based on a smooth variation of the dielectric constant over the transition region gives results in agreement with the measured values of this ratio to within a factor of 2. Whereas the model of electric double layer at the surface needs to be developed further to afford a close comparison with the experiments, the observations in this paper show that, for transparent insulators, the electric-field-induced second-harmonic generation within the surface double layer is probably more important than the quadrupolar nonlinearities. This effect due to the surface double layer may also be important in the reflected harmonics from the boundary of metals and semiconductors.[2,9]

---

# Measurement of $(\partial P/\partial T)_V$ and Related Properties in Solidified Gases. II. Solid $H_2$†

John F. Jarvis,* Horst Meyer, and Dietolf Ramm
*Department of Physics, Duke University, Durham, North Carolina*
(Received 18 July 1968)

We report measurements and their analysis of pressure changes with temperature and ortho-$H_2$ concentration in solid $H_2$ in both the hcp and cubic phases. The temperature range extended from 0.4 to 4.2°K, and the concentration $c$ of ortho-$H_2$ was between 0.005 and 0.94. The measurements were carried out by means of a sensitive capacitance strain gauge capable of resolving pressure changes of $2 \times 10^{-5}$ bar. The categories of experiments performed were (1) determination of the pressure $P$ in the hcp phase as a function of ortho concentration at several temperatures; (2) determination of the pressure difference $P$ (hcp) $-P$-(cubic) as a function of ortho concentration, and study of the hysteresis in both pressure and temperature of the hcp-to-cubic transition; and (3) measurement of $(\partial P/\partial T)_V$ at constant ortho concentration in the hcp phase at several different ortho concentrations. The results were analyzed in terms of a lattice contribution and an electric quadrupole-quadrupole (EQQ) interaction, neglecting any effects from other interactions and from crystalline fields. The EQQ interaction parameter determined experimentally was $\Gamma = 6e^2Q^2/25R^5$, where $eQ$ is the quadrupole moment of the orthomolecule in the state $J=1$, and $R$ is the nearest-neighbor distance. The theoretical value for a rigid lattice is $\Gamma/k_B = 1.00$°K. The results from (1) and (2), extrapolated to pure ortho-$H_2$, were analyzed using the theory of Miyagi and Nakamura and gave $\Gamma/k_B = 0.82 \pm 0.04$°K (value extrapolated to $P=0$). This value was confirmed from the temperature of the maximum of $(\partial P/\partial T)_V$ at low ortho concentrations. The discrepancy between the experimental and the theoretical values of $\Gamma$ is briefly discussed. From $(\partial P/\partial T)_V$ data with almost pure para-$H_2$ and from comparison with specific-heat data due to Ahlers, a lattice Grüneisen constant $\gamma_L = 2.06 \pm 0.1$ was found. The Grüneisen constant of the EQQ interaction was found to be $\gamma_{EQQ} = 1.62 \pm 0.1$, in agreement with the theoretically expected value. Evidence was found for redistribution of orthomolecules at low ortho concentration as a function of time. The theoretical expectations for a thermodynamic-equilibrium distribution of molecules in the lattice and that for a random high-temperature distribution are compared with experimental results.

## I. INTRODUCTION

IN the last few years, there has been a great deal of theoretical interest in the molecular ordering occurring in the cubic and hcp phases for pure ortho-$H_2$ and ortho-para mixtures.[1–7] These studies were prompted in part by recent experimental work showing a first-order crystalline phase transition in both solid $H_2$ [8,9] and solid $D_2$ [9,10] at high ortho-$H_2$ and high para-$D_2$ concentrations, respectively. It is now generally believed that the electric quadrupole-quadrupole (EQQ) inter-

† Work supported by the National Science Foundation and the Army Research Office (Durham). Preliminary results of part of this work have been reported by the same authors in Phys. Rev. Letters 18, 119 (1967) and in Ref. 17.
* Present address: Bell Telephone Laboratories, Holmdel, N. J.
[1] J. Felsteiner, Phys. Rev. Letters 15, 1025 (1965).
[2] H. Miyagi and T. Nakamura, Progr. Theoret. Phys. (Kyoto) 37, 641 (1967).
[3] W. M. Fairbairn and M. R. Steel, Proc. Phys. Soc. (London) 1, 34 (1968); G. M. Bell and W. M. Fairbairn, Phys. Rev. 158, 530 (1967), and references therein.

[4] H. M. James and J. C. Raich, Phys. Rev. 162, 649 (1967); H. M. James, ibid. 167, 862 (1968).
[5] J. C. Raich and R. D. Etters, Phys. Rev. 155, 457 (1967).
[6] S. Homma, K. Okada, and H. Matsuda, Progr. Theoret. Phys. (Kyoto) 38, 767 (1967).
[7] H. Ueyama and T. Matsubara, Progr. Theoret. Phys. (Kyoto) 38, 784 (1967); F. G. Mertens, W. Biem, and H. Hahn, Z. Physik 213, 33 (1968).
[8] M. Clouter and H. P. Gush, Phys. Rev. Letters 15, 200 (1965).
[9] R. L. Mills and A. F. Schuch, Phys. Rev. Letters 15, 722 (1965) (solid $H_2$); A. F. Schuch and R. L. Mills, Phys. Rev. Letters 16, 616 (1966) (solid $D_2$).
[10] K. F. Mucker et al., Phys. Rev. Letters 16, 799 (1966).

action between ortho-$H_2$ molecules, which have a rotational angular momentum $J=1$ in the solid state, is the dominant mechanism for the molecular alignment at low temperatures.[11,12] Theoretical calculations for pure ortho-$H_2$ have shown[1,2] that with such interactions the ground-state energy in the cubic phase is lower than that in the hcp phase at $T=0°K$, making the cubic phase the more stable one. NMR studies show evidence of cooperative molecular ordering in this phase,[13,14] while above the transition temperature $T_{trans}$, in the hcp phase, the rotational levels of the state $J=1$ are almost degenerate and the molecules are rotating almost freely.[15]

Although there appears to be no crystalline phase transition for ortho concentrations $c$ below about $c=0.6$,[16,17] the EQQ interaction must still be responsible for the specific-heat anomalies[16] that are observed at nonzero ortho concentrations in the hcp phase. The molecular alignment seems to be proceeding in a continuous way as the temperature is decreased. Solid para-$H_2$, where $J=0$, does not have an electric quadrupole moment, and hence its specific heat and the quantity $(\partial P/\partial T)_V$ should show only a lattice contribution.

In this paper we present measurements of the pressure at constant volume as a function of temperature in the range 0.4–4.2°K and for ortho concentrations up to 0.94. Furthermore, we investigate the change of pressure with ortho concentration at constant volume and temperature. Pressure measurements have the advantage that the sample to be investigated can be connected continuously to a temperature bath. Therefore $C_V$, which is related to $(\partial P/\partial T)_V$ assuming the validity of the Grüneisen equation, can be obtained both by decreasing and by increasing $T$. It is then possible to obtain information on phenomena not easily accessible by specific-heat measurements, namely, the hysteresis of the phase transition after successive warmings and coolings,[8,18,19] and also the effect of ortho-para conversion on pressure. The self-heating due to conversion makes specific-heat measurements rather difficult, at least at ortho concentrations above about $c=0.4$. By means of $(\partial P/\partial T)_V$ data at low ortho concentrations we have also obtained evidence of configurational rearrangement of ortho-$H_2$ molecules. Since at low ortho concentrations, the ortho-para conversion is small, although measurable, the effects of the

molecular rearrangement can be followed as a function of time. This motion of orthomolecules is unexpected in terms of classical thermally activated diffusion and is probably caused by ortho-para interchange effects.

Section II presents a short theoretical survey. In Sec. III, a brief description of the method of the pressure measurement and sample preparation is given. In Sec. IV we describe measurements of ortho-para-conversion-induced pressure changes. In Sec. V, the investigation of the hcp-to-cubic phase transition is described. Data for $(\partial P/\partial T)_V$ at constant ortho concentration are presented and discussed in Sec. VI, and the influence of molecular rearrangement on thermodynamic properties is described.

