PHYSICAL REVIEW B VOLUME 6, NUMBER 4 15 AUGUST 1972

Orientational Order Parameter in Cubic D_2 †

H. Meyer, F. Weinhaus, and B. Maraviglia*
Department of Physics, Duke University, Durham, North Carolina 27706
and
R. L. Mills
Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

(Received 23 March 1972)

We present a study of the orientational order parameter σ for D_2 molecules with both rotational angular momentum $J=1$ (para-D_2) and $J=0$ (ortho-D_2) in the ordered cubic phase. Our study covers the temperature range between 0.4 and 4 K at mole fractions X of ($J=1$) molecules $0.55 \le X \le 0.96$. The order parameters $\sigma_{(J=1)}(T, X)$ and $\sigma_{(J=0)}(T, X)$ are proportional to the respective doublet splitting observed in the NMR spectrum. In the ordered phase, two doublets spaced symmetrically around the central Larmor frequency are recorded. The outer one, with a splitting $\delta\nu_{(J=1)}$ up to about 78 kHz, represents the signal from the ($J=1$) molecules. The inner one, with splitting $\delta\nu_{(J=0)}$ an order of magnitude smaller than $\delta\nu_{(J=1)}$, is caused by polarization of the ($J=0$) molecules by the ($J=1$) field. A description is presented of the line shape as a function of T and X. Using the results from several samples, we obtain the extrapolated ($J=1$) order parameter for $X=1$ as a function of T. At the order-disorder transition temperature T_λ, the doublet structure suddenly disappears and is replaced by a sharp central line which is characteristic of the orientationally disordered phase. The first-order nature of the transition is thus clearly shown. The experimental order parameter for ($J=1$) molecules $\sigma_{(J=1)}(X=1, T)$ is compared with predictions from a mean-field and a cluster-variation theory, and also with results from Raman spectroscopy. As X decreases, the line structure shows a progressively greater temperature variation and becomes more smeared out as the order-disorder transition is approached. Below a critical mole fraction $X_c=0.54$, obtained by extrapolation, no doublet structure is observed. The limiting value of both $\sigma_{(J=1)}$ and $\sigma_{(J=0)}$ as a function of X at $T \ll T_\lambda(X)$ is in good agreement with predictions by Harris. A fit of the experiment to theory leads to a factor of about 0.02 for the reduction of the order parameter by the zero-point motion, in agreement with theoretical predictions. It is also shown that, within experimental error, the temperature variation of both order parameters $\sigma_{(J=1)}$ and $\sigma_{(J=0)}$ for a given X is the same. We briefly discuss the failure to observe the doublet splitting for the NMR pair spectrum of two neighboring ($J=1$) molecules in an hcp D_2 sample with $X=0.05$, and mention other peculiarities that at this time remain unexplained for dilute mixtures of ($J=1$) molecules in ($J=0$) D_2. The possible existence of a large crystalline field that might account for these anomalies is suggested.

I. INTRODUCTION

The orientational ordering of molecules with rotational angular momentum ($J=1$) in solid H_2 and D_2 is, in a number of ways, analogous to the spin ordering in antiferromagnets. This has been illustrated recently by Harris,[1] who summarized the properties of these two solids. In analogy to antiferromagnets, the ($J=1$) molecules in solid H_2 and D_2 undergo a cooperative transition at a temperature T_λ, and in their ordered state in the close-packed cubic structure $Pa3$ they appear to form sublattices.[2] In each of the four interpenetrating sublattices,[3] the molecular axes of the ($J=1$) molecules are aligned parallel to one of the body diagonals. We can define as order parameter[1] the quantity $\sigma_{(J=1)} = \langle 3\cos^2\theta - 1\rangle_T$, where θ is the angle between the molecular axis and the alignment direction in a particular sublattice. At $T=0$ and in a pure ($J=1$) solid, where $\theta=0$, one expects $\sigma_{(J=1)}$ to approach $2(\frac{2}{5})$, where the factor $\frac{2}{5}$ represents the average over the probability distribution of the molecular quantum states. In direct analogy to a diluted antiferromagnet, a ($J=1$) solid of mole fraction X diluted with ($J=0$) molecules shows a weakening of the effective interaction with dilution and there is a critical ($J=1$) mole fraction $X_c \approx 0.5$ below which no cooperative ordering transition is observed.[4,5]

Just as in a magnetic system where the order parameter is the average value of the magnetization $\langle S_z\rangle_T$, the quantity $\langle 3\cos^2\theta - 1\rangle_T$ can be conveniently measured by means of nuclear magnetic resonance (NMR).[1] The mechanism by which the rotational ordering can be detected is the dependence of the local intramolecular nuclear dipolar field on the molecular rotational state. This dependence was first demonstrated by Reif and Purcell[6] in their paper on the NMR line shape in solid H_2 in the ordered phase. At that time these authors were not aware of the interaction mechanism that brings about the orientational ordering.

It is now well established[1] that an electric quadrupole-quadrupole interaction between $(J=1)$ molecules is the dominant anisotropic interaction[7] responsible for orientational ordering.

One might argue that $(J=0)$ molecules are not expected *a priori* to experience orientational ordering because of the spherical nature of their ground state. However, these molecules experience a polarization caused by a slight admixture of the higher rotational state $J=2$ resulting from a perturbation due to the surrounding ordered $(J=1)$ molecules.[8] This polarization is evidenced by another doublet[9] with a splitting $\delta\nu_{(J=0)} \ll \delta\nu_{(J=1)}$ which we take to be proportional to a corresponding order parameter $\sigma_{(J=0)}$ to be defined below.

Unfortunately, the measurement of the order parameter by means of the doublet splitting in the NMR spectrum of H_2 and D_2 is less accurate than the determination of $\langle S_z \rangle$ by NMR in a number of antiferromagnets because the peak linewidth in the hydrogen is not negligible compared to the splitting. The situation becomes increasingly difficult as the $(J=1)$ solid is diluted with $(J=0)$ molecules and as the transition temperature T_λ is approached. Under these conditions there are distributed throughout the crystal various clusters of $(J=1)$ molecules, all with different degrees of orientation. Furthermore it is virtually impossible to carry out measurements on pure $(J=1)$ solid. Even if such an enrichment could be attained initially, the $(J=1)$ molecules would undergo a slow spontaneous conversion to $J=0$ in the solid sample. Hence experiments on a number of samples must be carried out and the results extrapolated to the limiting case of $X=1$. However, it will be shown that reliable extrapolations can be made for the splittings of pure $(J=1)$ D_2.

