conduction band. Each time this happens, as the temperature is raised for example, a magnetic ion is formed in the lattice. At higher temperature the extra entropy associated with the magnetic ion degeneracy favors its formation and the Sm becomes predominantly trivalent. While such a model is conceptually quite clear, its quantitative application to magnetic behavior is complicated by the uncertainty of the crystal-field splittings of the low-lying levels of the trivalent Sm ion. It may be surprising that the two configurations are so close in energy but actually we were more surprised that it was possible to form polycrystalline SmB_6 so well by simply reacting the elements that its intrinsic properties were not masked.

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OBSERVATION OF LIBRATIONAL WAVES IN THE ORDERED STATE OF SOLID HYDROGEN AND DEUTERIUM BY RAMAN SCATTERING

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The Raman spectra of high purity o-H_2 and p-D_2 at liquid-helium temperatures have been obtained. Features which appear below the ordering temperature are attributed to librational waves within the $J=1$ manifold of states. On the basis of a comparison with recent theories of the ordered state, a new structure is proposed.

We have observed[1] by laser Raman scattering the theoretically predicted[2-5] librational excitations of the ordered state of solid orthohydrogen and paradeuterium. The observations agree only qualitatively with existing theories and two possible explanations for the discrepancies are proposed. The first implies that the rigid-lattice, nearest-neighbor quadrupole-interaction model is inadequate in the present case. The second alternative explanation requires a crystal structure with symmetry lower than the previously assumed[2-5] $Pa3$ space group.

The ordered state of hydrogen is one in which the molecular axes assume preferential orientations with respect to the crystalline axes, analogous to the ordering of spins in an antiferromagnet. Because the anisotropic interactions are small compared with the separation of the J levels and because the temperature is low, only the $J=1$ manifold need be considered in solid o-H_2 and p-D_2 and therefore it is the axes of the $J=1$ molecular rotational wave functions that are ordered.

X-ray and neutron data[6] have shown that the molecular centers form an fcc lattice. Theories[7] based on such a rigid fcc lattice and electric quadrupole-quadrupole intermolecular coupling predict the structure of the ground state to be $Pa3$; the neutron-diffraction data are also consistent with this space group. In this structure the axes of the dumbbell-shaped $m_J=0$ wave functions are aligned along the four fcc body diagonals. The crystal is divided into four sublattices with the oriented molecules on a given sublattice being parallel. In the molecular-field approximation the $m_J=\pm1$ states of H_2 are degenerate and lie about 13 cm^{-1} above the ground state. In a more realistic description the low-lying excitations from the ground state are nonlocalized excitations of the $m_J=\pm1$ states (librational waves) and have been treated theoretically in a manner similar to spin waves in magnetism.

Recent theories[2-5] that have appeared are all based on the same physical model and differ only in the mathematical treatment. Except for the work of Homma, Okada, and Matsuda[2] the results of the linear spin-wave treatments are in mutual agreement, as are the more accurate nonlinear spin-wave treatments.[8] Both predict an energy gap for H_2 of about 8 cm^{-1} and a bandwidth for the excitations of about 11 cm^{-1}. At $k=0$ there are three distinct modes, all of which are Raman active, and their energies and symmetries are given in Table I. Using standard polarizability theory[9] we have calculated the relative intensities of the modes from the linear theory of Mertens, Biem, and Hahn.[5] The results are presented for a randomly oriented polycrystalline sample. The intensities were also calculated for a sample in which the [111] directions of the crystallites were oriented along the incident light beam, with results that do not differ significantly from the previous ones. The latter configuration was considered because of evidence[10] that the c axis of the hexagonal phase tends to orient along the direction of crystal growth. If the hcp-to-fcc transition takes place by the shifting of hexagonal planes[11] this results in a preferential ordering of the cubic body diagonals along the original c-axis direction.

High-purity samples (~98 %) of o-H_2 and p-D_2 were obtained using the method of Depatie and Mills.[12] They were solidified by slowly lowering the Raman cell into a Dewar containing a small amount of liquid helium. High-intensity ultrasonics[13] were applied during the growth in order to minimize cracking when the temperature was further lowered. The best samples were nearly free of cracks. Raman spectra were obtained using a Spectra-Physics model 125 He-Ne laser operating at 6328 Å with a power of 80 mW, and a Spex model 1400 double monochromator with an S-20 photomultiplier and current detection. Right-angle scattering was observed with the polarization of the incident light either parallel or perpendicular to the direction of observation. Above the transition temperatures (~2.8°K for H_2 and 3.8°K for D_2) there were no sharp features for small frequency shifts; however, single broad lines centered at 588 cm^{-1} for H_2 and 298 cm^{-1} for D_2 were observed. These correspond to the $J=1\rightarrow3$ transition reported by Bhatnagar, Allin, and Welsh[10] in normal hydrogen. Below the transition temperature, sharp features appear at low frequency shifts and the recorded spectra for $T\approx1.6$°K are shown in Figs. 1 and 2;

Table I. Comparison of theory and experiment for $k=0$ librational modes in solid o-H_2 and p-D_2. The mode degeneracies are given in parentheses. In the column labeled "Adjusted nonlinear," we have used the effective quadrupole coupling constant described in the text.