## II. THEORETICAL SURVEY

This section provides a short theoretical introduction, useful for the analysis of the results to be presented later.

As a first approximation, we assume that the contributions of the lattice and of the rotational motions to the free energy are independent of one another; thus

$$F(V,T,c) = F_L(V,T) + F_R(V,T,c),\qquad(1)$$

where the subscripts indicate, respectively, the lattice and the rotational energy. The quantity $F_L$ is assumed to be the same for both ortho- and para-$H_2$. For the latter molecules, the rotational energy in the solid is zero, if one neglects possible admixtures from excited states.

Nakamura[11] was first to show that at low pressures, EQQ interactions between orthomolecules are the dominant ones for the orientational alignment. We therefore assume that the rotational free energy is dependent on the EQQ interaction only and that it can be expressed as

$$\frac{F_R}{k_B T} = \frac{F_{EQQ}}{k_B T} = f(\Gamma/k_B T),\qquad(2)$$

where $\Gamma = 6e^2 Q^2/25R^5$ is the EQQ coupling parameter. Here $eQ$ is the electric quadrupole moment of the ortho-$H_2$ molecules, with[20] $Q=0.1368\times10^{-16}$ cm$^2$, and $R_0$ is the distance between nearest neighbors, 3.755 Å at pressures below about 10 atm,[9] and is closely the same for both phases. Assuming the lattice to be rigid and neglecting possible effects from zero-point vibrations, the EQQ coupling constant is then calculated to be $\Gamma/k_B = 1.00°K$. In Eq. (2) we assume that any other interaction effects such as dispersion and valence forces[12] give negligible splittings for all ortho concentrations. At low enough ortho concentrations, the crystalline field splittings are small, as was shown from an analysis of NMR relaxation times.[21] At higher ortho concen-

[11] T. Nakamura, Progr. Theoret. Phys. (Kyoto) 14, 135 (1955).
[12] W. H. Orttung, J. Chem. Phys. 36, 652 (1962).
[13] F. Reif and E. M. Purcell, Phys. Rev. 91, 631 (1953).
[14] L. I. Amstutz, H. Meyer, S. Myers, and D. C. Rorer, Phys. Rev. (to be published).
[15] J. Van Kranendonk, Physica 25, 1080 (1959).
[16] R. W. Hill and B. W. A. Ricketson, Phil. Mag. 45, 277 (1954); B. W. A. Ricketson, thesis, Oxford University, 1954 (unpublished).
[17] J. F. Jarvis, D. Ramm, H. Meyer, and R. L. Mills, Phys. Letters 25A, 692 (1967). In this paper, the change of pressure through the transition was not corrected to its value at constant volume.
[18] G. W. Smith and R. M. Housley, Phys. Rev. 117, 732 (1960).
[19] R. L. Mills, A. F. Schuch, and D. A. Depatie, Phys. Rev. Letters 17, 1131 (1966).
[20] G. Karl and J. D. Poll, J. Chem. Phys. 46, 2944 (1967).
[21] W. Hardy and J. R. Gaines, Phys. Rev. Letters 19, 1417 (1967).

trations, the recent analysis of Sung[22] shows that the crystalline field splittings are still small and in the analysis of our results they will be also neglected.

Similarly, we assume that the lattice below 4°K can be represented by the Debye approximation

$$F_L = k_B T \varphi(\Theta_D/T). \tag{3}$$

The theoretical dependence of the free energy on ortho-$H_2$ concentration has not been clarified yet, except at high temperatures, where Bellemans and Babloyantz[23] have made a calculation of the configurational free energy for mixtures. These authors found

$$\Delta F = F(V,T,c) - F(V, T, c=0) = Dc + Ec^2. \tag{4}$$

Here $D$ and $E$ are terms obtained taking into account directional intermolecular forces. The calculation of these factors is very involved, and their derivatives will be used as free parameters, to be determined from a best fit to the experimental data in Sec. IV.

The ground-state energy for EQQ interaction in solid ortho-$H_2$ at $T=0°K$ has been calculated by Miyagi and Nakamura.[2] Taking zero-point motion effects into account, these authors obtained $F_{EQQ}/k_B = -4.28°K$ for the hcp phase at $T=0°K$ and $F_{EQQ}/k_B = -4.85°K$ for the cubic phase. This energy is proportional to $\Gamma$, for which the authors have used the widely quoted value[11] $Q=0.11\times10^{-16}$ cm$^2$ instead of the correct value, $0.1368\times10^{-16}$ cm$^2$, recently calculated by Karl and Poll.[20] If we take this into account, the results can be written as

$$F_{EQQ}/k_B = -6.63(\Gamma/k_B), \quad °K, \text{ hcp phase}$$
$$(T=0)$$
$$F_{EQQ}/k_B = -7.51(\Gamma/k_B), \quad °K, \text{ cubic phase.} \tag{5}$$

Since $F_{EQQ}$ at $T=0$ is proportional to $V^{-5/3}$, one has

$$P_{EQQ} = -\left(\frac{\partial F}{\partial V}\right)_{T,EQQ} = -\frac{5}{3}\frac{F_{EQQ}}{V}$$
$$= -\frac{9.18\times10^2}{V}\left(\frac{\Gamma}{k_B}\right) \quad \text{h.c.p.}$$
$$\tag{6}$$
$$= -\frac{1.04\times10^3}{V}\left(\frac{\Gamma}{k_B}\right) \quad \text{cubic,}$$

where $P$ is expressed in bars, $\Gamma/k_B$ in °K, and $V$ in cm$^3$/mole. Under the assumptions made in Eqs. (1) and (2), we obtain

$$P = P_L(V,T) + P_{EQQ}(V,T,c) \tag{7}$$
and
$$V\left(\frac{\partial P}{\partial T}\right)_V = \gamma_L C_{V,L} + \gamma_{EQQ} C_{V,EQQ}, \tag{8}$$

where

$$\gamma_L = -\frac{d\ln\Theta_D}{d\ln V}, \quad \gamma_{EQQ} = -\frac{d\ln\Gamma}{d\ln V}. \tag{9}$$

The value for $\gamma_L$ is in the neighborhood of 2.[24] For a rigid classical lattice we expect $\gamma_{EQQ} = 5/3$, and we will show in Sec. VI that the experiment agrees well with this prediction.

At sufficiently low ortho concentrations, simple orthomolecule configurations have the highest random probability. If the energies of the configurations are known, then $(\partial P/\partial T)_{V,EQQ}$ can be calculated in terms of their respective contributions.

In close-packed structures the probability of having a single orthomolecule with no nearest orthoneighbor is given by the binominal distribution formula

$$P_s = (1-c)^{12}. \tag{10}$$

Furthermore, the probability of having two ortho-molecules forming an isolated pair of nearest ortho-neighbors is

$$P_p = 12c(1-c)^{18}. \tag{11}$$

The probabilities $P_{ti}$ that molecules form one of the six triangular configurations $i$ have been computed by Harris[25] and will not be presented here. It is sufficient to mention that for an ortho concentration $c=0.03$, one finds

$$P_t = \sum_{i=1}^{i=6} P_{ti} = 0.066;$$

for $c=0.01$ this number is 0.0118.

For $c<0.05$, we will for simplicity put

$$P_t = 1 - P_s - P_p. \tag{12}$$

In this simplification the molecules in configurations more complicated than isolated triangles are taken to have the same average internal energy per molecule as those in the triangles.

For isolated ortho-$H_2$ molecules, we make the approximation (reasonable in the temperature range that we have used) that the three energy levels are degenerate. Hence the partition function is

$$Z_s = 3. \tag{13}$$

For isolated pairs, the partition function, obtained from the known energy levels,[11,12] is

$$Z_p = [2e^{4\Gamma/k_B T} + 4 + 2e^{-\Gamma/k_B T} + e^{-6\Gamma/k_B T}]. \tag{14}$$

From this partition function, the quantities $C_{V,EQQ}$ and $(\partial P/\partial T)_{V,EQQ}$ are calculated and are found to have a maximum at $\Gamma/k_B T = 0.666$. This result is relevant for the determination of $\Gamma$ from experimental data.