After a short review in Sec. II of some of the properties of solid D_2 and a description in Sec. III of the experimental techniques, we describe in Sec. IV the determination of $\sigma_{(J=1)}$ and $\sigma_{(J=0)}$ in D_2 as measured by the separation of the Pake doublets in the NMR spectrum.[1] Both the temperature dependence at fixed mole fraction X and the dependence on X in the limit of $T=0$ are described and compared with theoretical predictions. In Sec. V we discuss briefly an unsuccessful attempt to observe the doublet splitting of the pair spectrum of two neighboring $(J=1)$ molecules in a dilute mixture with $X=0.05$. Section VI contains a summary and the conclusions. Some of the results presented here were the subject of preliminary reports.[9,10]

II. REVIEW

A. Orientational Ordering Transition: Experiment

It has been established experimentally,[11] that upon cooling a solid H_2 or D_2 sample of suitably large X, the hcp phase which forms at the triple point is stable down to a temperature $T_{h\text{-}c}$ where a transition to a cubic structure is observed. In this cubic phase, orientational ordering apparently takes place.[12] When the cubic solid is then warmed, there is an indication that an order-disorder transition occurs[5] together with a partial reconversion to the hcp phase[11] at a temperature $T_{c\text{-}h} > T_{h\text{-}c}$. Upon repeatedly cycling the sample through the transition,[5,11] one observes that the cubic phase becomes stabilized to an increasing fraction at temperatures well above $T_{c\text{-}h}$ while the order-disorder transition remains[5] at $T_{c\text{-}h}$. From the repeatability of the thermodynamic behavior during the warming part of the cycle, it appears reasonable to consider this process as being representative of the order-disorder transition and consequently we take $T_{c\text{-}h}$ to be identical to T_λ. One can, at least in solid D_2 after repeated cyclings, make the reasonable assumption that the orientational transition takes place on the cubic lattice only, without the complication of an additional crystalline phase change. There is evidence from several experiments, however, that the disordered structure does not completely disappear even in the ordered phase[13,14] and this evidence will be further discussed below.

The hysteresis in the structure change may arise from the Martinsitic nature of the transition. In the orientationally disordered phase, the hcp and cubic structures apparently have almost identical free energies. It is observed in electron-diffraction experiments[15] that solid films of D_2 and H_2 with $X>0.3$, frozen directly from the gas on a cold substrate below 8 K, exhibit cubic structure. When warmed to temperatures where diffusion readily takes place, the films transform to the hcp structure and remain so when cooled well below the initial substrate temperature.

B. Orientational Ordering Transition: Theory

A number of theories have dealt with the orientational ordering transition. The first successful one[2] used a self-consistent rigid-lattice molecular-field model for the close-packed cubic structure in $Pa3$ space group. Later theories[16] considered various other cubic and hcp space groups. Also random-field approximation calculations were carried out.[17] Recently, Lee and Raich[18] used a cluster-variation method and considered only nearest-neighbor interactions to calculate the ordering of pure $(J=1)$ H_2 and D_2 on hcp and cubic lattices. These authors also gave a comprehensive summary of previous theories. They calculated the rotational free energy of the $Pa3$ structure and various hcp space groups as a function of a reduced temperature T/T_b, where $T_b = \frac{19}{3}\Gamma_{\text{eff}}$. Here Γ_{eff} is the electric quadrupole-quadrupole interaction parameter[2] which for nearly pure para-D_2 is[19] $\Gamma_{eff}/k_B = 1.15 \pm 0.06$ K. For the *Pa*3 structure the order-disorder transition temperature T_λ was found to occur at $0.75 T_b$. A crossing of the various free-energy curves signifies a first-order transition to another space group, and it appears from the calculation that an hcp space group is more stable than the cubic one for $0.715 < T/T_b$. However, as mentioned before, the experimental evidence seems to favor an order-disorder transition within the cubic phase, at least for D_2, and we will use the calculations of Lee and Raich for the *Pa*3 structure only.

A calculation[18] of the long-range order parameter for the cubic *Pa*3 structure shows only a very small temperature variation in the ordered phase. This is quite different from the result of the molecular-field-[2,20] and random-phase[17]-approximation theories where $\sigma_{(J=1)}$ shows a considerable decrease as T is increased to T_λ. In the random-phase approximation,[17] the energies $E_i(\vec{k}, T)$ of the rotational excitations, termed librons, are shown to be proportional to the order parameter. Here i denotes the mode, and $\vec{k}$ is the wave vector. Hence in this approximation one has

$$\sigma_{(J=1)}(T)/\sigma_{(J=1)}(T=0) = E_i(\vec{k}, T)/E_i(\vec{k}, T=0) \ . \qquad (1)$$

Thus the temperature variation of the libron energy is the same as that of the order parameter.

Recently, Cullen *et al.*[21] discussed the nature of the orientational order-disorder transition, showing that it should be first order, even in the absence of a crystallographic change or a change in volume.

C. NMR Spectrum in Ordered D_2

In solid D_2 the para molecules have a rotational angular momentum $J = 1$ and a nuclear spin $I = 1$. Of the ortho molecules, with $J = 0$, a fraction $\frac{5}{6}$ have a nuclear spin $I = 2$ and the remainder have spin zero. Hence both ortho and para molecules will show NMR absorption. As mentioned before, the local field on each nuclear spin is a function of the rotational state characterized by the projection J_z of the angular momentum on the axis of alignment. At temperatures where orientations are almost random and $J_z^2 \approx \frac{2}{3}$, the effect of the local hyperfine field on each spin is averaged out, and a sharp line is observed. However, in the ordered state, where $J_z^2 = 0$, a doublet structure can be expected in the NMR spectrum for the $(J = 1)$ molecules. Reif and Purcell[6] showed that for H_2 the splitting between the doublet peaks in a powdered sample should be $\delta\nu_{(J=1)} = 3d$, when $J_z^2 = 0$ is assumed for the ground state. Here d is the intramolecular splitting constant. For D_2, $d = 25.25$ kHz is taken to be the sum of the contributions $d_M = 2.74$ kHz and $d_Q = 22.50$ kHz which are, respectively, the intramolecular-nuclear-dipole coupling constant and the nuclear-quadrupole coupling constant.[22] Hence the expected splitting is close to 76 kHz, a value that was first observed by Gaines *et al.*[23] for ordered D_2 at $X = 0.81$. Actually the whole line structure[6] extends over a frequency range of about $6d$, but the signal intensity is largest at the two satellite peaks.

