

[25] J. C. Raich and R. D. Etters (unpublished).

[26] W. M. Fairbairn, W. S. Lounds, and M. R. Steel, in Proceedings of the Eleventh International Conference on Low Temperature Physics, 1968 (unpublished).

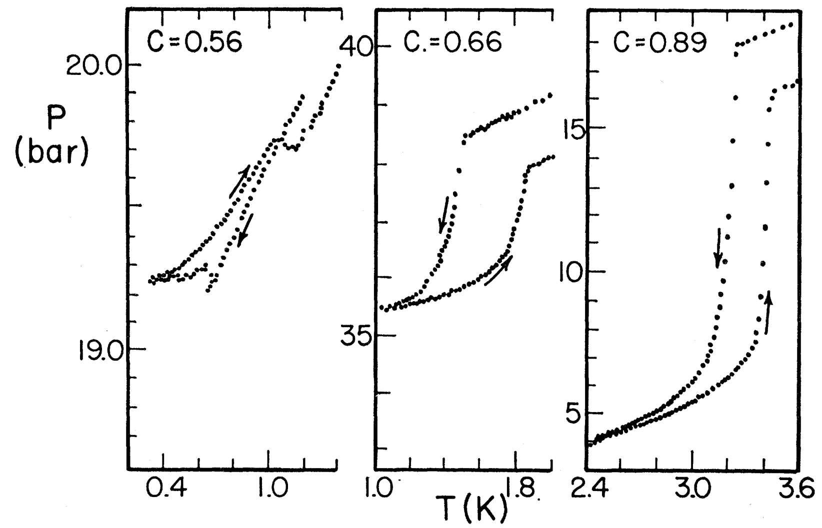

FIG. 2. Pressure $P(T)$ during first thermal cycling through the transition for various p-D_2 concentrations.

III. EXPERIMENTAL METHODS

The apparatus uses a strain gauge that can resolve pressure changes of 10^{-5} bar. The sensitivity of the particular guage is limited by the outer wall thickness of the sample container which is required to withstand pressures up to 150 bar during condensation of the sample. Appreciably higher sensitivities are attainable with thinner membranes for experiments at low pressure.

The apparatus and the technique of taking data have been described elsewhere.[4,13] As mentioned in Ref. 13, the change in pressure with temperature does not take place at exactly constant volume, and a correction must be applied to convert the measured dP/dT to $(\partial P/\partial T)_V$. We have

$$(\partial P/\partial T)_V=(1+a)dP/dT\,, \qquad (10)$$

where the quantity a is inversely proportional to the compressibility of the solidified gas, being about 1% for the helium isotopes and 7% for solid H_2 in that particular chamber. For D_2, however, the isothermal compressibility coefficient is only half that for solid H_2, namely,[27] $K_T=3\times10^{-4}$ bar^{-1}, and its value is known to about 30% in the pressure range of the present measurements. The quantity a is then of the order of 0.2. Because of the large uncertainty in a, we have computed it empirically by normalization. Through Eqs. (2a), (2b), (3a), (3b), and (10), the specific-heat data[12] when combined with dP/dT data are sufficient to determine a. Since $\gamma_{\mathrm{EQQ(expt)}}$ is found to equal $\gamma_{\mathrm{EQQ(theoret)}}=5/3$ for H_2,[4] this agreement has been taken as justification for use of the same value for D_2. Choosing arbitrarily $c=0.33$ and $3<T<4$°K, we found $a=0.26\pm0.05$. To obtain $C_{V,\mathrm{EQQ}}$ from C_V via Eq. (2a), we used the $C_{V,L}$ data given by Hill and Lounasmaa.[28] The uncertainty in our $(\partial P/\partial T)_V$ data is dependent on the magnitude of (dP/dT) and is estimated to average 2–3% except near the ordering transition and below 0.4 K, where it is larger.

Gas samples with concentrations between $c=0.33$ (normal deuterium n-D_2) and $c=0.90$ were made up by mixing enriched p-D_2, prepared by selective adsorption,[29] with commerically available n-D_2.[30] Concentrations in the range $0.02<c<0.33$ were obtained by mixing n-D_2 with nearly pure o-D_2, prepared at 20 K on Cryenco catalyst. As stated by Grenier and White,[12] the para-enrichment process reduces the HD impurity from that in the n-D_2, where it was about 0.4%.

The preparation of the solid sample and the determination of c were carried out as for H_2.[4] The un-

TABLE I. The crystalline-phase transition temperatures and the pressure changes during the first thermal cycling.[a]

c	$T_{\mathrm{h-c}}$ (K)	$T_{\mathrm{c-h}}\cong(T_\lambda-0.004)$ (K)	$(\delta P_{\mathrm{h-c}})_{\mathrm{I}}$ (bar)	$(\delta P_{\mathrm{c-h}})_{\mathrm{I}}$ (bar)
1.00	(3.90)	(4.05)	(19)	(17)
0.95	(3.50)	(3.70)	(16.4)	(14.0)
0.90	3.17	3.40	13.6	11.5
0.85	2.83	3.07	11.0	9.2
0.80	2.50	2.75	8.4	6.8
0.75	2.15	2.43	6.1	4.9
0.70	1.82	2.10	4.4	3.0
0.65	1.48	1.80	2.8	1.6
0.60	1.15	1.46	1.5	0.9
0.58	0.97	1.30	0.4	0
0.56	0.73	1.10	−0.25	−0.2
0.55	0.50	1.00	−0.1	−0.2
0.54	(0)	(0.85)		
0.53		(0.7)		
0.52		(0.3)		

[a] Values in parentheses are extrapolations.

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

[28] R. W. Hill and O. V. Lounasmaa, Phil. Mag. **4**, 786 (1959).

[29] D. A. Depatie and R. L. Mills, Rev. Sci. Instr. **39**, 105 (1968).

[30] Deuterium, C. P. Grade, Matheson Products, East Rutherford, N. J. 07073.

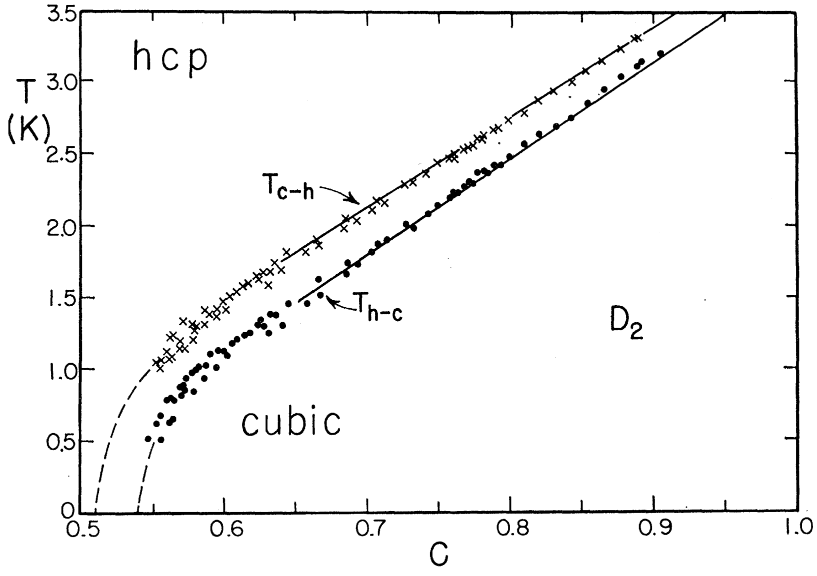

FIG. 3. Phase diagram for solid D_2. Cross, cooling transition; full circle, warming transition; solid line, Ref. 2. The lower line also coincides with the results of Ref. 12.

certainty in c was about ±1.5 and ±0.5% at the highest and lowest concentrations, respectively. For experiments where measurements were taken over an extended period such that the concentration varied by as much as 0.05 due to self-conversion, the value of c at a given time was obtained by linear interpolation in time between those values measured at the beginning and at the end of the experiment. Such an interpolation is justified according to the theory of Motizuki.[11]

Because of the slow para-ortho conversion rate, no isothermal measurements of P versus c were carried out. Such measurements were feasible in H_2 and led to a determination of Γ for this solid.[4] No efforts were made to obtain $(\partial P/\partial T)_V$ above 4.2 K, where specific-heat data[12] are available.