Harris[25] has determined the energy levels for the six isolated triangular configurations of nearest ortho-$H_2$ molecules, each one having 27 states. Although the

[22] C. C. Sung, Phys. Rev. 167, 271 (1968).
[23] A. Bellemans and A. Babloyantz, Mol. Phys. 2, 169 (1959); A. Babloyantz and A. Bellemans, ibid. 3, 313 (1960).
[24] G. Ahlers, J. Chem. Phys. 41, 86 (1964).
[25] A. B. Harris (unpublished).

energies of these systems are somewhat different, the energy levels of the isosceles triangle are representative for most configurations and will be used in the calculations below. These levels, expressed in units of $\Gamma$, and their degeneracies (in parentheses) are[25] $-7.289(2)$, $-7.112(1)$, $-6.431(1)$, $-4.750(1)$, $-4.024(1)$, $-3.620(2)$, $-3.078(2)$, $-0.792(1)$, $0(3)$, $+0.093(2)$, $1.060(1)$, $1.390(2)$, $1.534(1)$, $4.114(2)$, $5.024(2)$, $7.349(1)$, $8.739(1)$, and $11.176(1)$. The $(\partial P/\partial T)_{V,\mathrm{EQQ}}$ calculated from the partition function $Z_t$ has a broad maximum for $\Gamma/k_B T = 0.625$.

So far it has been tacitly assumed[12] that the ortho-molecules are distributed in the random way given by Eqs. (10) and (11). Since classical diffusion is negligible below about $8°\mathrm{K}$,[26,27] it has been taken for granted that the random distribution persists down to the absolute zero. However, as will be shown later, there is strong evidence of molecular rearrangement with temperature towards a state of thermodynamic equilibrium. Hence we must consider the properties of dilute ortho-$H_2$ alloys for two extreme cases: (a) The time to perform the experiment is short in comparison with the time constant $\tau$ of rearranging the molecules in the lattice; (b) the experiment is performed over a period long in comparison with $\tau$, so that the system is always in equilibrium.

For the first case, the different configurations coexist in "frozen equilibrium" and the partition function of the system is

$$Z_{\mathrm{EQQ}}{}^{Nc} = (Z_s)^{NP_sc} \times (Z_p)^{NP_pc/2} \times (Z_t)^{NP_tc/3}, \quad (15)$$

where $N$ is the total number of $H_2$ molecules present.

For the second case, the partition function for the three configurations in thermodynamic equilibrium is found from standard statistical methods to be

$$Z_{\mathrm{EQQ}}{}^{Nc} = [Z_s P_s + Z_p{}^{1/2} P_p + Z_t{}^{1/3} P_t]^{Nc}. \quad (16)$$

The relative number of orthomolecules forming isolated singles, pairs, and triangles is given by

$$\frac{N_s}{Nc} = \frac{P_s Z_s}{Z_{\mathrm{EQQ}}}; \quad \frac{N_p}{Nc} = \frac{P_p Z_p{}^{1/2}}{Z_{\mathrm{EQQ}}}; \quad \frac{N_t}{Nc} = \frac{P_t Z_t{}^{1/3}}{Z_{\mathrm{EQQ}}}. \quad (17)$$

In Sec. VI, we present for a given concentration $c$ the calculated $(\partial P/\partial T)_{V\,\mathrm{EQQ}}$ for the two limiting cases given by Eqs. (15) and (16). It is clear that these two equations can be extended in a straightforward fashion to include the contribution of more complicated molecular configurations, once their energy levels are known.

## III. EXPERIMENTAL

Since the cryostat and the method of taking and analyzing data have been described in detail in a previ-

[26] B. V. Rollins and E. Watson, in *Conference de Physique des basses Temperatures, Paris, 1955* (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956), p. 474.
[27] M. Bloom, Physica 23, 767 (1957).

ous paper,[28] they will be reviewed only briefly. The experiment consists in measuring the pressure in an annular space containing the sample of solid $H_2$. The outer wall consists of a stainless-steel membrane that is displaced very slightly as the pressure inside the sample space changes. The other walls are of copper and are in thermal contact with a temperature-regulated bath operating between 0.4 and $20°\mathrm{K}$. The stainless-steel membrane together with a concentric rigid stainless-steel tube forms a capacitor that is part of an $LC$ resonant circuit.

The circuit is made to oscillate by a tunnel diode mounted on the sample cell. The frequency of oscillations is about 14 MHz and is measured by an electronic counter. Frequency drifts are measured to be less than 1 Hz over periods of several hours. The sensitivity of this strain gauge is about 5 KHz/bar from calibration of the apparatus with liquid helium under pressure. This calibration is checked every time the apparatus is cooled for a series of experiments. Because of the stability of the oscillator, pressure changes as small as $2 \times 10^{-5}$ bar can be detected. The automatic data-recording technique used in this experiment makes it possible to gather a large number of data of the pressure $P$ as a function of temperature and time.

The procedure in forming a solid sample of $H_2$ is as follows. The entire cryostat is first cooled to $4.2°\mathrm{K}$. The sample chamber is then thermally insulated from the main bath and heated to about $20°\mathrm{K}$. $H_2$ gas under a pressure of 120 bar is introduced into the strain gauge via the capillary heated by means of an inserted resistance wire. The strain gauge heater and the capillary heater are then turned off and the cell, initially filled with liquid, is cooled along the melting curve. In the neighborhood of the triple point, the capillary is heated again and there is a sudden rush of $H_2$ into the cell, resulting in a pressure 40–100 bar in the solid. The $H_2$ is then frozen in the capillary by turning off the capillary heater. Then the sample is warmed until liquid is present in order to remove strains that were introduced by the very rapid compression of the solid. After about 15 min of annealing the sample is cooled to $4.2°\mathrm{K}$. The total time taken to form the sample from the initial condensing of the gas until the time when measurements can be started is approximately 1 h. The high initial pressure at the melting curve is necessary since the pressure drops by about 25 bar upon cooling to $4.2°\mathrm{K}$, and up to 10 bars more between 4.2 and $0.5°\mathrm{K}$ for the highest ortho concentrations. Data taking of the pressure versus temperature is carried out as described for solid $He^4$ except that the cooling or warming rate is between 10 and 15 $m°\mathrm{K}/min$. This larger rate, is necessary because of the substantial ortho-para conversion during the experiment. Rates higher than these are not used, because this would disturb the equilibrium of the system. Data taking of

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

the pressure versus ortho concentration at fixed temperature is carried out over periods up to 110 h. In both $P$-versus-$c$ and $P$-versus-$T$ measurements, a correction[28] has to be applied to take into account the finite compressibility[29] of solid $H_2$ as compared with the elasticity of the strain gauge.

The correction gives

$$\frac{(\partial P/\partial T)_{V,c}}{dP/dT} = \frac{(\partial P/\partial c)_{V,T}}{dP/dc} = 1.07. \qquad (18)$$

Here $dP/dT$ and $dP/dc$ are the quantities directly observed. The corrected derivatives $(\partial P/\partial T)_{V,c}$ and $(\partial P/\partial c)_{V,T}$ are integrated to obtain the isochores of $P$ versus $c$ and $P$ versus $T$.

Since the ortho-para conversion rate may be strongly dependent on magnetic impurities in the system, extensive checks were made to determine if excessive conversion occurred during the sample formation. No changes in the ortho concentration in excess of those given by the well-known rate equation were noticed. The hydrogen gas used was an ultra pure grade from the Matheson Company containing less than 1 ppm of $O_2$ and less than 10 ppm of total impurities. The analysis of ortho-para conversion was by means of the heat conductivity of $H_2$ gas[30] and was carried out by L. Amstutz of this laboratory.

## IV. ISOTHERMAL CHANGE OF PRESSURE WITH ORTHO CONCENTRATION

When the temperature was held constant for a sample of solid $H_2$, the pressure was found to increase with time. This is readily explained by the assumption that a given density and temperature, the pressure in the pure para-$H_2$ is larger than in ortho-$H_2$. As the ortho-para conversion proceeds with time, the pressure increases to a limiting value, corresponding to the pressure in pure para-$H_2$.