A generalization[14] of the expression for the splitting in a powder sample, that uses the thermal average over the rotational states J_z, gives

$$\delta\nu_{(J=1)}(X, T) = 3d\langle 1 - \tfrac{3}{2} J_z^2 \rangle_T \quad . \qquad (2)$$

Relating J_z^2 to $\cos^2\theta$, one finally has

$$\delta\nu_{(J=1)}(X, T) = \tfrac{15}{4} d \, \langle 3\cos^2\theta - 1 \rangle_T = \tfrac{15}{4} d \, \sigma_{(J=1)} \ . \qquad (3)$$

Recently, Harris[24] considered in detail the D_2 ground state in the cubic phase near $X = 1$. Considering the dependence on X, he obtained

$$\sigma_{(J=1)}(X, T=0) = \tfrac{4}{5}(1 + 0.066\, X - a/X)\xi \ . \qquad (4)$$

Here the second term in the parentheses takes into account admixtures of the higher rotational state $J = 3$ and also includes the contributions to the electric field gradient at the nucleus from neighboring molecules. The third term corrects for the zero-point motion of the rotational angular momentum and the factor a has been calculated by several authors[24-26] to be approximately 2×10^{-2}. The factor ξ expresses the influence of the interaction between the lattice vibrations and the rotational motion and is expected to be slightly smaller than unity.

For the rotationally ordered phase, Harris[8] has also predicted a doublet structure for the NMR spectrum of the $(J = 0)$ molecules. As mentioned before, this structure arises because the $(J = 0)$ molecules are slightly polarized, the ground state being an admixture with higher rotational states due to a perturbation from the ordered $(J = 1)$ molecules. Using an effective-field model, Harris calculated the doublet splitting for a powdered sample to be

$$\delta\nu_{(J=0)}(X, T=0) = X \tfrac{95}{6} d_Q (\Gamma_{eff}/B) \ , \qquad (5)$$

where Γ_{eff}/k_B, the renormalized value of the electric quadrupole-quadrupole interaction parameter, has been divided by B/k_B, the rotational constant. From the most recent values[19,27] of these quantities, respectively, 1.15 ± 0.06 and 43.0 K, one then obtains for the right-hand side of Eq. (5) the quantity $(9.5 \pm 0.6)X$ kHz. In analogy to the ordering in the $(J = 1)$ system, it seems appropriate to define a normalized order parameter for the polarized $(J = 0)$ molecules, which we take to be

$$\sigma_{(J=0)}(X, T) = \frac{\delta\nu_{(J=0)}(X, T)}{\delta\nu_{(J=0)}(X=1, T=0)} \quad . \qquad (6)$$

There have been no quantitative predictions on the

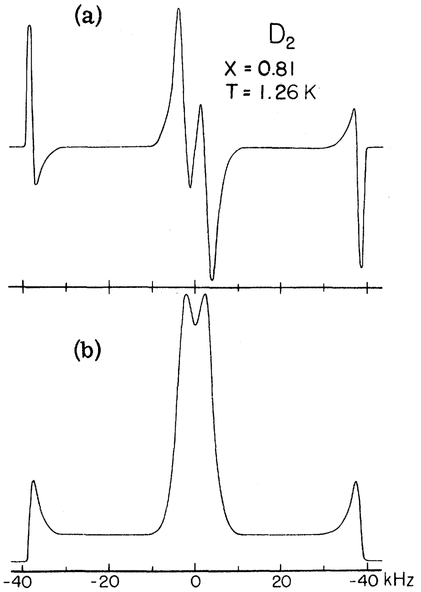

FIG. 1. Observed derivative and integrated shape of a representative NMR line in orientationally ordered D_2, for $X = 0.81$ and $T = 1.26$ K. The outer peaks form the Pake doublet representing the signal from the $(J = 1)$ molecules. The inner doublet is the signal from the polarized $(J = 0)$ molecules.

temperature dependence of $\sigma_{(J=0)}$, but it seems reasonable for a given X to expect $\sigma_{(J=0)}$ to be proportional to $\sigma_{(J=1)}$.

The effective-field model that Harris used is expected to be nearly correct for high mole fractions X. However, it is obvious that this approximation becomes worse as X decreases. We make, therefore, the *ad hoc* suggestion that an improved representation will be obtained by replacing X with the ratio $T_\lambda(X)/T_\lambda(X=1)$. We have then at $T \approx 0$ and for X not too close to X_c the predictions

$$\delta\nu_{(J=1)}(X,\ T=0) = 75.72\left(1 + 0.066\ \frac{T_\lambda(X)}{T_\lambda(X=1)} - a\ \frac{T_\lambda(X=1)}{T_\lambda(X)}\right)\xi \text{ kHz}\ , \tag{7a}$$

$$\delta\nu_{(J=0)}(X,\ T=0) = 9.5\,\frac{T_\lambda(X)}{T_\lambda(X=1)} \text{ kHz}\ . \tag{7b}$$

We must point out, however, that in the hcp phase $(X < 0.53)$, orientational ordering from electric quadrupole interaction does also occur. The NMR line from the $J = 1$ molecules broadens considerably[14] as T decreases to zero and the NMR spectrum in the ground state of hcp D_2 may well show a doublet structure similar to that in the cubic phase.[9,23]

III. EXPERIMENTAL TECHNIQUE

The experimental arrangement is the same as that given in a previous report,[14] and hence the present description will be brief. Deuterium samples of enriched para-D_2 were prepared by selective adsorption.[28] Analysis of the mole fraction X was made before and after each experiment using the method of differential thermal conductivity of the gas. In addition, the value of X could be checked from the temperature T_λ at which the splitting disappeared, using the table in Ref. 5 of T_λ vs X. The samples were liquefied in the radio-frequency cavity, then frozen quickly to achieve powder form. The cryostat operated over a temperature range between 0.45 and 20 K. The NMR line shapes were obtained using a continuous-wave Robinson spectrometer operating at low rf levels by sweeping the frequency slowly through the line, whose center was at about 5.5 MHz. The line derivative was recorded electronically on a chart recorder, frequency markers being used at regular intervals. In order to stabilize the cubic phase above T_λ, some of the samples were cycled between five and ten times through the transition. For the study of $\sigma_{(J=1)}$ as a function of T, the line shapes were recorded with increasing temperature, since this was convenient and the transition on warming is believed to be representative of the order-disorder phenomenon. The slow para-ortho conversion limited the time for a transition study and only the $(J = 1)$ Pake-doublet splitting was closely followed near the transition. Except for a few samples, the line-structure center was not observed in detail. For mole fractions near X_c where the line structure varies strongly with X, the experiments were carried out with the same sample over a period of several days. The mole fraction at a given time was then interpolated from the initial and final X values.