IV. EXPERIMENTAL RESULTS: hcp-TO-CUBIC PHASE TRANSITION

A detailed study of the phase transition as a function of c was made in two parts. In Sec. IV A, the sample was freshly prepared at the freezing curve and was cooled and then warmed through the transition. The pressure changes and temperatures associated with the cooling and warming are presented in Table I. In Sec. IV B, the quantity $P(T)$ and its derivative $(\partial P/\partial T)_V$ were observed during several successive thermal cyclings through the transition at different p-D_2 concentrations.

A. Phase Diagram

The experiments consisted in cooling the hcp sample from its freezing point into the cubic phase, warming it back into the hcp phase, and finally to its melting point. Such temperature cycles took place at practically constant c because of the slow para-ortho conversion rate. Representative $P(T)$ curves for cooling and warming through the transition on this first thermal cycle are shown in Fig. 2 and appear to be very similar to those for H_2 except that the transition on warming is more sharply defined. The pressure drops sharply at the first hcp-cubic cooling and increases on warming, but does not attain its original value at a corresponding temperature in the hcp phase. Just as in solid H_2,[4] there is a small concentration region where the pressure difference $\delta P=(P_{\mathrm{hcp}}-P_{\mathrm{cubic}})$ becomes negative. This effect has been observed repeatedly and is believed to be real. Its unique concentration range extends from $c=0.58$ to 0.55, below which no transition from hcp to cubic is observed. Figure 3 shows the phase diagram and a comparison of our data with those of other authors.[2,12] Preliminary data over a smaller concentration range have been presented elsewhere.[31] As in the experiments[4] on solid H_2, the pressure change through the transition was defined as follows: A line was drawn tangent to the $P(T)$ curve in the cubic phase and parallel to that in the hcp phase. The separation of the lines was then defined as $(\delta P_{\mathrm{c-h}})_1$ and $(\delta P_{\mathrm{h-c}})_1$, for warming and cooling, respectively. The subscript 1 denotes the first thermal cycling. The transition temperature was chosen as the temperature at which half the pressure change had taken place. As for H_2, there is a hysteresis in the transition temperature between cooling $T_{\mathrm{h-c}}$ and warming $T_{\mathrm{c-h}}$. Each $P(T)$ curve upon warming exhibited a slope whose maximum occurred at a sharply defined temperature T_λ. It is the temperature of this maximum that Grenier and White[12] have presented in tables of C_V as a function of c. The temperature at the maximum of $(\partial P/\partial T)_V$ was found usually to be about 3–4 mK higher than

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[31] J. F. Jarvis, D. Ramm, H. Meyer, and R. L. Mills, Phys. Letters **25A**, 692 (1967).

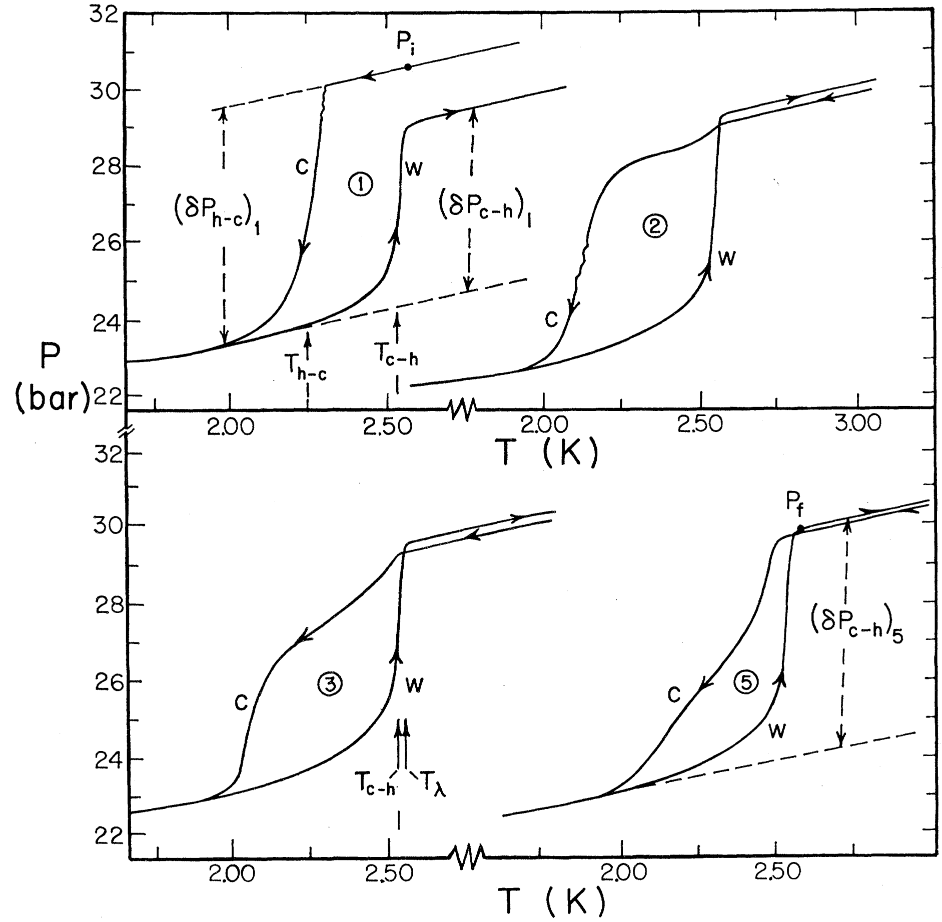

FIG. 4. Pressure $P(T)$ for p-D_2 concentration $c=0.77$ during several thermal cyclings through the transition. The labels on the curves number the thermal cycle and indicate whether it is cooling (C) or warming (W). The different symbols are described in the text.

T_{c-h} as defined above, and agreed with T_λ of Grenier and White[12] who report an average uncertainty of ±7 mK.

Experiments of the type that were carried[4] out on solid H_2 very close to the critical $(J=1)$ concentration $c=0.55$, could not be carried out on solid D_2 because of the slow para-ortho D_2 conversion. Nevertheless, we expect the behavior of D_2 to be similar to that of H_2 and have determined the critical p-D_2 concentration for the cubic-to-hcp transition $c=0.52$ by extrapolation in a way consistent with that for H_2. The results are presented in Table I.

The phase diagram for D_2, extrapolated to $c=1$, leads to $T_{h-c}=3.90$ K and $T_{c-h}=4.05$ K. Furthermore, the pressure change, as defined previously and extrapolated to $c=1$, gives $(\delta P_{h-c})_1=19\pm1$ bar and $(\delta P_{c-h})_1=17\pm1$ bar. From the experiments with several thermal cyclings (see below) it is apparent that T_{c-h} is closely representative of the order-disorder transition in the cubic phase.