The conversion rate appeared well represented by the relation[31]

$$dc/dt = -Kc^2, \qquad (19)$$

at least at concentrations larger than about 0.25. The constant $K$ seemed to be temperature-independent in the solid phase according to several experiments in this laboratory. There was no pressure dependence within experimental error in the range of pressures covered in this work. The value of $K$ obtained from more than 20 experiments over various time intervals was found to be $K = 0.0185 \pm 0.001$ h$^{-1}$, in excellent agreement with the results of previous authors.[19,32]

Figure 1 shows the pressure changes versus ortho concentration for representative experiments at four
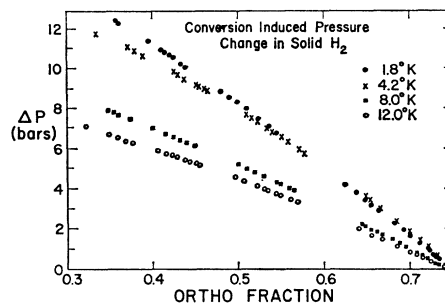


Fig. 1. Pressure changes versus ortho concentration in the hcp phase at four different temperatures. For simplicity, the pressure has been arbitrarily shifted to $P=0$ for $c=0.74$, i.e., at the beginning of the experiment.

different temperatures in the hcp phase. The pressure was measured as a function of time starting with $c=0.74$ and the concentration was then calculated from Eq. (19) after determining the ortho concentration of the gas removed from the sample cell.

The experimental results, corrected to pressures at constant volume, could be fitted by least squares to the relation

$$P(c) = P(c=0) + D'c + E'c^2, \qquad (20)$$

as one would expect from differentiation of Eq. (4). The quantities $P(c=1) - P(c=0)$, $D'$, and $E'$ are presented in Table I as a function of temperature. In Fig. 2, $[P(c=0) - P(c=1)]_{hcp}$ is plotted versus temperature. At high temperatures, this quantity tends to a value different from zero. To obtain this curve below 1.8°K and between 1.8 and 4.2°K, data of $(\partial P/\partial T)_V$ at various ortho concentrations in the hcp phase were extrapolated to $c=1$ and integrated. These results are described in detail in Sec. VI. We obtain

$$[P(c=0) - P(c=1)]_{hcp}{}^{T=0} = 34.6 \pm 1.5 \text{ bar} \qquad (21)$$

as the extrapolated value for $c=1$, were the hcp phase stable at 0°K. This extrapolation does not take into account an order-disorder transition that may increase somewhat the value obtained in Eq. (21). We hence regard the results of Eq. (21) as a lower limit, and because of this uncertainty we will not use it for the determination of $\Gamma$. Since it is known[19] that the hcp phase is in fact not stable below about 2.9°K for $c=1.0$, we also drew the difference $P(c=0)_{hcp} - P(c=1)_{cubic}$ as a function of temperature using an extrapolation of the data described in Sec. V. For this extrapolation, the data obtained upon cooling through the transition were used, since it was thought that these data were more truly representative of the hcp-cubic transition than the data obtained upon increasing the temperature in the first thermal cycle (see Sec. V). Extrapolation to $T=0$°K gives

$$[P(c=0)_{hcp} - P(c=1)_{cubic}] = 39.7 \pm 2 \text{ bar}. \qquad (22)$$

One now makes the reasonable assumption that the pressure change is entirely due to the alignment of

[29] H. D. Megaw, Phil. Mag. **28**, 129 (1939).
[30] See, e.g., E. R. Grilly, Rev. Sci. Instr. **24**, 72 (1953).
[31] E. Cremer and M. Polanyi, Z. Physik. Chem. (Frankfurt) **B21**, 459 (1936).
[32] G. Ahlers, J. Chem. Phys. **40**, 3123 (1964), and references therein.

Table I. Pressure difference between solid ortho- and para-H₂ as a function of temperature, as given in column 4. The numbers in columns 2–4 were obtained from a fit of Eq. (20). The standard deviation of this fit is shown in column 5. The pressure difference between solid ortho-H₂ at 2.9°K and at $T$ in the cubic phase is given in column 6.

| $T$ (°K) | $D'$ | $E'$ | $[P_{(c=0)} - P_{(c=1)}]_{hcp}$ (bar) | Std. dev. (bar) | $P_{(c=1)}(2.9°K) - P_{(c=1)\ cubic}(T)$ (bar) |
|---|---|---|---|---|---|
| 12.0 | −6.71 | −9.55 | +16.2 | 0.018 | |
| 8.0 | −10.03 | −9.02 | +19.0 | 0.014 | |
| 4.2 | −9.66 | −17.25 | +26.8 | 0.034 | |
| 4.2 | −8.90 | −16.55 | +25.5 | 0.075 | |
| 2.9 | | | +28.6 | | 0 |
| 2.7 | | | +29.1 | | 8.9 |
| 2.5 | | | +29.5 | | 10.0 |
| 2.0 | | | +30.5 | | 10.8 |
| 1.8 | −21.9 | −8.95 | +30.8 | 0.032 | 10.9 |
| 1.0 | | | +32.8 | | 11.1 |

orthomolecules, the effect from intrinsic lattice changes being negligible. Using Eqs. (6) and (22), a value of $\Gamma/k_B = 0.85 \pm 0.04°K$ is obtained. This value is representative for the molar volume $V = 22.1$ cm³/mole that corresponds to the experimental average pressure of 40 bar.

We now calculate the changes of molar volume between solid ortho- and para-H₂ at a given low pressure. Assuming the compressibility coefficient to be the same for both ortho- and para-H₂, and taking the value $k_T = 5.0 \pm 0.5 \times 10^{-4}$ bar⁻¹, which is the average value for the range 0–100 bar as obtained by Megaw,[29] we find with the aid of Eqs. (21) and (22)

$$(V_{ortho} - V_{para})/\bar{V} = -1.7 \times 10^{-2} \quad \text{at} \quad T = 0°K$$
$$\text{hcp phase.} \quad (23)$$

Assuming the same compressibility in both hcp and cubic phases for ortho-H₂, we obtain at $T = 0°K$

$$(V_{ortho\ (hcp)} - V_{ortho\ (cubic)})/\bar{V} = 0.28 \times 10^{-2}. \quad (24)$$

This last result illustrates the sensitivity of the strain-gauge method. Such a small volume change cannot be resolved using the techniques of x-ray[9] or neutron[10] diffraction.
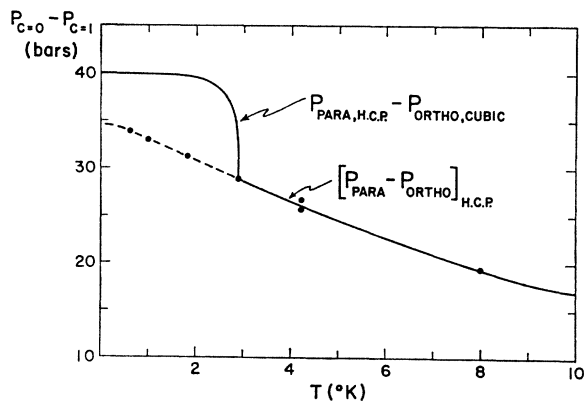


Fig. 2. $P(c=0) - P(c=1)$ versus temperature. The curve $P(c=1)_{hcp} - P(c=1)_{cubic}$ was obtained by extrapolation to $c=1$ of results in Sec. V.

## V. hcp-fcc PHASE TRANSITION

The measurements of the temperature dependence of $P$ are the most meaningful when they are carried out at constant ortho concentration $c$. However, such measurements are complicated at high ortho concentrations by the steady pressure increase with time, described in Sec. IV. In order to correct the actual data to results at constant $c$, the following procedure was used. During each $P(T)$ experiment, the pressure change with time $(\partial P/\partial t)_T$ was measured over a short period of time before and after each cycling through the transition and these two determinations of $(\partial P/\partial t)_T$ were averaged. A computer program took the conversion pressure changes into account to correct the data to values of $P$ versus $T$ at constant ortho-H₂ concentration. The procedure could typically compensate for 90% of the conversion-induced pressure change. The ortho concentration labeling the curves and tabulations presented in this section and in Sec. VI is the average ortho concentration during the experiment.