IV. RESULTS

A. General Observations

First, it should be pointed out that for all of the lines, we recorded conventional derivatives, a representative example of which is shown in Fig. 1 for $T \ll T_\lambda$. "Shoulders" of the doublet structure having a frequency splitting twice the value of the main Pake doublet[6] were observed several times for both the $(J = 0)$ and the $(J = 1)$ signals. However their intensity was often weak, and a systematic study was not made. In the absorption line shape plotted in Fig. 1, the shoulders for the $(J = 0)$ and $(J = 1)$ signals were not recorded. Saturation effects and signal deterioration between successive measurements were less pronounced in the present experiments than in those reported by Gaines *et al.*[23] at $X = 0.82$. However, as anticipated from relaxation theory in the ordered phase,[8,29] the saturation effects became more severe as X approached unity and recording was made at pro-

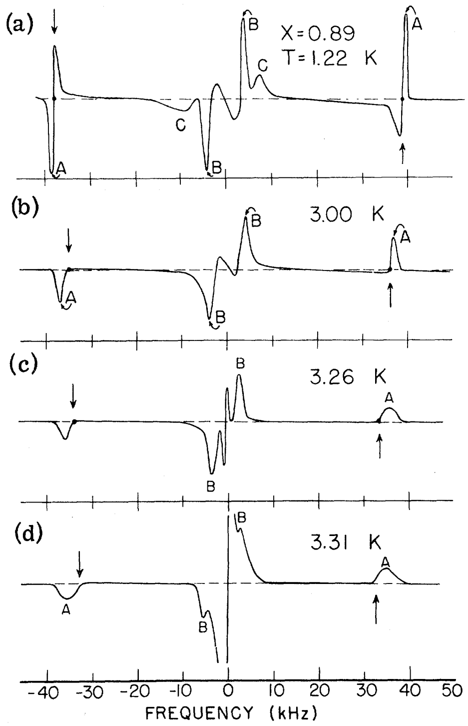

FIG. 2. Derivative traces of the NMR line for $X=0.89$ as a function of T. The solid circles mark the position of the absorption peaks, as explained in the text. The arrows mark the position of the flattened peaks as the temperature increases. The symbols A and B denote the maxima in the derivative trace for the $(J=1)$ and $(J=0)$ signals, respectively. The frequency differences $A-A$ and $B-B$ then represent the respective linewidths. Close to $T_\lambda=3.33$ K, the appearance of a sharp central line indicates the presence of clusters of disordered D_2 molecules.

gressively lower rf levels as X was increased.

The principal features observed were as follows.

(i) For $X \gtrsim 0.78$ and $T < T_\lambda$ two pairs of satellites were observed. The two outer peaks represent[23] the signal from the $(J=1)$ molecules with a splitting $\delta\nu_{(J=1)}$, and the inner doublet is interpreted as that from the $(J=0)$ molecules with a splitting $\delta\nu_{(J=0)}$. At $X=0.79$ this assignment was confirmed by a careful examination of the intensity ratio of the inner and the outer structures. For $X \lesssim 0.78$ the $(J=0)$ structure became too narrow for the inner doublet to be resolved. Resolution of this inner doublet was further hampered by the residue of a central line which partially masked the $\delta\nu_{(J=0)}$ splitting over the whole temperature range.

(ii) For a given X, the peaks of the absorption spectrum became less sharp as T approached T_λ. This is shown in Fig. 2 where smoothed recording traces of the absorption derivatives are presented for $X=0.89$. The peaks of the absorption spectrum, namely the points where the derivative crosses the horizontal "base lines," are denoted by solid circles. As T was increased, these points became less distinct and at the same time the maxima in the derivative tracing became broader. This broadening, which is not too noticeable for $X=0.96$, became more evident as X decreased. One can with some justification continue to define as "splitting" $\delta\nu$, the frequency difference between the flattened peaks in the absorption spectrum. Their positions are indicated by arrows on the derivative plot in Fig. 2, and it is clear that $\delta\nu$ so defined decreases noticeably as T approaches T_λ. Another way of describing the temperature variation of the doublet structure involves recording the structure widths $W_{(J=1)}$ and $W_{(J=0)}$ of the respective signals, as defined by the separation $A-A$ and $B-B$ on the tracings of Fig. 2. The humps marked by C in Fig. 2(a) represent the shoulders[6] of the $(J=0)$ structure with a splitting of about $2\delta\nu_{(J=0)}$.

(iii) For a given sample, the $(J=0)$ line structure was found to contract with increasing temperature in a manner similar to the $(J=1)$ structure. For the two mole fractions $X=0.89$ and 0.79 the ratio $\delta\nu_{(J=0)}/\delta\nu_{(J=1)}$ was measured, and was found to be constant for $T \lesssim 0.9T_\lambda$. The determination of the ratio became rather uncertain as T_λ was approached.

(iv) For temperatures close to T_λ, there appeared in the center of the structure a sharp line having a linewidth of the same magnitude as that in the disordered phase[30] above T_λ. This observation is identical to that[14] in solid H_2 and is attributed to the presence of clusters of orientationally disordered D_2. The temperature difference $t = (T_\lambda - T)/T_\lambda$ at which this sharp line appeared is a strong function of X. For $X=0.9$, the central line was observed for $t \lesssim 0.02$ [Fig. 2(c)], while for $X=0.74$, it started growing steadily for $t \lesssim 0.07$.

(v) The splitting $\delta\nu_{(J=1)}$ as defined above is presented in Fig. 3. With decreasing T, the various samples behave quite differently. By plotting the normalized splitting $\delta\nu_{(J=1)}(T)/\delta\nu_{(J=1)}(T=0)$ vs T/T_λ for all samples, we have been able to extrapolate the results to $X=1$ shown as the solid line in Fig. 3. Judging from the increased sharpness of the recorded derivative spectrum as one approaches $X=1$, it is conjectured that for the pure $(J=1)$ solid the Pake-doublet peaks should be well defined up to T_λ exhibiting only a slight broadening.

(vi) In contrast to the splitting $\delta\nu_{(J=1)}$, the linewidth $W_{(J=1)}$ showed a temperature variation between T and T_λ that was approximately the same for all X at a given reduced temperature T/T_λ. This is shown in Fig. 4 where the normalized width $W_{(J=1)}(T)/W_{(J=1)}(T=0)$ is plotted against T/T_λ. The first-order nature of the transition is clearly shown here for all mole fractions X.

(vii) The normalized $(J=1)$ splitting for $X=0.74$ when plotted versus T/T_λ is found to agree with

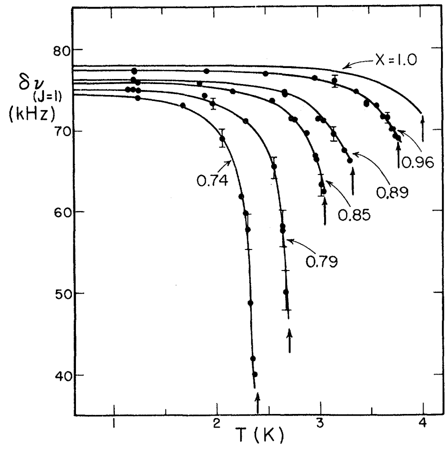

FIG. 3. Doublet splitting $\delta\nu_{(J=1)}$ as a function of T for samples at a given mole fraction X. During each experiment, X decreased by about 5×10^{-3} and the label for each curve represents the average X. The solid line with no experimental points is the splitting for $X=1$, obtained by extrapolation of the data.

the solid H_2 results for $X=0.73$, shown in Fig. 6 of Ref. 14. Thus at least for this mole fraction (the highest for which the temperature dependence of $\delta\nu_{(J=1)}$ was investigated in solid H_2) the results for H_2 and D_2 scale.