B. Experiments with Repeated Thermal Cycling

Schuch *et al.*[2] made a careful study of successive thermal cycling of both H_2 and D_2 through the transition. The partial concentrations of the hcp and cubic phases were estimated from the intensities of the corresponding x-ray diffraction lines. The very striking result was that upon warming through the transition on the first cycle, only about 20% of the original hcp phase reappeared, while about 10% of the cubic phase still remained at 0.8 K above T_{c-h}. This result is consistent with that from neutron diffraction studies,[1] where a reflection from the hcp phase only was monitored. Repeated thermal cyclings[2] further diminished the hcp phase above T_{c-h} and stabilized the cubic phase. After the third cycle, about 50% of the material remained cubic at ~0.8 K above T_{c-h}. It appears probable that after many thermal cycles all of the cubic solid would remain stable in this region. As the temperature was increased well above T_{c-h}, the cubic structure went over gradually to hcp.

We have carried out measurements of $P(T)$ at constant molar volume through as many as six thermal cycles for various p-D_2 concentrations. Experiments of this kind lasted about 15 h. A representative set of curves is shown in Fig. 4 for $c=0.77$. Practically the same curves were obtained on a second experiment

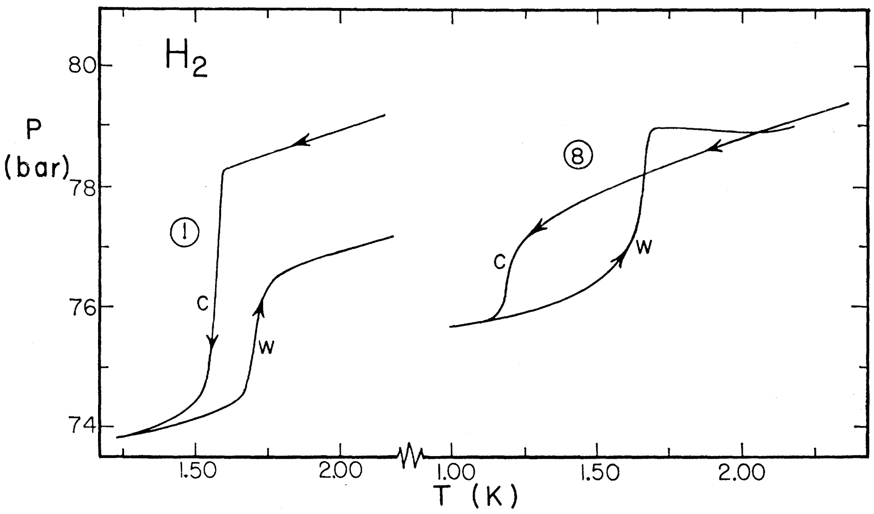

FIG. 5. Pressure $P(T)$ for H_2 during repeated thermal cycling through the transition. Labeling identical to Fig. 4. The decrease with cycling of the transition temperature results from the decrease with time of the o-H_2 concentration which was initially $c=0.74$.

after annealing the sample at the melting point. Curves at higher p-D_2 concentrations are quite similar.

As shown in Fig. 4, the first cooling exhibits a discontinuity in slope $(\partial P/\partial T)_V$ when the hcp-cubic transition starts. Some instabilities in the transition are reflected by the sawtooth pattern over a small region of the $P(T)$ curve where its slope is largest. Upon warming, the slope again changes quite sharply, and above $T_{\text{c-h}}$ it assumes the same value as on cooling. The pressure change $(\delta P_{\text{c-h}})_1$ is only about 80% of $(\delta P_{\text{h-c}})_1$, where the subscript 1 denotes the first thermal cycle. On cooling during the second cycle, there is a small pressure drop near $T_{\text{c-h}}$ followed by a large drop near $T_{\text{h-c}}$ of the first cycle, again with some jagged behavior of the $P(T)$ curve. On warming the sample, the pressure exceeds that reached after the first cycle. During the third and subsequent cycles, the pressure drop on cooling starts at higher temperatures, but the cubic-to-hcp transition is the same as before with $(\partial P/\partial T)_V$ being reproducible well below $T_{\text{h-c}}$.

From Fig. 4 we conclude that, after the nth thermal cycle, one has approximately

$$(\delta P_{\text{h-c}})_n \cong (\delta P_{\text{c-h}})_n \cong (\delta P_{\text{h-c}})_1 .$$

It is quite possible that after still more thermal cycles the final pressure P_f above $T_{\text{c-h}}$ reaches the initial pressure P_i in the pure hcp phase before the first transition. P_f is then the pressure of the disordered, almost entirely cubic phase. Since $P_i \approx P_f$, we conclude that the pressure of disordered cubic and hcp phases must be closely the same.

Based on evidence from cycling experiments with x rays and with pressure, it appears that the pressure change at the transition is mainly due to the rotational order-disorder transition in the cubic phase. This is consistent with the suggestion of Mucker *et al.*[1] that the peak in specific heat is due to rotational disordering rather than to a purely crystalline-phase change. Furthermore the temperature of this disordering corresponds to the maximum in both the specific heat and $(\partial P/\partial T)_V$. This temperature after repeated cycling coincides with the temperature at which the pressure starts to drop upon cooling (Fig. 4).

We have also carried out systematic thermal-cycling experiments on solid H_2, the sample being cooled and warmed 18 times through the transition. The initial concentration was $c=0.74$. The $P(T)$ curves are presented with numbers labeling the thermal cycles in Fig. 5. The time interval between the second and fifteenth cycles was held to about 1 h to minimize effects of conversion. The most striking observations were the following: (a) after repeated cycling, just as for D_2, $(\delta P_{\text{h-c}})_n \approx (\delta P_{\text{c-h}})_n$; (b) the transition on warming became sharper after repeated cycling; (c) there was a region just above $T_{\text{c-h}}$, where the slope $(\partial P/\partial T)_V$ became negative. This last observation is unexpected since a negative slope indicates a negative thermal expansion or a negative specific heat and suggests that thermodynamic equilibrium was not reached during the rapid cyclings and the subsequent pressure measurements.

V. MEASUREMENT OF $(\partial P/\partial T)_V$ IN hcp PHASE

All data below 4 K were taken at an average pressure of about 20 bar. Smoother values of $(\partial P/\partial T)_V$ at regular temperature intervals and various p-D_2 concentrations are presented in Table II. From this table, one can obtain the isobaric coefficient of thermal expansion α_p, using the relation $\alpha_p = (\partial P/\partial T)_V K_T$. The isothermal compressibility coefficient K_T is assumed to be constant below 4.2 K, where its average value is $(3.3 \pm 1.0) \times 10^{-4}$ bar^{-1} from density experiments between 20 and 100 bar.[27]

A. Lattice Contribution

The lowest $(J=1)$ concentration available by simple catalytic conversion of gaseous D_2 at low temperature

TABLE II. $(\partial P/\partial T)_V$ in bar K^{-1} for various low concentrations of paradeuterium in the hcp phase.