Measuring the value of the pressure change $\Delta P_{trans}$ through the transition is somewhat difficult because the slopes $dP/dT$ on either side of the transition differ considerably. The procedure used was to draw a line tangent to the low-temperature portion of the $P(T)$ curve parallel to the $P(T)$ curve just above the transition. The separation of the lines was taken to be the pressure change $\Delta P_{trans}$. The transition temperature $T_{trans}$ was chosen as the temperature at which half of the pressure change had taken place. This definition makes $T_{trans}$ upon cooling about 5–20 m°K lower than the temperature at which $(\partial P/\partial T)_V$ is maximum. Figure 3 shows three typical transitions; there is a marked hysteresis in the transition temperature between cooling and warming. Such a hysteresis has been noted by several authors in various experiments.[8,17–19,33]

As well as could be ascertained from the data of a given sample, the features of the initial transition upon cooling were unique. The second and following cooling transitions had characteristics that were more like

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

those of the warming transitions. It was therefore thought that after thermal cycling the cubic phase was not removed entirely above $T_{\text{trans}}$. This view is borne out by the observation that the pressure change on warming is only $\frac{1}{2}$ to $\frac{2}{3}$ of the pressure change that occurs when cooling through the transition with a freshly prepared sample. This observation led to the procedure of annealing or partially melting the solid sample between each cooling-warming cycle through the transition. Upon cooling, the refrozen sample then reproduced the same features as the initial cooling through the transition. The slow rate of data taking made it difficult to perform several thermal cyclings through the transition without an appreciable change in ortho concentration due to ortho-para conversion. Therefore, curves corresponding to those of Fig. 3 of Ref. 33 were not obtained for $H_2$. However, in solid $D_2$, where the conversion rate is much slower, a detailed study of the transition after repeated cycling has been made. These measurements will be reported elsewhere.[34]

*Note added in proof.* A study of fast successive thermal cyclings through the transition has subsequently been made for $H_2$ and the analysis of the results will be compared with that for $D_2$ in a forthcoming paper[34] and correlated with the x-ray data.[33]

Neither upon cooling nor upon warming through the transition have we observed evidence for more than one peak in the derivative $(\partial P/\partial T)_V$. Three maxima were expected according to the specific-heat data of Ahlers and Orttung,[35] since $C_V$ is related to $(\partial P/\partial T)_V$ via Eq. (8). We conclude tentatively that the existence of their three maxima may have been an apparatus effect. Perhaps the differences have been due to the nature of the container and the mechanical history of the respective $H_2$ samples. The possibility of such an effect is apparent from the result of a very interesting x-ray study of solid $H_2$.[36]

One feature of the $P(T)$ curve that was intensively investigated and is considered to be accurate is the



Fig. 4. Negative pressure drop for $c < 0.62$ and absence of transition for $c = 0.58$. The correction described by Eq. (18) has not been applied to this figure.

existence of a small concentration range between $c = 0.60$ and $c = 0.62$ where $\Delta P_{\text{trans}} = P_{\text{hcp}} - P_{\text{cubic}}$ becomes negative. In this range the cubic phase must have a larger molar volume than the hcp phase. The large quantity of data, both cooling and warming, show that this is not a spurious effect. A representative transition in this concentration range is shown in Fig. 4.

A second feature of the experiment is the lack of a transition below $c = 0.59$ upon cooling and below $c = 0.55$ upon warming. The curve of $T_{\text{trans}}$ versus $c$ upon warming below $c = 0.59$ was obtained as follows: Solid $H_2$ with an ortho concentration of 0.61 was cooled through the transition to a predetermined temperature which was kept constant, and the pressure was monitored as a function of time, while the ortho-para conversion proceeded. Eventually, a sharp change in pressure took
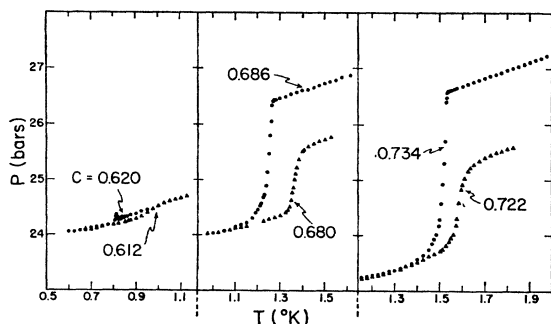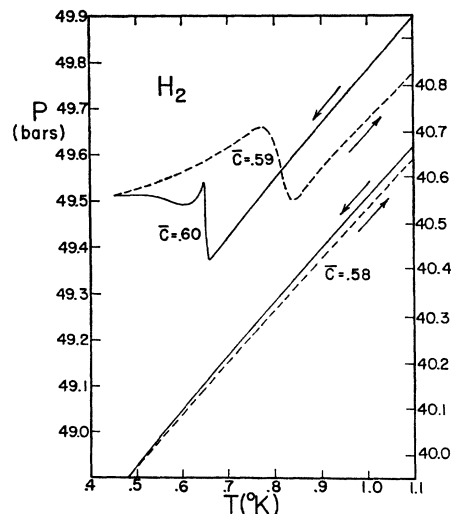


Fig. 3. Typical $P$-versus-$T$ data upon first cooling and first warming through the hcp-cubic transition. The correction described by Eq. (18) has not been applied to this figure.

[34] D. Ramm, H. Meyer, and R. L. Mills (unpublished).
[35] G. Ahlers and W. H. Orttung, Phys. Rev. **133**, A1642 (1964).
[36] C. S. Barrett, L. Meyer, and J. Wasserman, J. Chem. Phys. **45**, 834 (1966).

TABLE II. Pressure drop $\Delta P_{\text{trans}}$ and transition temperature $T_{\text{trans}}$ versus ortho-$H_2$ concentration.

| | $T$ (°K) | | $P_{\text{trans}}$ (bar) | |
|---|---|---|---|---|
| $c$ | Cooling | Warming | Cooling | Warming |
| 1.00 | 2.88 | 2.92 | 10.7 | 8.4 |
| 0.95 | 2.58 | 2.70 | 9.3 | 7.2 |
| 0.90 | 2.38 | 2.45 | 7.9 | 6.0 |
| 0.85 | 2.10 | 2.22 | 6.6 | 4.8 |
| 0.80 | 1.82 | 1.96 | 5.2 | 3.6 |
| 0.75 | 1.58 | 1.72 | 3.8 | 2.4 |
| 0.70 | 1.30 | 1.48 | 2.5 | 1.4 |
| 0.67 | 1.15 | 1.30 | 1.7 | 0.9 |
| 0.65 | 0.98 | 1.18 | 1.2 | 0.4 |
| 0.63 | 0.90 | 1.07 | 0.7 | 0.05 |
| 0.62 | 0.82 | 1.00 | 0.4 | −0.16 |
| 0.61 | 0.73 | 0.92 | 0.11 | −0.32 |
| 0.60 | 0.65 | 0.85 | −0.21 | −0.48 |
| 0.59 | 0.55 | 0.80 | ⋯ | ⋯ |
| 0.58 | <0.4 | 0.74 | ⋯ | ⋯ |
| 0.57 | <0.4 | 0.69 | ⋯ | ⋯ |
| 0.56 | <0.4 | 0.63 | ⋯ | ⋯ |
| 0.55 | <0.4 | 0.90 | ⋯ | ⋯ |

TABLE III. Slope $(dP/dT)_{trans}$ for various
ortho concentrations at low pressures.

| $c$ | $\Delta S$ (joule/mole °K) | $\Delta P_{trans}$ (bar) | $(dP/dT)_{trans}$ (bar °K$^{-1}$) |
|---|---|---|---|
| 0.73 | 1.6[a] | 1.8 | 890 |
| 0.73 | 1.34[b] | 1.8 | 750 |
| 0.69 | 1.17[b] | 1.3 | 900 |
| 0.65 | 0.8[b] | 0.5 | 1600 |
| 0.63 | 0.3[b] | 0 | very large |
| 0.68 | | | 820[c] |
| 0.68 | | | 1000[d] |
| 0.75 | | | 400[e] |

[a] Based on Fig. 4 of Ref. 35.
[b] By integration of the specific heat of Ref. 16.
[c] From extrapolation at low pressures of data in Table III of Ref. 37.
[d] From extrapolation at low pressures of data in Fig. 9 of Ref. 35.
[e] From Ref. 19.

place that signaled the transition from the cubic phase back into the hcp one. From an analysis of the sample after the experiment, the concentration $c$ at the time of the transition could be determined. The concentration of 0.55 appears to be the critical one. Table II gives a summary of the phase transition curve upon cooling and warming and shows the pressure change $\Delta P_{trans}$. It also gives the extrapolated pressure change upon first cooling between $T_{trans}$ and $T = 0$ as a function of ortho concentration. The results so presented are an average over about 40 cooling and 40 warming passes through the transition. A graphical representation of the results and comparison with other recent work has been presented elsewhere. A recent publication[33] has summarized all previous experiments near the transition.