(viii) We now make an observation of the line shape in the two orientationally disordered phases of D_2. The NMR line shape was recorded on a fresh sample with $X=0.85$ at $T=3.3$ K before the sample was cooled below T_λ. The crystalline phase was then disordered hcp. After six thermal cycles of the solid through the ordering transition, the line shape was again recorded at $T=3.3$ K, where the phase was presumed[5,11] to be disordered cubic. No difference in the line shape could be detected between the two recordings. This experiment shows that the line shape in the disordered state is apparently independent of the crystalline structure of the sample.

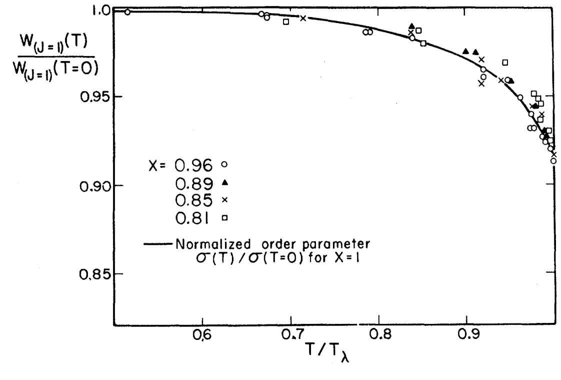

FIG. 4. Normalized linewidth $W_{(J=1)}(T)/W_{(J=1)}(T=0)$ plotted against T/T_λ for various samples of different mole fraction X.

B. Order Parameter for ($J=1$) Molecules

It is clear from Eq. (3) that a proper definition of the order parameter σ rests on the observability of sharp Pake doublets. From our remarks above it appears that σ can be defined in the following limiting situations: (i) for $X\approx1$ over the whole temperature range $T/T_\lambda\leq1$; (ii) for $X>X_c$ at $T\lesssim\frac{2}{3}T_\lambda$. Fortunately theoretical predictions have been made for these two cases.

For all other conditions, an interpretation of the experimental results in terms of $\sigma_{(J=1)}$ is not so clear. However, because of the striking temperature variation shown by the linewidths in Fig. 4, an order parameter might still be defined by

$$\sigma_{(J=1)}(X,\ T)=\sigma_{(J=1)}(X,\ T=0)\,\frac{W_{(J=1)}(X,\ T)}{W_{(J=1)}(X,\ T=0)}\ . \quad (8)$$

With this definition one sees that the temperature variation of σ is the same regardless of X, and this conclusion is different from the one reached if $\delta\nu$ is taken to be proportional to the frequency difference between the flattened peaks (see Fig. 3).

We have plotted in Fig. 5 the extrapolated normalized splitting for $X=1$ versus a reduced temperature scale. It should be noted that, within experimental uncertainty, the temperature variation of $\delta\nu_{(J=1)}(X=1)$ is the same as that of $W_{(J=1)}$ $(X=1)$. This indicates that, for the pure $J=1$ solid, there is little broadening of the individual doublet peaks as T_λ is approached, and hence the order parameter $\sigma_{(J=1)}$ is well defined. In Fig. 5 the normalized order parameter $\sigma_{(J=1)}(T)/\sigma_{(J=1)}$ $(T=0)$ is compared with the results from the molec-

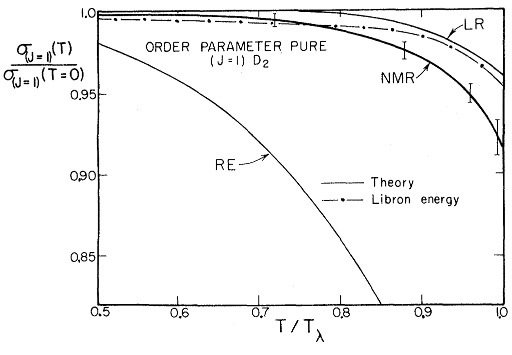

FIG. 5. Normalized splitting of order parameter $\delta\nu_{(J=1)}(T)/\delta\nu_{(J=1)}(T=0)=\sigma_{(J=1)}(T)/\sigma_{(J=1)}(T=0)$ as a function of T/T_λ for pure ($J=1$) solid D_2. Solid lines, NMR experiments described in this paper and theoretical predictions, Refs. 18 and 20; dash-dot curve, normalized libron energy of the E_g mode, Ref. 31. If the libron data are normalized to unity at $T/T_\lambda=0.7$ (which is permitted within their experimental error), they coincide with the Lee and Raich predictions.

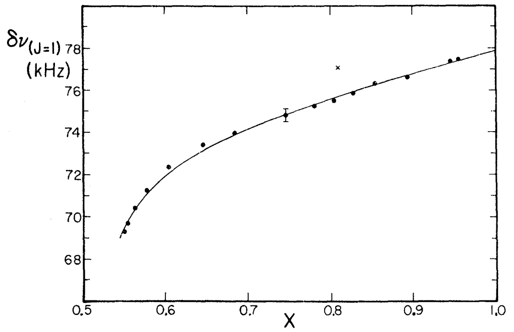

FIG. 6. Limiting Pake splitting $\delta\nu_{(J=1)}(X,\ T=0)$ in D_2, plotted as a function of X. Solid circles, experimental points; cross, Gaines *et al.*, Ref. 23; solid line, calculated curve from Eq. (7a) with $a=0.021$ and $\xi=0.985$.

ular-field calculations (labeled RE for Raich and Etters[20]) and the cluster-variation method (labeled LR, for Lee and Raich[18]). Agreement is best with the theory of Lee and Raich. Furthermore, we show a plot of the normalized libron energy[31] $E_t(\vec{k}=0, T)/E_t(\vec{k}=0, T=0)$ for the E_g mode (8.9 cm^{-1}) in D_2 with $X=0.97$. This last plot shows a temperature variation about half that for $\delta\nu_{(J=1)}(T)$. The comparison between the curves from NMR and Raman results leads to the conclusion that Eq. (1) is verified to within about 5%. The conclusion from Figs. 4 and 5 is that the orientational transition in D_2 is first order, at any rate for $X \gtrsim 0.8$. Hence Raman and NMR experiments appear to give clearer evidence as to the nature of the transition than do measurements[32,5] of C_p and $(\partial P/\partial T)_v$. These latter quantities show a smooth rise to a peak at T_λ, then a sharp drop at T_λ to a constant value. Except for this last feature, the behavior resembles that for a higher-order transition. The rise is to be attributed to the population of the librons and the peak can be understood as representing a somewhat broadened first-order transition, the end of which is clearly shown by the sharp drop in C_P and $(\partial P/\partial T)_v$. Arguments in a preliminary communication[9] favoring a higher-order transition at $X=0.74$ and 0.79 apparently do not apply to D_2 near $X=1$ and must be considered as probably incorrect.