T (K) \ $c=$	0.018	0.025	0.033	0.05	0.060	0.090	0.128	0.180	0.233	0.295	0.330	0.380	0.415	0.48	0.524	0.550	0.59
0.35	0.000	0.00045	0.0180	0.039	0.053	0.0832	0.148	0.202	0.244	0.318	0.316	0.388	0.294	0.379	0.374		
0.40	0.0035	0.0070	0.0202	0.042	0.0565	0.0876	0.156	0.214	0.266	0.364	0.376	0.438	0.458	0.440	0.468		
0.45	0.0072	0.0120	0.0225	0.044	0.0585	0.0920	0.164	0.229	0.294	0.407	0.440	0.506	0.555	0.560	0.592		
0.50	0.0112	0.0153	0.0248	0.046	0.0610	0.0965	0.172	0.245	0.320	0.445	0.490	0.576	0.646	0.705	0.755	0.783	
0.55	0.0135	0.0176	0.0270	0.0485	0.0643	0.101	0.178	0.261	0.344	0.477	0.530	0.640	0.721	0.815	0.905	0.946	
0.60	0.0150	0.0195	0.0282	0.052	0.0665	0.105	0.188	0.277	0.366	0.507	0.564	0.689	0.772	0.895	1.035	1.105	
0.65	0.0162	0.0206	0.0293	0.054	0.069	0.110	0.196	0.292	0.385	0.532	0.593	0.717	0.815	0.965	1.14	1.230	
0.70	0.0162	0.0220	0.0304	0.0565	0.072	0.115	0.205	0.305	0.402	0.553	0.617	0.740	0.840	1.02	1.205	1.32	
0.75	0.0162	0.0226	0.0316	0.058	0.0745	0.120	0.212	0.318	0.420	0.572	0.638	0.755	0.856	1.05	1.24	1.36	
0.80	0.0162	0.0234	0.0327	0.060	0.077	0.125	0.222	0.329	0.435	0.590	0.655	0.770	0.868	1.06	1.260	1.38	
0.85	0.0163	0.0238	0.0338	0.062	0.080	0.130	0.229	0.339	0.445	0.605	0.671	0.782	0.876	1.065	1.260	1.38	
0.90	0.0164	0.0240	0.0349	0.063	0.0825	0.134	0.237	0.349	0.460	0.617	0.685	0.792	0.885	1.062	1.260	1.365	
0.95	0.0163	0.0244	0.0360	0.0655	0.0845	0.139	0.244	0.359	0.472	0.631	0.697	0.802	0.892	1.060	1.25	1.35	
1.00	0.0162	0.0246	0.0360	0.067	0.0865	0.143	0.250	0.368	0.482	0.642	0.708	0.810	0.898	1.060	1.235	1.335	
1.10	0.0160	0.0251	0.0372	0.070	0.091	0.151	0.261	0.386	0.502	0.658	0.730	0.830	0.914	1.062	1.23	1.315	
1.20	0.0160	0.0255	0.0383	0.072	0.095	0.1575	0.272	0.400	0.521	0.678	0.748	0.845	0.924	1.07	1.23	1.31	1.42
1.40	0.0172	0.0267	0.0406	0.078	0.100	0.1675	0.287	0.321	0.549	0.704	0.781	0.882	0.954	1.10	1.24	1.31	1.42
1.60	0.0199	0.0298	0.0440	0.0825	0.1025	0.173	0.296	0.435	0.567	0.724	0.805	0.899	0.979	1.15	1.26	1.325	1.42
1.80	0.0244	0.0354	0.0497	0.087	0.105	0.177	0.298	0.442	0.577	0.739	0.823	0.924	1.005	1.19	1.285	1.35	1.43
2.00	0.0302	0.0415	0.0542	0.090	0.106	0.179	0.298	0.444	0.584	0.748	0.836	0.945	1.03	1.22	1.31	1.365	1.445
2.20	0.0380	0.0475	0.0598	0.093	0.107	0.180	0.296	0.443	0.584	0.753	0.844	0.957	1.045	1.24	1.34	1.385	1.46
2.40	0.0459	0.0529	0.0642	0.095	0.1085	0.180	0.292	0.438	0.582	0.754	0.845	0.960	1.055	1.25	1.36	1.40	1.475
2.60	0.0505	0.0576	0.0689	0.097	0.1095	0.179	0.287	0.431	0.575	0.750	0.842	0.961	1.055	1.25	1.365	1.41	1.490
2.80	0.0532	0.0604	0.0722	0.098	0.110	0.177	0.280	0.420	0.564	0.742	0.832	0.960	1.055	1.24	1.365	1.415	1.50
3.00	0.0592	0.0640	0.0756	0.0995	0.1115	0.175	0.274	0.411	0.522	0.729	0.822	0.958	1.052	1.225	1.365	1.415	1.51
3.40	0.0730	0.0805	0.0881	0.101	0.1175	0.173	0.266	0.396	0.535	0.710	0.802	0.958	1.050	1.20	1.365	1.41	1.515
3.80	0.097	0.0960	0.1010	0.106	0.1285	0.184	0.264	0.390	0.525	0.692	0.797	0.962	1.050	1.19	1.365	1.41	1.53
4.20	0.120	0.1300	0.1310	0.135	0.146	0.210	0.275	0.386	0.521	0.689	0.800	0.965	1.052	1.19	1.37	1.41	1.56

is $c=0.02$, and thus even here molecular rotations will contribute along with lattice vibrations to the observed values of $(\partial P/\partial T)_V$. In an attempt to separate the rotational contribution, we fit the data for four concentrations ranging from $c=0.018$ to 0.050 to the expression

$$(\partial P/\partial T)_V = AT^3 + BT^{-2} \tag{11}$$

at temperatures between 2.5 and 4.2 K. The terms in T^3 and T^{-2} represent the lattice contribution and the high-temperature EQQ contribution, respectively. The factors A and B were evaluated and plotted as a function of c. As expected, A was constant and B was approximately proportional to c^2. The value of A, which is the only term of interest here, was found to be $(1.75 \pm 0.10) \times 10^{-3}$ bar K^{-4}. The lattice specific heat is then calculated from an average $\Theta_D = 105$ K below $T=4$ K.[28] From Eq. (3a) we obtain $\gamma_L = 2.0 \pm 0.1$, which is similar to $\gamma_L = 2.1$ for solid H_2.[4] From measurements on D_2 of $(\partial P/\partial T)_V$, C_V, and K_T, one finds that, just as for solid H_2, the quantity $(C_p - C_V)/C_V$ is negligibly small for temperatures at least up to 5 K, in agreement with previous estimates.[28]

B. Concentration Range $0.02 < c < 0.07$

In this concentration range, it was expected that an analysis of the $(\partial P/\partial T)_V$ data could be carried out in

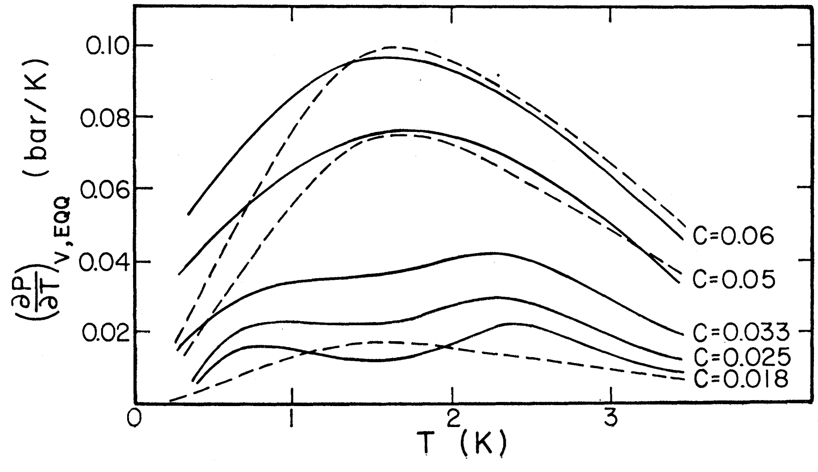

FIG. 6. $(\partial P/\partial T)_{V,EQQ}$ for D_2 at several low para concentrations. Solid line, experimental data; dashed curve, theory using $\gamma_{EQQ} = 5/3$ and $\Gamma_{eff}/k_B = 1.05$ K, and nearest pair interaction only, as described in text.