An extrapolation to $c = 1$ of several experimental $P(T)$ curves for the first cooling through the transition is presented in Table I, last column. This extrapolation has been used for the calculation of $\Gamma$ in Sec. IV.

The molar volume change at constant pressure $\Delta V = V_{hcp} - V_{cubic}$ is given to a good approximation by

$$\Delta V_{trans} = k_T V \Delta P_{trans}. \tag{25}$$

This quantity can now be used in conjunction with entropy data to obtain the slope of the hcp-cubic phase
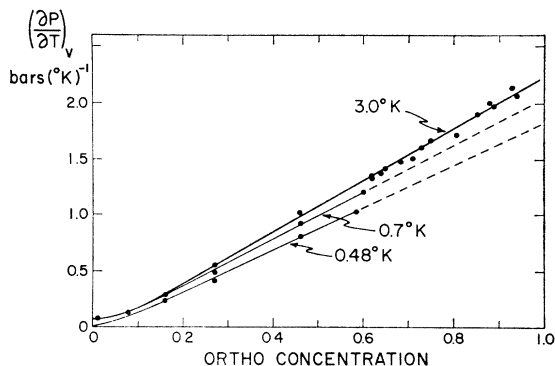


FIG. 5. $(\partial P/\partial T)_V$ versus concentration for different temperatures in the hcp phase. The solid lines cover the range over which experiments were carried out. The dashed lines are the extrapolations of these lines.

transition $(dP/dT)_{trans}$. In order to make a meaningful comparison only warming data are considered, since the entropy results are obtained under the same conditions of heating. For concentrations above 0.62, the entropy changes over the smeared transition are obtained from the specific-heat data of Hill and Ricketson[16] and of Ahlers and Orttung.[35] Table III gives the slope $(dP/dT)_{trans}$ so obtained using the Clausius-Clapeyron equation. For comparison the slopes measured directly[19,35,37] are presented in the three bottom rows. With the exception of Ref. 19, the agreement is considered very satisfactory in view of the large uncertainties, especially for $c < 0.68$. At $c = 0.6$ there is still an indication of a positive latent heat.[16] Also, from our method of recording pressure and temperature at regular time intervals, there is good evidence that the specific heat goes through a maximum at the transition for any ortho concentration. Hence the latent heat over the smeared-out transition must be positive; it follows that $(dP/dT)_{trans}$ must become infinite and then negative as $c$ is decreased through the value 0.62.

## VI. $(\partial P/\partial T)_V$ RESULTS AND THEIR ANALYSIS

This section presents the results for $(\partial P/\partial T)_V$ for various ortho concentrations $c$ as a function of temperature. The lowest concentration used represents the closest approach to para-$H_2$ that was achieved in the preparation of the samples. Although para-$H_2$ gas with $c = 0.002$ was prepared by the usual catalytic conversion method near 20°K, the subsequent compression of the gas to about 150 bar in the metal cryostat before the formation of the solid allowed the conversion of a small amount of para-to-ortho-$H_2$.

For data with $c \gtrsim 0.3$, where ortho-para conversion is appreciable, corrections for this phenomenon were made, as outlined in Sec. V. Below about $c = 0.15$, there was also a change of pressure with time due to molecular rearrangement, as will be described later in this paper, and a similar correction to the data for this effect was made. All the derivative results, shown in Table IV, represent data obtained from averaging equal numbers of warming and cooling $(\partial P/\partial T)_V$ curves. This averaging eliminated the remaining drift with time due to ortho-para conversion or molecular rearrangement. Further results at concentrations above 0.71 were obtained from 40 cooling and warming experiments through the hcp to cubic transition. Part of these results are shown in Fig. 5. A number of $(\partial P/\partial T)_V$ curves for $0.46 < c < 0.56$ will be presented in another

[37] S. Dickson and H. Meyer, Phys. Rev. **138**, A1293 (1965).
The transition temperatures tabulated in this article were obtained upon *warming* through the transition. We also note that the slope $d \ln T_{trans}/d \ln V = 2.0$ quoted in this paper applies mainly to the pressure range $P = 1000$ bar, where interactions other than EQQ become important (Ref. 12). At pressures below about 1000 bar, where only EQQ interactions need being considered (Refs. 11 and 12), there are too few experimental points to define such a slope; hence the NMR results are not inconsistent with a slope of 5/3 that one would expect from EQQ interaction only.

TABLE IV.  $(\partial P/\partial T)_V$ data, expressed in bars $(°K)^{-1}$, for different ortho-$H_2$ concentrations.

| $T\backslash c$ (°K) | 0.038 | 0.042 | 0.071 | 0.082 | 0.118 | 0.156 | 0.162 | 0.27 | 0.47 | 0.65 | 0.71 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.4 |  | 0.032 | 0.066 | 0.087 | 0.148 | ⋯ | 0.186 | ⋯ | ⋯ | ⋯ | ⋯ |
| 0.6 |  | 0.057 | 0.100 | 0.120 | 0.208 | 0.244 | 0.269 | 0.438 | 0.92 | 0.13 | 0.07 |
| 0.8 |  | 0.066 | 0.121 | 0.138 | 0.242 | 0.295 | 0.305 | 0.510 | 0.96 | 0.37 | 0.18 |
| 1.0 | 0.045 | 0.069 | 0.128 | 0.147 | 0.260 | 0.330 | 0.324 | 0.564 | 0.99 | 1.22 | 0.44 |
| 1.2 | 0.050 | 0.071 | 0.129 | 0.151 | 0.270 | 0.353 | 0.334 | 0.602 | 1.02 | ⋯ | 1.30 |
| 1.4 | 0.052 | 0.070 | 0.128 | 0.151 | 0.274 | 0.365 | 0.339 | 0.627 | 1.04 | 1.21 | ⋯ |
| 1.6 | 0.053 | 0.068 | 0.127 | 0.150 | 0.273 | 0.367 | 0.340 | 0.636 | 1.06 | 1.27 | 1.37 |
| 1.8 | 0.0535 | 0.067 | 0.125 | 0.148 | 0.270 | 0.361 | 0.337 | 0.634 | 1.06 | 1.32 | 1.41 |
| 2.0 | 0.0535 | 0.067 | 0.122 | 0.144 | 0.264 | 0.349 | 0.331 | 0.628 | 1.07 | 1.35 | 1.45 |
| 2.2 | 0.0535 | 0.066 | 0.118 | 0.140 | 0.255 | 0.335 | 0.323 | 0.615 | 1.06 | 1.38 | 1.48 |
| 2.4 | 0.054 | 0.066 | 0.114 | 0.135 | 0.246 | 0.321 | 0.313 | 0.601 | 1.06 | 1.40 | 1.50 |
| 2.6 | 0.055 | 0.066 | 0.111 | 0.130 | 0.238 | 0.308 | 0.302 | 0.585 | 1.05 | 1.40 | 1.51 |
| 2.8 | 0.056 | 0.067 | 0.108 | 0.125 | 0.230 | 0.297 | 0.291 | 0.569 | 1.04 | 1.40 | 1.51 |
| 3.0 | 0.058 | 0.068 | 0.106 | 0.121 | 0.222 | 0.287 | 0.280 | 0.553 | 1.03 | 1.39 | 1.50 |
| 3.2 | 0.060 | 0.069 | 0.105 | 0.119 | 0.216 | 0.278 | 0.271 | 0.539 | 1.02 | 1.38 | 1.50 |
| 3.4 | 0.063 | 0.071 | 0.104 | 0.118 | 0.210 | 0.271 | 0.264 | 0.528 | 1.01 | 1.37 | 1.49 |
| 3.6 | 0.067 | 0.074 | 0.105 | 0.117 | 0.206 | 0.265 | 0.258 | 0.518 | 1.00 | 1.36 | 1.48 |
| 3.8 | 0.072 | 0.078 | 0.106 | 0.118 | 0.202 | 0.262 | 0.253 | 0.510 | 0.98 | 1.35 | 1.47 |
| 4.0 | 0.078 | 0.083 | 0.109 | 0.120 | 0.199 | 0.259 | 0.247 | 0.506 | 0.97 | 1.35 | 1.46 |
| 4.2 | 0.083 | 0.090 | 0.114 | 0.124 | 0.197 | 0.257 | 0.242 | 0.500 | 0.95 | 1.34 | 1.44 |