In Fig. 6 the experimental results for the limiting splitting $\delta\nu_{(J=1)}$ for $T \ll T_\lambda$ are presented. A small adjustment has been made to the observed data to correct for line pulling by intermolecular dipolar interaction. This method of correction is similar to that made for the solid H_2 spectrum,[14] but the amount involved is smaller, being of the order of 0.5 kHz. The splittings were well determined at all mole fractions above $X=0.55$ although the individual peaks were found to broaden somewhat as X decreased, reflecting a random distribution throughout the sample of $(J=1)$ molecular configurations. With a limiting lowest temperature of 0.4 K in the present cryostat, it was difficult to reach the ordered phase for $X=0.55$ but an extrapolation of the results to zero splitting is not inconsistent with the critical molefraction $X_c=0.53$ obtained from $(\partial P/\partial T)_v$ measurements.[5] The splitting data for a given X after melting and recrystallizing the D_2 sample were quite reproducible. By contrast, variations up to 10 kHz were observed[14] between two different recrystallizations in solid H_2. For comparison, the result by Gaines *et al.*[23] for solid D_2 at $X=0.81$ is also shown in Fig. 6, where it has been similarly corrected for dipolar interaction.

The experimental data for D_2 were fitted to Eq. (7a) using a least-squares method with a and ξ as variable parameters. Values of $T_\lambda(X)$ were taken from Ramm *et al.*[5] whose measurements extend to X_c. Using all the data, we obtained $a=0.021$ and $\xi=0.985$. There are possible systematic errors in the points closest to the critical mole fraction which tend to make the splitting too small. Therefore, a second least-squares fit was made, in which the three lowest points were discarded. This fit gave $a=0.020$ and $\xi=0.983$. The difference between the two values of a and ξ are representative of the uncertainties in these parameters. As already reported,[10] a fit using Eq. (4) proved much less satisfactory.

We have advanced the same arguments that were given in the derivation of Eq. (7a) to modify Harris's relation for the order parameter in H_2 [Eq. (E16) in Ref. 24] and have used this new relation together with $a=0.02$ to fit our earlier results for H_2 in the range $0.70 \leq X \leq 0.87$. Although the variation in frequency over this mole-fraction range is only ~ 2.5 kHz and the scatter is somewhat larger than for D_2, the fit of the modified theory to the experiment is substantially better than that of the original relation.

C. Order Parameter for $(J=0)$ Molecules

The same remarks made above for the definition of $\sigma_{(J=1)}$ apply equally for $\sigma_{(J=0)}$. Here again the linewidth of the $(J=0)$ signal structure is useful in interpreting the degree of polarization of the $(J=0)$ molecules at intermediate molefractions and temperatures.

In Fig. 7 we present the splitting $\delta\nu_{(J=0)}(T\approx 0.4)$ vs X, where a correction has been applied to take into account the pulling together of the two peaks. This correction is of the order of 1 kHz and is quite important because the width of the $(J=0)$ structure is comparable with the splitting, and the relative magnitude of the correction increases as X decreases. Assuming a linear extrapolation to $X=1$, we obtain $\delta\nu_{(J=0)}(X=1)=9.0 \pm 0.7$ kHz which is in good agreement with the value 9.5 ± 0.6 kHz

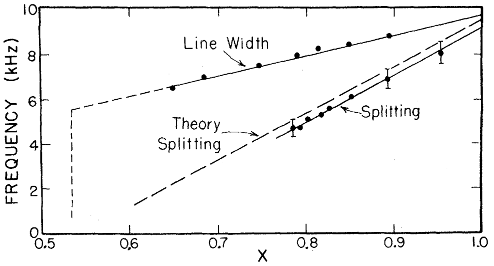

FIG. 7. Limiting Pake splitting $\delta\nu_{(J=0)}(X,\ T=0.4\ \mathrm{K})$ in D_2 (corrected for mutual attraction of the peaks) and corresponding linewidth $W_{(J=0)}$ of the central structure, plotted versus X. Solid circles, experimental points; lower dashed line, calculated from the theory of Harris, Ref. 8, using Eq. (7b). Upper dashed line conjectured extrapolated behavior of $W_{(J=0)}$.

predicted by Harris.[8] A plot of Eq. (7b) in Fig. 7 shows consistency with the experimental results within the uncertainties involved. Also in Fig. 7 we plot the linewidth of the structure from the ($J=0$) signal. This plot is useful in the concentration region $X \leqslant 0.79$ where the splitting can no longer be observed. As $X \to 1$, the linewidth is approximately given by the Pake-doublet splitting $\delta\nu_{(J=0)}$ plus the width from intermolecular broadening, which is of the order of 0.7 kHz. But as $X \to X_c$ in the ordered phase, the Pake-doublet splitting becomes much smaller than the linewidth. This effect is probably caused by a distribution of the doublet splittings throughout the crystal, depending on the configuration of nearest ($J=1$) neighbors, and is no doubt related to the broadening observed for the individual ($J=1$) Pake-doublet peaks with decreasing X.

Based on the observations mentioned before, it is very likely that the extrapolated order parameter $\sigma_{(J=0)}(X=1)$ for polarized ($J=0$) molecules is well defined over the whole temperature range in the ordered phase and that the temperature variation is closely the same as for $\sigma_{(J=1)}$.

V. ORDER PARAMETER OF ISOLATED PAIRS OF INTERACTING ($J=1$) NEIGHBORS IN hcp D_2

It was first shown by NMR techniques in hcp H_2 for $X \leqslant 0.1$ that nearest ($J=1$) neighbors forming isolated pairs in a background of ($J=0$) molecules undergo orientational ordering.[33] The energy levels for such ($J=1$) pairs coupled by electric quadrupole-quadrupole interaction were calculated by Nakamura.[7] Associated with this ordering is a satellite structure in the NMR spectrum where the frequency of the splittings increases with decreasing T until a limiting value is reached for $k_BT/\Gamma_{\mathrm{eff}}=0.7$. The observed spectrum consists of (a) an intense central line representing the ($J=1$) molecules having only ($J=0$) nearest neighbors, and (b) three peaks on each side of this central line, separated by about 8 kHz, which represent the pair spectrum. Other configurations, such as three nearest ($J=1$) neighbors, give a less distinct spectrum that forms a background to the lines just mentioned.