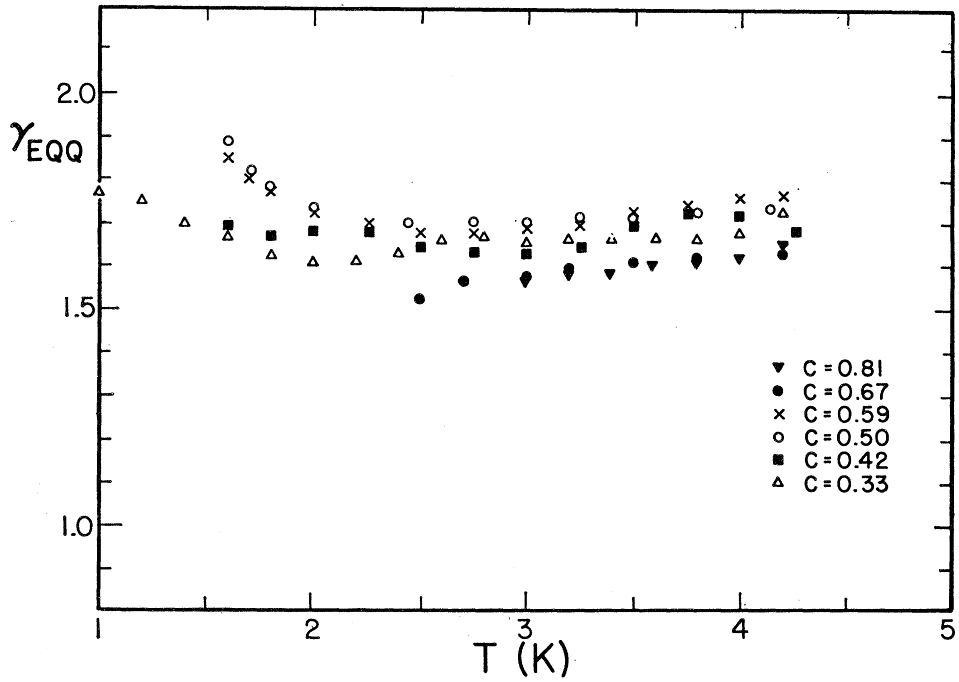

FIG. 7. Grüneisen constant γ_{EQQ} as a function of T for several p-D_2 concentrations in the hcp phase.

terms of contributions from isolated pairs and triangles of ($J=1$) molecules. For this purpose, $(\partial P/\partial T)_{V,EQQ}$ was obtained from $(\partial P/\partial T)_V$ by subtracting the lattice contribution AT^3 of Eq. (11). The results are shown in Fig. 6. The two distinct maxima at the lowest para concentrations are found to merge into a single one as c increases. In Fig. 6 we have also plotted values of the theoretical $(\partial P/\partial T)_{V,EQQ}$ calculated by Harris[20] and compared them with the experimental data at $c=0.06$ and $c=0.05$. The fit was best for a value of $\Gamma_{\mathrm{eff(pair)}}/k_B = 1.05\pm0.07$ K. The theoretical prediction by Harris,[5] including phonon effects and screening is $\Gamma_{\mathrm{eff(pair)}}/k_B = 1.11$ K.

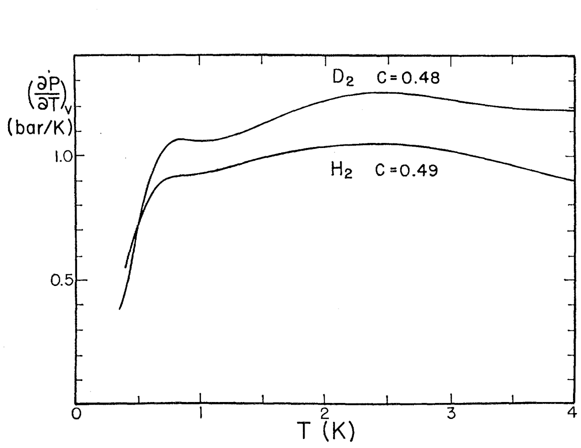

FIG. 8. Representative curves of $(\partial P/\partial T)_V$ for D_2 and H_2 in the range of intermediate ($J=1$) molecule concentrations.

The behavior at the lowest ($J=1$) concentrations is totally unexpected and has not been clarified at the present time. The specific-heat measurements[28] on D_2 at comparable ($J=1$) concentrations have not been extended to low enough temperatures to show evidence of the double maximum in $C_{V,EQQ}$.

C. Concentration Range $0.07<c<0.55$

The $(\partial P/\partial T)_V$ values presented in Table II can be compared with the corresponding specific heats[12] at the same ($J=1$) concentrations. After making use of Eqs. (2a) and (2b) and subtracting the appropriate lattice contributions from both C_V and $(\partial P/\partial T)_V$, we obtained the effective γ_{EQQ} from Eq. (3b) for several values of c using appropriate interpolations. Figure 7 shows the results as a function of temperature. We have already pointed out that the strain-gauge correction-constant a in Eq. (10) was determined by assuming thermodynamic correspondence between $(\partial P/\partial T)_V$ and C_V data at $c=0.33$ for $3<T<4$ K. As can be seen, γ_{EQQ} varies only slightly with T and c. The apparent dependence on c might be due to concentration errors in both C_V and $(\partial P/\partial T)_V$ experiments.

In the concentration range up to $c=0.52$, the hcp phase appears to be stable at all temperatures below the freezing point. As can be seen from Fig. 8 and Table II, there is a broad maximum in $(\partial P/\partial T)_V$ around 2.5 K, but a sharper peak appears in the region $0.7<T<1.0$ K for concentrations between 0.40 and 0.55. This sharper peak was observed during both cooling and warming experiments. It is tempting to suggest

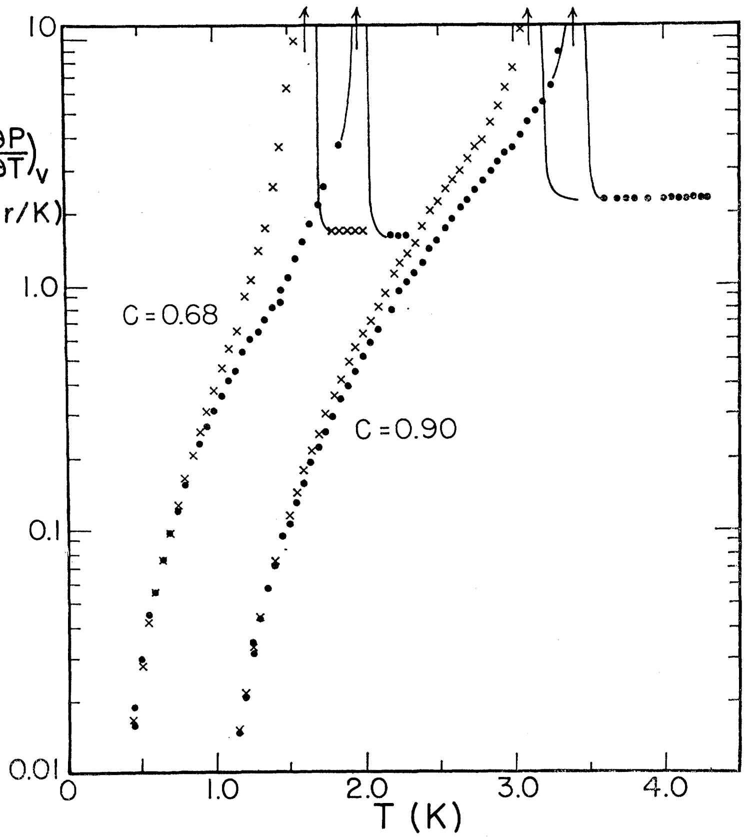

FIG. 9. $(\partial P/\partial T)_V$ in the cubic phase for two representative concentrations, $c=0.90$ and $c=0.68$.