paper[34] where they will be compared with data on $D_2$ over a similar concentration range of $(J=1)$ molecules.

## A. Results of Para-$H_2$

Two samples with ortho concentrations $c=0.005$ and 0.011 were investigated. The respective pressures of these samples at 4.2°K were 58 and 16 bar. In order to account for the rotational contribution of the ortho-molecules, the data were analyzed using the relation

$$(\partial P/\partial T)_V = AT^3 + BT^{-2}, \qquad (26)$$

where the terms represent, respectively, the lattice contribution and the first term in the high-temperature expansion of $(\partial P/\partial T)_V$ EQQ. The term in $T^{-2}$ describes the EQQ contribution at temperatures higher than about 2.5°K. The factor $B$ will not be discussed, being of no further use in the analysis. A least-squares fit, carried out between 4.2 and 2.5°K, gave for the $c=0.005$ and 0.011 samples, respectively, $A = (9.2\pm0.5)\times10^{-4}$ and $(1.05\pm0.03)\times10^{-3}$ bar $(°K)^{-4}$. The specific-heat data of Ahlers[24] over the same temperature range gave $C_V = 1.00\times T^3$ mJ/mole °K for a sample under a pressure of about 55 bar at 4°K, comparable with that of our $c=0.005$ sample. Hence from Eq. (8) we obtain $\gamma_L = 2.06\pm0.1$. This result is in good agreement with that obtained by Ahlers[24] ($\gamma_L \simeq 2.15$) from measurements of $C_V$ at different molar volumes. Furthermore, using the value of $(\partial P/\partial T)_V$ and Megaw's[29] value of $k_T = 5\times10^{-4}$ bar$^{-1}$ one obtains over the temperature range up to 4.2°K

$$\frac{C_P - C_V}{C_V} = \left(\frac{\partial P}{\partial T}\right)_V^2 \frac{k_T V T}{C_V} = 9.3\times10^{-7}T^4 \qquad (27)$$

($T$ in °K). This difference would be undetectable at these temperatures and our conclusion is consistent

with the tentative calculation of Hill and Lounasmaa[38] that $C_P \simeq C_V$, based on their $C_P$ data on para-$H_2$.

It follows that samples having a pressure difference of 40 bar will have a $\Theta_D$ different by the amount $\delta P k_T \gamma_L = 4.2\%$ with the lower pressure sample having the larger value. Therefore, their respective $(\partial P/\partial T)_V$ at low temperatures will differ by about 12%, in agreement with our observations on both samples. This remark explains the difference between $C_P$ and $C_V$ below 4°K in Fig. 2 of Ref. 24 since the $C_P$ measurements were taken at "zero" pressure while the $C_V$ data were taken at pressures higher than about 55 bar. It is concluded, therefore, that the Grüneisen relation is valid for solid para-$H_2$ at least in the temperature range below 4.2°K. What is inconsistent in Ahler's Fig. 2 is the attribution of a molar volume of 22.56 cm$^3$ to the sample measured at 55 bar $(T=4°K)$ since this would imply a molar volume of 23.14$\pm$0.05 cm$^3$ at $P=0$. This is appreciably larger than obtained from recent precise x-ray determinations[9] giving $V=22.52$ $\pm$0.05 cm$^3$/mole at $P=0$.

## B. Concentration Range 0.01 < c < 0.07

This concentration range was covered in detail because it was initially hoped that an analysis of the $(\partial P/\partial T)_V$ data in terms of contributions from isolated orthopairs and triangles could be carried out. Figure 6 shows the averaged $(\partial P/\partial T)_V$ EQQ results over warming and cooling for the concentration $c=0.038$ after subtracting the lattice term from the measured $(\partial P/\partial T)_V$. Both cooling and warming experiments were carried out over a time interval of 3 h. It was only after these measurements were completed that direct evidence was obtained[39] that a redistribution of orthomolecules

[38] R. W. Hill and O. Lounasmaa, Phil. Mag. **4**, 785 (1959).
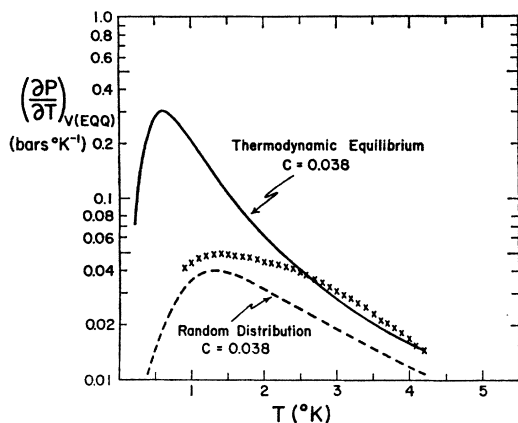[39] L. I. Amstutz, J. R. Thompson, and H. Meyer, Phys. Rev. Letters **21**, 1175 (1968).

FIG. 6. $(\partial P/\partial T)_V$ EQQ as a function of temperature for the ortho concentration of 0.038. Crosses, experimental points after subtraction of the lattice contribution; solid curve, calculated for thermodynamic equilibrium within the orthoconfigurations assuming only the presence of isolated single orthomolecules and isolated pairs; dashed curve, calculated for high-temperature random distribution of orthomolecules (see text).

took place with time as a function of temperature at low ortho concentrations. The redistribution time constant $\tau$ (corresponding to $c=0.04$) is on the order of 0.5 h at $4°$K, and increases to about 5 h at $0.5°$K. These observations[39] explained the pressure drift with time, since a molecular rearrangement that strives to achieve a minimum in the free energy causes a change of pressure in the system. Hence the $(\partial P/\partial T)_V$ data are expected to fall between the two theoretical curves in Fig. 6 corresponding, respectively, to thermodynamic equilibrium (measurement time $\gg\tau$) and to high-temperature random distribution of orthomolecules (measurement time $\ll\tau$). The curves were calculated, respectively, from the partition functions in Eqs. (16) and (15), where a value $\Gamma/k_B=0.84°$K was used. As can be seen in Fig. 6, the experiment is in fair agreement with the upper curve between 3 and $4.2°$K, where $\tau$ is short. However, below about $3°$K, the orthomolecule distribution becomes "frozen in" and a curve approximately parallel to that of the calculated random distribution is obtained. It means that there are more isolated pairs and triangles present than in the random distribution. The maximum of the experimental curve coincides well with that of the calculated one, which confirms the value $\Gamma/k_B=0.85°$K obtained in Sec. IV. Similar results were obtained for the ortho concentrations of 0.042 and 0.07, all of them showing a maximum for $(\partial P/\partial T)_V$ EQQ near $T=1.30°$K.