The centers of gravity of the three-line structures on each side of the central line are separated according to Eq. (2). For the ground state of a ($J=1$) pair, it is found[33] that $\langle J_Z^2\rangle = \frac{1}{2}$. Hence one obtains, neglecting zero-point motion,

$$\delta\nu_{\mathrm{pair}} = \tfrac{3}{4}d = \begin{cases} 43\ \text{kHz for } H_2 \\ 19\ \text{kHz for } D_2\ . \end{cases}$$

In H_2 the additional ~ 8-kHz splitting into a three-line structure is caused by intermolecular dipolar interaction.[33] In D_2 one also expects to see the pair ordering but, because the intermolecular dipolar interaction is much smaller, the three-line satellite structures are calculated to collapse into one line each, approximately 1 kHz wide. The Pake-doublet splitting is hence expected to be much larger than the 1-kHz linewidth of the central line, the shape of which is closely Gaussian. On the basis of the statistical probability of isolated pairs $P = 12X(1-X)^{18}$, and the respective values of the nuclear spins for ($J=1$) and ($J=0$) species, the integrated intensity ratio of each Pake-doublet peak to the central line for $X=0.05$ is calculated to be $\approx 1:400$. In spite of this low ratio, estimates based on the performances of the rf spectrometer with D_2 and with H_2 show that the D_2 Pake doublet should be observable. Furthermore, experiments[33] on the pair spectrum in H_2 with the same spectrometer lead us to believe that under the same conditions the doublet signal in D_2 should not be saturated by rf power.

We have made a careful scan of the NMR spectrum for $X=0.05$ at $T=0.6$ K, under optimum signal-to-noise conditions of the NMR detection system. As can be seen in Fig. 8 the signal derivative from the central line has fallen to the noise level at a distance of 4 kHz from the center. The doublet, however, is not observed at the expected frequency.

We suggest tentatively that a broadening mechanism in solid D_2 prevents detection of the Pake-doublet peaks at least for $T \geqslant 0.6$ K. Suppose for instance a crystalline field introduces a splitting ϵ of the two lowest rotational states (energy $= -4\Gamma$), where ϵ has a random distribution throughout the crystal with an average of the order of $\epsilon/k_B \approx 0.5$ K. It is then conceivable that the Pake-doublet peaks will be broadened for $k_BT \approx \epsilon$ and could only be observed for $k_BT \ll \epsilon$ when only the ground state is populated. However, such a large value of ϵ for D_2 cannot be explained in the light of the small value calculated[34] for solid H_2.

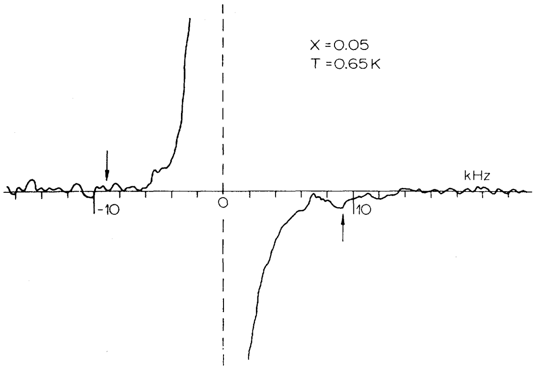

FIG. 8. Derivative of the absorption line for $X = 0.05$ at 0.6 K. Only a small portion of the intense central line with linewidth 0.8 kHz representing the signal from $(J=0)$ and $(J=1)$ molecules is shown. Arrows show the place where the Pake doublet for the pair spectrum should have been observed.

Nevertheless, in support of the hypothesis of the broadening mechanism, we mention other evidence that was observed in solid D_2 with low $(J=1)$ mole fractions.

(i) An anomaly in $(\partial P/\partial T)_v$ for $X < 0.03$ and $T \geqslant 0.9$ K, where a double maximum, unexpected for the pair-level configuration, was reported.[5] A splitting from a sufficiently large crystalline field could account for the double maximum.

(ii) For $X = 0.03$ and $T < 1$ K, there exist[35] anomalous contributions to C_p that are not explained by the properties of $(J=1)$ nearest-neighbor "pairs" and "triplets." Such anomalies are also evident in $(\partial P/\partial T)_v$ measurements when analyzed in a manner similar to that for C_p. It is not excluded, however, that they might be due to next-nearest-neighbor "pairs."

(iii) The value of Γ obtained from the Raman-pair spectrum,[36] $\Gamma\,\text{pair}/k_B = 0.98 \pm 0.03$ K, is substantially different from that[19] for pure $(J=1)$ D_2, where $\Gamma_{(X=1)}/k_B = 1.15 \pm 0.05$ K. In solid H_2, Γ_{pair} and $\Gamma_{(X=1)}$ are in closer agreement being, respectively, $\Gamma_{\text{pair}}/k_B = 0.79 \pm 0.03$ and $\Gamma_{(X=1)}/k_B = 0.84 \pm 0.04$ K.[19,33,36] Perhaps a substantial crystalline field that either varies with X or does not affect the more symmetrical cubic phase could account for the difference in solid D_2.

The linewidth of the Raman-pair-spectrum transition[36] $\delta E = 10\Gamma$ gives no clue, however, to a possible splitting of the ground state. The observed limiting low-temperature linewidth in D_2, 1.3 cm^{-1}, is mainly determined by the experimental resolution evidenced by the width of the scattered laser line, 1.0 cm^{-1}. However, in H_2, the transitions seems sharper. It is hoped that further experimental refinements in this very difficult field can be made to better determine the pair-spectrum linewidth.

VI. SUMMARY AND CONCLUSIONS

The principal results of this research can be summarized as follows.

(i) The investigation of the NMR line shape in the ordered state in solid D_2 gives direct information on the order parameter for both the $(J=1)$ and $(J=0)$ molecules, the latter being slightly polarized by ordering of the former. The order parameter, which is proportional to the doublet splitting in the absorption spectrum, is well defined in only two limiting situations: (a) for nearly pure $(J=1)$ solid at all temperatures in the ordered state, and (b) for mixtures at temperatures less than about $\frac{2}{3}$ of the transition temperature, where the doublet peaks are clearly resolved.

(ii) The orientation transition appears to be a first-order process, at least for $X \gtrsim 0.8$, judging from the sharpness of the structure disappearance. This is in agreement with theoretical expectations.[2,17,18] At lower X, where considerable washing out of the line structure is observed at T increases, conclusions on the nature of the transition are less certain, even though the transition temperature is well defined from other experiments.[5,11,32]

(iii) The order parameters $\sigma_{(J=1)}$ and $\sigma_{(J=0)}$ at $T \ll T_\lambda$ are in good agreement with Harris's theoretical predictions which we have modified using a reasonable assumption pertaining to the dependence of σ on X. The experimental value of the zero-point motion of the rotational angular momentum J_z is in agreement with predictions.