that the peak arises from a rotational ordering transition in the hcp phase. However, nuclear-magnetic-resonance (NMR) experiments for $c=0.49$, carried out in this laboratory,[32] failed to show any significant change in the line shape at T below 1 K. One would expect the appearance of satellite absorption lines in the NMR spectrum in the rotationally ordered hcp solid, just as for the cubic phase of D_2.[33] Hence an interpretation of the peaks below 1 K is unclear.

After the maximum in $(\partial P/\partial T)_V$ near 0.8 K was repeatedly observed in solid D_2, a systematic survey was made to see whether it could also be detected in solid H_2 for comparable concentrations of the $(J=1)$ species. The results are shown also in Fig. 8 where the maximum is seen to be less pronounced for H_2. Just as in D_2, there is a rapid decrease of $(\partial P/\partial T)_V$ below about 0.8 K.

VI. MEASUREMENT OF $(\partial P/\partial T)_V$ ON CUBIC PHASE

These measurements, reported briefly elsewhere,[34] were made during the first thermal cycle through the transition. The time interval in cooling from the transition to the lowest temperatures was on the average 3–4 h, corresponding to about 10 mK/min. A similar rate was used to warm the sample into the rotationally disordered state. Typical results showing both cooling and warming are presented in Fig. 9 for two concentrations. The systematic difference between cooling and warming is found to disappear at the lowest temperatures, where the cubic phase is the only one present. At these low temperatures, the excitation-dispersion spectrum can be expected to be temperature independent and the simple analysis outlined in Eq. (7) can be performed. In Table III smoothed values of $(\partial P/\partial T)_V$ from warming experiments are presented at regular temperature intervals for some of the concentrations studied.

As a first step in analyzing the data, the value of γ_{EQQ} for the cubic phase was checked as before by making the assumption that both $(\partial P/\partial T)_{V,L}$ and $C_{V,L}$ were the same as in the hcp phase. The specific-heat data used were again those of Grenier and White,[12] extending down to 1.6 K. The average value of γ_{EQQ} was found to be 1.75 ± 0.2 compared with the theoretical value of 5/3 or 1.67. The large uncertainty in the experimental value is attributed to strong T and c dependence of the two quantities C_V and $(\partial P/\partial T)_V$, which enter into the calculation. Within experimental

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[32] B. Maraviglia, F. Weinhaus, and H. Meyer (unpublished).

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

[34] D. Ramm, H. Meyer, J. F. Jarvis, and R. L. Mills, Solid State Commun. **6**, 497 (1968).

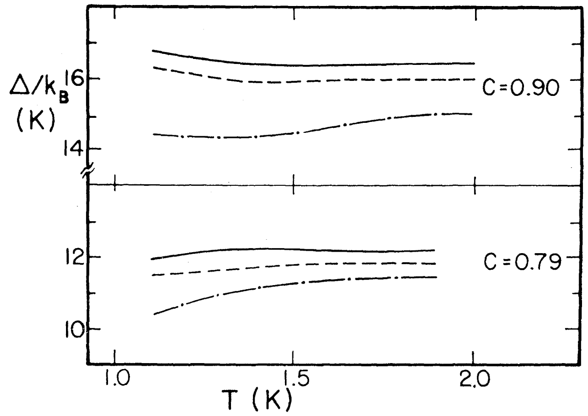

FIG. 10. Splitting Δ/k_B as obtained from a fit of the experimental data to theories of rotational excitation. For an explanation, see text. Solid line, theory Ref. 9; dashed line, theory Ref. 8; dotted line, theory Ref. 7.

error, the value of γ_{EQQ} is the same in both cubic and hcp phases. In the following analysis we use the theoretical value of $\gamma_{\mathrm{EQQ}}=5/3$.

We find that for $c \gtrsim 0.79$, the data can be adequately fitted by a theoretical specific heat of the form $C_V(k_BT/\Delta)$. The quality of the fits for various theories is shown for $c=0.90$ and $c=0.79$ in Fig. 10 where the splitting Δ/k_B, as derived from the data through Eq. (8), is plotted versus T. A constant value of Δ/k_B indicates a perfect fit. As mentioned in Sec. II, the actual splitting Δ/k_B so obtained depends on the theoretical approximation used. The fit with the theory of Ueyama and Matsubara[8] and of Mertens *et al.*[9,10] appears to be the best. We find that for $c \gtrsim 0.79$ the splitting increases linearly with p-D_2 concentration, as given by the expressions

TABLE III. $(\partial P/\partial T)_V$ in bar K^{-1} in solid D_2 for various high concentrations of paradeuterium.[a]

T \ $c=$ 0.66	0.68	0.74	0.79	0.80	0.83	0.86	0.90
0.45		0.018	0.003					
0.50		0.030	0.008					
0.55		0.043	0.011					
0.60		0.056	0.022					
0.65		0.076	0.030					
0.70		0.096	0.043					
0.75		0.122	0.054					
0.80		0.152	0.068					
0.85		0.187	0.090					
0.90		0.223	0.113					
0.95		0.260	0.135					
1.00		0.30	0.158					
1.10	0.467	0.41	0.225	0.083		0.0418	0.025	0.0095
1.20	0.570	0.50	0.315	0.148		0.081	0.046	0.0193
1.30	0.695	0.63	0.418	0.226		0.130	0.075	0.0418
1.40	0.88	0.81	0.540	0.320	0.286	0.197	0.125	0.071
1.50	1.33	1.06	0.700	0.440	0.395	0.277	0.181	0.110
1.60	1.90	1.45	0.880	0.588	0.515	0.367	0.254	0.152
1.80	7.8	2.90	1.35	0.940	0.860	0.610	0.452	0.294
2.0	[b]	[b]	2.20	1.46	1.33	0.965	0.745	0.495
2.20	1.55	1.60	4.11	2.20	2.01	1.50	1.16	0.770
2.40	1.56	1.60	[b]	3.45	3.06	2.26	1.74	1.27
2.60	1.57		1.68	10.0	5.35	3.31	2.53	1.85
2.80	1.58		1.69	[b]	[b]	5.40	3.68	2.60
3.00	1.58		1.70	1.89	1.86	[b]	[b]	3.60
3.20	1.59		1.71	1.91	1.89	2.00	2.15	[b]
3.40	1.60		1.72	1.93	1.91	2.02	2.16	[b]
3.60	1.62		1.73	1.95	1.93	2.04	2.16	2.20
3.80	1.63		1.74	1.95	1.94	2.06	2.16	2.22
4.00	1.64		1.75	1.97	1.96	2.08	2.17	2.24
4.20	1.85		1.76	1.99	1.98	2.08	2.18	2.26

[a] Values from warming through cubic-hcp transition during first thermal cycle. More detailed tabulation available from authors.