It should be noted that the $(\partial P/\partial T)_V$ EQQ observed between 4.2 and $0.5°$K corresponds to the removal of only a fraction of the rotational entropy $S_R=cR\ln3$ for the state $J=1$. If the $(\partial P/\partial T)_V$ measurements had been extended rapidly to temperatures below $0.4°$K, other maxima would have been observed corresponding to the splitting of the lowest levels in the pair and triangular configurations and of all the other configu-

rations such as next-nearest neighboring pairs, etc. The crystalline field splittings of the "isolated" single orthomolecules[21] will give a contribution below about $10\,m°$K.

### C. Concentration Range $c\gtrsim0.07$

As the ortho concentration increased above about 0.07, the $(\partial P/\partial T)_V$ data were relatively less affected by the drift due to molecular rearrangement. One may tentatively offer the following explanation for this observation: Isolated molecules are much more likely to diffuse through the lattice than are clusters of orthomolecules. As the ortho concentration increases, the relative number of molecules forming clusters becomes larger and hence it becomes progressively more difficult for the system to rearrange. The $(\partial P/\partial T)_V$ data (as well as $C_V$ data) may then be representative for a frozen-in distribution formed at the melting point.

From Table IV it can be seen that, at temperatures between 4.2 and $1.5°$K, $(\partial P/\partial T)_V$ in the hcp phase for $c\gtrsim0.4$ is approximately independent of temperature for a given ortho concentration. From Fig. 5, where $(\partial P/\partial T)_V$ is plotted as a function of $c$ at different temperatures, it appears that $(\partial P/\partial T)_V$ at a given temperature is approximately proportional to the ortho concentration. The results, extrapolated to $c=1.0$, have been used for the calculation of the dashed curve below $4.2°$K in Fig. 2. The assumption for this extrapolation has been that no sharp order-disorder transition occurs in the hcp phase, but rather a continuous ordering into the ground state at $T=0°$K. This assumption differs from theoretical expectations that are based on molecular-field-type calculations[40] and where the order-disorder transition temperature $T_c(\text{hcp})$ is slightly below that in the cubic phase. Such a transition, which cannot be observed, would raise somewhat the dashed part of the curve in Fig. 2; therefore, as pointed out before, the value of $[P_{\text{para}}-P_{\text{ortho}}]_{\text{hcp}}$ at $T=0°$K, presented in Eq. (21), must be considered to be a lower limit.

The value of the Grüneisen constant $\gamma_{\text{EQQ}}$ has been obtained from the $(\partial P/\partial T)_V$ data and the $C_P$ data of Hill and Ricketson,[16] using the conclusion of Eq. (27) that $C_P=C_V$. The $C_P$ data for the ortho concentrations of 0.205, 0.33, and 0.427 between 0.6 and $2°$K were used. At these concentrations, self-heating effects become small and the $C_P$ curves show a regular behavior. Further use was made of the data[16] at the ortho concentrations of 0.25, 0.41, and 0.56 between 2 and $3°$K. In order to calculate $\gamma_{\text{EQQ}}$, the values of $(\partial P/\partial T)_V$ were interpolated to give values at the same ortho concentration as the $C_P$ values. No systematic variation of $\gamma_{\text{EQQ}}$ with ortho concentration or temperature was found, and the average was $\gamma_{\text{EQQ}}=1.62\pm0.1$, which is in excellent agreement with the theoretical value 5/3 considering the combined uncertainties of both experi-

[40] H. James, Phys. Rev. **167**, 862 (1968); W. M. Fairbairn, W. Lounds, and M. R. Steel (unpublished).

ments. This evidence justifies in part the assumption made in writing Eq. (5). It might be mentioned that as the ortho concentration increases above about 0.35 and the relative number of isolated orthomolecules diminishes, the rotational entropy below 0.3°K becomes negligible in comparison with that above this temperature. The Schottky anomaly in the specific heat, as measured[16] between 0.3 and 10°K, gives a rotational entropy equal to $Rc \ln 3$ to within experimental error.[16]

The derivative $(\partial P/\partial T)_V$ on the cubic side of the transitions for ortho concentrations of 0.65 and above decreases rapidly with decreasing $T$. The exact temperature dependence a few tenths of a degree below $T_{\text{trans}}$ is quite uncertain, because the conversion-induced pressure change is much larger than $(\partial P/\partial T)_V \delta T$ over the same period of time, where $\delta T$ is the controlled temperature change. The compensation for the ortho-para conversion is not sufficiently accurate to remove the uncertainty in the $(\partial P/\partial T)_V$ curve. In solid $D_2$, the para-ortho conversion is much slower and in this solid an analysis of the specific heat in the cubic phase has been carried out.[34]

## VII. SUMMARY

Our investigation of pressure at constant volume as a function of temperature and ortho-$H_2$ concentration in solid $H_2$ has given the following results, which we summarize below.

(a) From the pressure difference between ortho- and para-$H_2$ extrapolated to $T=0$, we have obtained a value of the EQQ interaction constant $\Gamma/k_B = 0.85 \pm 0.03$ °K at an average pressure of $P=40$ bar. This value will decrease by the amount $\delta \ln \Gamma = k_T P \gamma_{\text{EQQ}} = 0.03$ when the average pressure is normalized to $P=0$; one then obtains $\Gamma/k_B = 0.82 \pm 0.03$°K, in excellent agreement with the results from NMR[41] taken at $P=0$. Hence $\Gamma$ is smaller by about 18% than the theoretical value for a rigid lattice, $\Gamma/k_B = 1.00$°K. The reason for this decrease has been attributed[42] to the interaction between zero-point lattice vibrations and the rotation. A similar result is found for $D_2$ where an analysis of $(\partial P/\partial T)_V$ data[43] in the cubic phase using the theory of Ref. 7, and $(\partial P/\partial T)_V$ data at low para-$D_2$ concentrations[34] give $\Gamma/k_B = 1.05$°K, while the theory of a rigid lattice gives $\Gamma/k_B = 1.18$°K.

(b) We have studied systematically the hcp-cubic phase transition and found that the transition disappears below about $c=0.59$ upon cooling and $c=0.55$ upon warming. The pressure drop $P_{\text{hcp}} - P_{\text{cubic}}$ is positive except over the very small concentration range $0.60 < c < 0.62$.

(c) The slope $(dP/dT)_{\text{trans}}$ is about 1000 bar/°K and is consistent with measurements from both specific heat and NMR under pressure at $c=0.7$. It becomes very large and seems to change sign as the concentration decreases.

(d) Measurements of $(\partial P/\partial T)_V$ and their comparison with specific-heat data have shown that the lattice Grüneisen constant is $\gamma_L = 2.06 \pm 0.1$ and have demonstrated that the Grüneisen equation is valid for solid para-$H_2$, at least below 4.2°K. Furthermore, $\gamma_{\text{EQQ}}$ was found very close to the value of 5/3 expected for EQQ interaction.

(e) Measurements of $(\partial P/\partial T)_V$ have been affected by molecular rearrangement that takes place as a function of time, the effect increasing in importance as the ortho concentration is decreased. Therefore, the data at concentrations below about 0.07 can only be given qualitative theoretical significance. The temperature, however, at which the maximum $(\partial P/\partial T)_{V \text{ EQQ}}$ is found is consistent with that calculated for a frozen-in distribution of the orthomolecules for a value of $\Gamma/k_B = 0.85$°K $(P=40$ bar). At higher concentrations, where the relative effect of this molecular motion is reduced, we believe that the data are representative for a random distribution of orthomolecules that remains frozen in as the temperature changes. This configuration, however, may not have as low a free energy per molecule as that where the solid sample is divided into a pure ortho-$H_2$ and a para-$H_2$ phase. Further studies of this motion and the time constant $\tau$ in both solid $H_2$ and also in $D_2$ are being planned.

[41] A. B. Harris, L. I. Amstutz, H. Meyer, and S. Myers, Phys. Rev. **175**, 603 (1968).
[42] A. B. Harris, Intern. J. Quantum Chem. (to be published).
[43] D. Ramm, H. Meyer, J. F. Jarvis, and R. L. Mills, Solid State Commun. **6**, 497 (1968).