(iv) The temperature dependence of $\sigma_{(J=1)}$ for $X = 1$ is in rough agreement with predictions by Lee and Raich[18] based on a cluster-variation method describing the orientational transition. From the polarization model of $(J=0)$ molecules it is likely that $\sigma_{(J=0)}$ has the same temperature variation as $\sigma_{(J=1)}$ for X close to unity.

(v) In ordered D_2 at moderate X, observation of a sharp central NMR absorption line indicates the presence of a non-negligible fraction of orientationally disordered phases. The intensity of this signal which could arise from either disordered cubic or hcp D_2 becomes larger as X decreases and is a function of temperature.

(vi) The failure to observe the order parameter for oriented isolated $(J=1)$ pairs in the hcp phase suggests a line-broadening mechanism that makes the Pake doublet difficult to detect, at least at temperatures above 0.6 K. Such broadening may be the result of crystalline fields that cause additional splitting of the rotational energy states. Other anomalies in the thermodynamic properties might be explained by this splitting which is much larger than that calculated for H_2. Experiments at temperatures below, say, 0.1 K aimed at observing the Pake doublet in the ordered orientational state of the ($J = 1$) pairs could contribute to the elucidation of this question and are planned in this laboratory.

ACKNOWLEDGMENTS

The authors are indebted to Dr. A. B. Harris and Dr. S. Myers for a number of stimulating discussions. The first draft of the manuscript was written at the Department of Engineering Science, Osaka University. One of the authors (H. M.) acknowledges a travelling fellowship from the Japanese Society for Promotion of Science that made this visit possible and expresses his gratitude for the hospitality shown and for many stimulating discussions with Professor T. Nakamura and his co-workers. The authors also wish to thank Professor J. P. McTague for communicating his Raman data and for informative discussions on the observation of the pair spectra.

[†] Supported in part by a grant from the Army Research Office (Durham) and a contract with the Office of Naval Research. The work at Los Alamos was done under the auspices of the U. S. Atomic Energy Commission.

[*] Present address: Instituto di Fisica, Universita di Roma, Rome, Italy.

[1] A. B. Harris, J. Appl. Phys. 42, 1574 (1971).

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

[3] J. Felsteiner, Phys. Rev. Letters 15, 1025 (1965).

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

[5] D. Ramm, H. Meyer, and R. L. Mills, Phys. Rev. B 1, 2763 (1970), and references therein.

[6] F. Reif and E. M. Purcell, Phys. Rev. 91, 631 (1953).

[7] T. Nakamura, Progr. Theoret. Phys. (Kyoto) 14, 135 (1955); Suppl. 46, 343 (1970).

[8] A. B. Harris, Phys. Rev. B 2, 3495 (1970).

[9] B. Maraviglia, F. Weinhaus, H. Meyer, and R. L. Mills, Solid State Commun. 8, 815 (1970).

[10] B. Maraviglia, F. Weinhaus, H. Meyer, and R. L. Mills, Solid State Commun. 8, 1683 (1970).

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

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

[13] R. L. Mills, A. F. Schuch, and J. L. Yarnell (unpublished).

[14] L. I. Amstutz, H. Meyer, S. M. Myers, and D. C. Rorer, Phys. Rev. 181, 589 (1969).

[15] O. Bostanjoglo and R. Kleinschmidt, J. Chem. Phys. 46, 2004 (1967).

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

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

[18] R. J. Lee and J. C. Raich, Phys. Rev. Letters 27, 1137 (1971). The order parameter $\overline{n}$ defined in this article by $\overline{n} = \frac{1}{2}(1 + \frac{1}{3}\langle 0 \rangle)$ is incorrect and should be $\overline{n} = \frac{1}{3}(1 + \frac{1}{2}\langle 0 \rangle)$ [J. Raich (private communication)]. This parameter $\overline{n}$ is related to $\sigma_{(J=1)}$ by the equation $\sigma_{(J=1)} = \frac{4}{5}[1 - 3\overline{n}]$.

[19] C. F. Coll and A. B. Harris, Phys. Rev. B 4, 2781 (1971). This paper describes the analysis of Raman scattering data by W. N. Hardy, I. S. Silvera, and J. P. McTague, Phys. Rev. Letters 26, 127 (1971). The value for Γ calculated by Coll and Harris was based on an incorrect extrapolation of the Raman data to $X = 1$, and we find that a reanalysis gives $\Gamma/k_B = 1.15 \pm 0.06$ K for D_2 and $\Gamma/k_B = 0.84 \pm 0.04$ K for H_2, which we quote throughout the paper. A new analysis of $(\partial P/\partial T)_v$ data (Ref. 5) using the anharmonic one-libron spectrum in D_2 by A. J. Berlinsky and C. F. Coll [Phys. Rev. B 5, 1587 (1972)] gives $\Gamma/k_B = 1.15 \pm 0.05$ K.

[20] J. C. Raich and R. D. Etters, Phys. Rev. 155, 457 (1967); 161, 493 (1967).

[21] J. R. Cullen, D. Mukamel, S. Shtrikman, L. C. Levitt, and E. Callen, Solid State Commun. (to be published).

[22] N. F. Ramsey, *Molecular Beams* (Oxford U.P., London, 1956).

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

[24] A. B. Harris, Phys. Rev. B 1, 1881 (1970).

[25] J. C. Raich and R. D. Etters, Phys. Rev. 168, 425 (1968); and private communication regarding some numerical corrections.

[26] H. Miyagi and T. Nakamura, Progr. Theoret. Phys. (Kyoto) 44, 833 (1970).

[27] B. P. Stoicheff, Can. J. Phys. 35, 730 (1957).

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

[29] S. Homma, Progr. Theoret. Phys. (Kyoto) 40, 1 (1968).

[30] F. Weinhaus, S. M. Myers, B. Maraviglia, and H. Meyer, Phys. Rev. B 3, 3730 (1971).

[31] The temperature dependence of the libron energies [W. N. Hardy, I. S. Silvera, and J. P. McTague (unpublished)] was communicated to the authors by Dr. J. P. McTague.

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

[33] A. B. Harris, L. I. Armstutz, H. Meyer, and S. M. Myers, Phys. Rev. 175, 603 (1968).

[34] J. Noolandi, Can. J. Phys. 48, 2032 (1970), and references therein.

[35] J. Roberts and J. G. Daunt, J. Low Temp. Phys. 6, 97 (1971).

[36] I. Silvera, W. Hardy, and J. McTague, Phys. Rev. 4, 2724 (1971).