[b] Region of transition where $(\partial P/\partial T)_V$ becomes very large.

$$\Delta/k_B=37.3c-18.1\ \mathrm{K},\quad \text{(theory Ref. 8)} \qquad (12a)$$

$$\Delta/k_B=38.9c-19.0\ \mathrm{K}\quad \text{(theory Refs. 9 and 10)}. \qquad (12b)$$

Hence the splitting of pure p-D_2 extrapolates to $\Delta_{\mathrm{BZ}(c=1)}/k_B=19.2\pm1.0$ K and 19.9 ± 1.0 K from Eqs. (12a) and (12b), respectively. Using Eq. (7), one obtains the corresponding results $\Gamma_{\mathrm{eff}(c=1)}/k_B=0.91$ and 0.94 K. The theory of Homma *et al.*,[7] who pioneered the concept of librons, gives a relatively small width for the excitation band. The value of $\Delta_{\mathrm{BZ}(c=1)}/k_B$ obtained from a fit using this theory is 17.4 K.

We have also analyzed the data by plotting $(\partial P/\partial T)_{V,\mathrm{EQQ}}$ at a given T as a function of c and extrapolating to $c=1$. The analysis gave $\Delta_{\mathrm{BZ}(c=1)}/k_B$ in agreement with the results above.

The best evidence in favor of the dispersion spectra of Refs. 8 and 9 is given by their prediction of the relative spacing of the libron energy levels $(J=1)$ at $\mathbf{k}=0$, observed in Raman experiments.[6] A refined analysis of this spectrum by Berlinsky, Harris, and Coll,[21] assuming the cubic structure of Ref. 22, gives $\Gamma_{\mathrm{eff}(c=1)}/k_B=0.96$ K. Hence, there is excellent agreement among the various experimental determinations, giving an average value of $(\Gamma_{\mathrm{eff}(c=1)}/k_B)_{\mathrm{expt}}=0.94\pm0.05$ K. This value can be compared with $(\Gamma_{\mathrm{eff}(c=1)}/k_B)_{\mathrm{theoret}}=1.01$ K calculated for pure p-D_2 in the cubic phase.[5]

For pure p-D_2, the ration $T_{\mathrm{c-h}}/(\Gamma_{\mathrm{eff}(c=1)}/k_B)$ is $4.1/0.94 \cong 4.4$, whereas it is $3.0/0.7 \cong 4.3$ for solid o-H_2.[6,21] Although these ratios are somewhat lower than those predicted from the various models (Sec. II), they appear reasonable.

VII. ROTATIONAL ENTROPY

In this section we examine the entropy difference $[S_{\mathrm{EQQ}(T=\infty)}-S_{\mathrm{EQQ}(T=0.37)}]/Rc\ln 3 \equiv \sigma_\infty-\sigma_{0.37}$. Here σ_∞ is the extrapolated high-temperature limit of the reduced rotational entropy, assuming that no odd rotational levels above $J=1$ are excited. The expected value of σ_∞ is unity. The temperature $T=0.37$ K is the lowest one reached in our experiments on which the entropy calculations are based.

For concentrations below $c=0.55$, where the solid is apparently always hcp and where no transition occurs, $(\partial P/\partial T)_V$ was found to be the same for both cooling and warming. Hence, the computation of entropy from these data is straightforward. However, for $0.55<c$, there is a thermal hysteresis and therefore an irreversibility near T_λ. The exact cause of this phenomenon

is still unclear and, under these circumstances, a reliable estimation of entropy change δS is excluded in the neighborhood of T_λ. It is apparent from Fig. 4 that the $P(T)$ curves obtained on warming are the more reproducible ones. Hence, in order to get at least an estimate of the entropy change near T_λ, we use the warming curves corresponding to the first cycle through the transition. This change δS is to be regarded as a lower limit, since Fig. 4 shows that the pressure change $\delta P_{\text{c-h}}$ and the related entropy change increase with the number n of thermal cycles.

To calculate σ_∞, we make use of the strain-gauge data up to 4.2 K. At concentrations below $c=0.55$, $(\partial P/\partial T)_{\text{V,EQQ}}$ is transformed into $C_{\text{V,EQQ}}$ by means of Eq. (3b), using $\gamma_{\text{EQQ}}=5/3$. At higher concentrations, $(\partial P/\partial T)_{\text{V,EQQ}}$ values are used except in the temperature regions where they become very large and hence uncertain, usually $(T_\lambda-\delta T)<T<T_\lambda$, where $\delta T\approx 0.02$ K. Over this temperature interval, the directly recorded pressure difference corrected to that at constant volume, is used and the approximate change in entropy is calculated from the expression

$$\delta S=\int_{T_\lambda-\delta T}^{T_\lambda}\frac{C_V dT}{T}=\frac{V[P(T_\lambda)-P(T_\lambda-\delta T)]}{\gamma_{\text{EQQ}}[T_\lambda-\frac{1}{2}\delta T]}. \quad (13)$$

Between 4.2 and 13 K, $T_\lambda-\delta T$ and for $c\geqslant 0.33$ we use the specific-heat C_P data of Grenier and White[12] and subtract the lattice contribution $C_{P,L}$ of Hill and Lounasmaa[28] to obtain $C_{P,\text{EQQ}}$ which is approximately $C_{\text{V,EQQ}}$. For higher temperatures, we use the series expansion of $C_{\text{V,EQQ}}$ in powers of Γ/k_BT in addition to the result of a Padé-approximant method, devised by Berlinsky and Harris,[35] using $\Gamma/k_B=0.94$ K. For $c<0.33$, there is a scarcity of C_P data and we therefore use the series expansion[35] for $C_{\text{V,EQQ}}$ above 4 K to obtain the entropy $\sigma_\infty-\sigma_{4.2}$. The results are presented in Tables IV and V, where for convenience, we have tabulated the entropy at $T_{\text{c-h}}\simeq T_\lambda$. It is immediately apparent that $\sigma_\infty-\sigma_{0.37}$ increases systematically with c and tends toward unity. In view of the various uncertainties, some of them discussed above, the limiting entropy could be in error by about 5%. At low $(J=1)$ concentrations the small value computed for $\sigma_\infty-\sigma_{0.37}$ is expected for D_2, as it is for solid H_2, because there is a large number of $(J=1)$ isolated molecules, pairs, triangles, etc., among the $(J=0)$ molecules and the entropy of these is removed only at temperatures well below 0.37 K,[20,36] because of the near degeneracy of their lowest-energy states. At $c\gtrsim 0.5$, the ground state of the mixture is apparently well separated from the first excited state and $\sigma_{0.37}\approx 0$.

We have also calculated the entropy of the rotational motion from the specific-heat measurements of Grenier and White[12] over their complete temperature range. At their highest concentration $c=0.81$ the entropy is negligible below 1.6 K and we obtain $(\sigma_\infty-\sigma_{1.6})=0.98$ in satisfactory agreement with the result from the pressure measurements of Table V. Using the specific heat of Gonzales *et al.*[37] on normal D_2, we have extended the entropy calculations down to 0.3 K at $c=0.33$. At this concentration, again the entropy change $(\sigma_\infty-\sigma_{0.37})=0.83$ is in good agreement with that calculated from pressure data, where we obtained 0.86.

TABLE IV. The reduced rotational entropy $\sigma_T=S_{\text{EQQ}}/Rc\ \ln 3$ for various low concentrations of paradeuterium in the hcp phase.[a]

c	$\sigma_{4.2}-\sigma_{0.37}$	$\sigma_{13}-\sigma_{4.2}$	$\sigma_\infty-\sigma_{13}$	$\sigma_\infty-\sigma_{0.37}$
0.018	0.227	0.014	0.002	0.24
0.025	0.246	0.020	0.003	0.27
0.033	0.290	0.026	0.003	0.32
0.060	0.408	0.042	0.006	0.46
0.085	0.474	0.056	0.009	0.54
0.128	0.565	0.077	0.013	0.66
0.180	0.602	0.102	0.018	0.72
0.233	0.628	0.128	0.023	0.78
0.295	0.647	0.155	0.028	0.83
0.326	0.655	0.170	0.031	0.86
0.380	0.667	0.183	0.035	0.89
0.415	0.673	0.190	0.038	0.90
0.480	0.682	0.200	0.043	0.93
0.524	0.687	0.206	0.047	0.94

[a] Various quantities obtained as described in text.

We hope to present in a technical report a detailed tabulation of the rotational entropy as a function of temperature, as obtained from specific heat[12,38,39] and from strain-gauge data for both solid D_2 and H_2.

VIII. SUMMARY

The research described in this paper has given results that can be summarized in the following way:

(1) A study of the hcp-to-cubic and cubic-to-hcp phase transitions shows that these occur at p-D_2 concentrations of $0.55\lesssim c\leqslant 1.0$. There is a hysteresis between transitions for cooling and for warming over the whole concentration range. The hysteresis is still more pronounced than in solid H_2.

TABLE V. The reduced entropy $\sigma_T=S_{\text{EQQ}}/Rc\ \ln 3$ for various high concentrations of paradeuterium in the solid phase.[a]

c	$\sigma_{T_\lambda}-\sigma_0$	$\sigma_{4.2}-\sigma_{T_\lambda}$	$\sigma_{13}-\sigma_{4.2}$	$\sigma_\infty-\sigma_{13}$	$\sigma_\infty-\sigma_0$
0.67	0.38	0.22	0.23	0.056	0.91
0.73	0.47	0.15	0.23	0.061	0.93
0.80	0.53	0.10	0.24	0.065	0.94
0.83	0.57	0.08	0.25	0.066	0.97
0.86	0.59	0.08	0.25	0.068	1.00
0.90	0.60	0.05	0.25	0.070	0.99

[a] Various quantities obtained as described in text.

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[35] A. J. Berlinsky and A. B. Harris, Bull. Am. Phys. Soc. **14**, 334 (1969).

[36] W. N. Hardy and J. R. Gaines, Phys. Rev. Letters **19**, 1417 (1967).

[37] O. D. Gonzales, D. White, and H. L. Johnston, J. Phys. Chem. **61**, 773 (1957).

[38] R. W. Hill and B. W. A. Ricketson, Phil. Mag. **45**, 277 (1954).

[39] B. W. A. Ricketson, thesis, Oxford University, 1954 (unpublished).

(2) A detailed study of the pressure $P(T)$ at constant volume, as the sample is thermally cycled through the transition, has been compared with similar cycling results from x-ray work that earlier established the relative fractions of the crystalline phases. The conclusion is that the pressure change is due mainly to ordering of the rotational-momentum component J_Z in the cubic phase. The temperature labeled $T_{\text{c-h}}$ is reproducible upon successive thermal cycles as the cubic phase becomes stabilized to an increasing degree above $T_{\text{c-h}}$. The temperature T_λ of the maximum in $(\partial P/\partial T)_V$, which is about 4 mK above $T_{\text{c-h}}$, agrees well with that from specific-heat data and is believed to represent the order-disorder transition in the cubic phase. Its extrapolated value to $c=1$ is $\sim$4.05 K, which confirms previous estimates.

(3) From measurements of $(\partial P/\partial T)_V$ at the low p-D_2 concentrations of $c=0.06$ and 0.05, we obtain a value of $\Gamma_{\text{eff(pair)}}/k_B=1.05\pm0.07$ K. According to a recent theory by Harris that takes into account quantum effects, dielectric screening, and differential attraction between neighboring $(J=1)$ molecules, $\Gamma_{\text{eff(pair)}}/k_B$ is predicted to be about 1.11 K, while the classical value for a rigid lattice with no screening effects is 1.20 K.

From extrapolation of $(\partial P/\partial T)_V$ data in the cubic phase to the limiting case of pure p-D_2 solid, we obtain $\Gamma_{\text{eff}(c=1)}/k_B=0.93\pm0.05$ using the densities of state of Ueyama and Matsubara and of Mertens *et al.* The theoretical prediction by Harris is $\Gamma_{\text{eff}(c=1)}/k_B=1.01$ K.

(4) The quantity $(\partial P/\partial T)_{\text{V,EQQ}}$ as a function of T for $c<0.05$ shows two maxima, at 0.9 and 2.5 K, rather than the one expected theoretically around 1.7 K. This behavior is not understood at present.

Furthermore, a maximum in $(\partial P/\partial T)_{\text{V,EQQ}}$ is detected in the hcp phase for $0.40<c<0.55$ near 0.9 K, in addition to the broad maximum near 2.5 K. It is attractive to associate this lower-temperature maximum with rotational ordering in the hcp phase, but previous NMR experiments[32] in this laboratory at $c=0.45$ do not substantiate the idea of such ordering.

(5) The value of the rotational Grüneisen-constant γ_{EQQ} determined from a combination of $(\partial P/\partial T)_{\text{V,EQQ}}$ and $C_{\text{V,EQQ}}$ data is found to be almost independent of p-D_2 concentration and temperature, as one would expect. The lattice Grüneisen constant γ_L is 2.0 ± 0.1 for D_2 and, hence, agrees with that of H_2 within experimental error.

(6) The rotational entropy $S_{T=\infty}-S_{T=0.37}/Rc\ln 3$ obtained from a combination of $(\partial P/\partial T)_{\text{V,EQQ}}$ and $C_{p,\text{EQQ}}$ measurements increases systematically with c and tends to unity only above $c\gtrsim 0.6$. We assume that $S_{T=\infty}=Rc\ln 3$, and therefore a considerable change in entropy for $c\lesssim 0.6$ takes place below 0.37 K. This can be interpreted as follows: at small c, isolated $(J=1)$ molecules, isolated pairs and triangles of these molecules are relatively abundant. These configurations are almost degenerate in their lowest states, the splittings being of the order of 10^{-2} cm^{-1}.[20,37] Hence the entropy is appreciable at 0.4 K. As the concentration of $(J=1)$ molecules increases, clusters with larger numbers of $(J=1)$ molecules become more abundant and the average spacing between the nondegenerate ground state and the first excited state becomes gradually larger. At $c>0.5$, the entropy at $T=0.37$ K is close to zero. In the cubic phase, the average libron energy becomes $\Delta_{\text{BZ}(c=1)}=20\ k_B$ as c tends to unity, a result obtained from $(\partial P/\partial T)_V$ data and from direct optical observation. The situation in solid H_2 is similar.

ACKNOWLEDGMENTS

The authors wish to thank Dr. J. F. Jarvis for advice and experimental help and Gregory Goellner for assisting during several of the experiments and for calculation of the entropies. They are indebted to Dr. A. Brooks Harris for many useful discussions and for providing unpublished results. Finally, the authors acknowledge support by the U. S. Atomic Energy Commission for the part of the work done at Los Alamos.