	Mode symmetry	Theoretical intensity (relative) $Pa3$	Theoretical $k=0$ frequencies[a] (cm^{-1})			Experiment		Proposed assignment C_{3i}^2
			Linear	Nonlinear	Adjusted nonlinear	Frequency (cm^{-1})	Intensity	
H_2	$E_g(2)$	1.00	8.40	7.09	6.05	6.1 ± 0.5	1.00	$E_g(2)$
	$T_g(3)$	0.413	10.2	9.75	8.33	7.1 ± 0.5	0.18	$E_g(2)$
						10.8 ± 0.5	0.05	$A_g(1)$
	$T_g(3)$	0.088	18.8	17.9	15.2	14.8 ± 1	0.13	$A_g(1)+E_g(2)$
D_2	$E_g(2)$	1.00	10.3	8.72	8.36	8.3 ± 0.5	1.00	$E_g(2)$
	$T_g(3)$	0.413	12.5	12.0	11.5	10.3 ± 0.5	0.34	$E_g(2)$
						14.4 ± 0.5	0.12	$A_g(1)$
	$T_g(3)$	0.088	23.1	22.0	21.1	21.1 ± 1	~0.2	$A_g(1)+E_g(2)$

[a] These frequencies are calculated for $Q/e=0.1348\times10^{-16}$ cm^2 for H_2 and 0.1327×10^{-16} cm^2 for D_2. The lattice parameter was taken to be 5.312 and 5.081 Å for fcc o-H_2 and p-H_2, respectively.

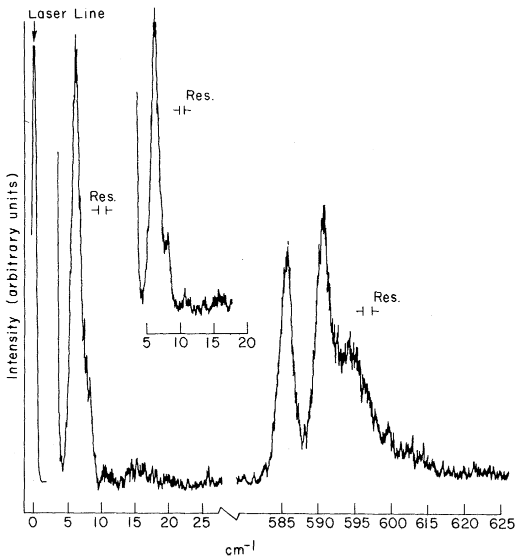

FIG. 1. Raman spectrum of solid o-H_2 at 1.6°K (ortho purity ≈ 98%). The sharp rise in intensity below 5 cm^{-1} is due to the intense Rayleigh line whose center is recorded at a greatly reduced gain. The absolute scale for high frequency shifts is accurate to ~1 cm^{-1}.

the frequencies and approximate integrated intensities are listed in Table I. Within experimental error, these lines were completely depolarized. We identify them with the librational waves. The broad $J=1\rightarrow 3$ lines are observed to sharpen into at least three distinguishable peaks. These transitions correspond to the nonlocalized rotational excitons studied in great detail by Van Kranendonk and co-workers[14] for the $J=0\rightarrow 2$ transition in solid p-H_2. In the high temperature phase of o-H_2 the $J=1$ manifold forms a broad band[15] giving a large width to the $J=1\rightarrow 3$ transition. At low temperatures in the ordering phase the ground state is nondegenerate and sharp, and the splitting of the exciton state becomes observable as in p-H_2. The exciton splitting can be obtained in a manner analogous to that for p-H_2, and such a calculation is in progress elsewhere.[16]

An inspection of Table I shows that the observed spectra for the librational waves cannot be completely explained by existing theories based on the $Pa3$ structure. We consider two possible approaches for reconciling the experimental results with theory, allowing the Q-Q coupling constant to be an adjustable parameter.[17] The first is to assume that $Pa3$ is indeed the proper space group for the crystal. In this case one of the lines must be attributed to something other than a $k=0$ librational mode since symmetry does not allow more than three of these modes. An extra line could possibly arise from a two-libron excitation. The only lines that can be suppressed in order to give reasonable agreement for the relative frequencies are the 10.8-cm^{-1} line for H_2 and the 14.4-cm^{-1} line for D_2. The intensities for the remaining lines then agree poorly with the calculated ones. Suppressing the highest frequency lines for H_2 and D_2 gives approximate agreement for the intensities, but then the frequencies are in serious disagreement.

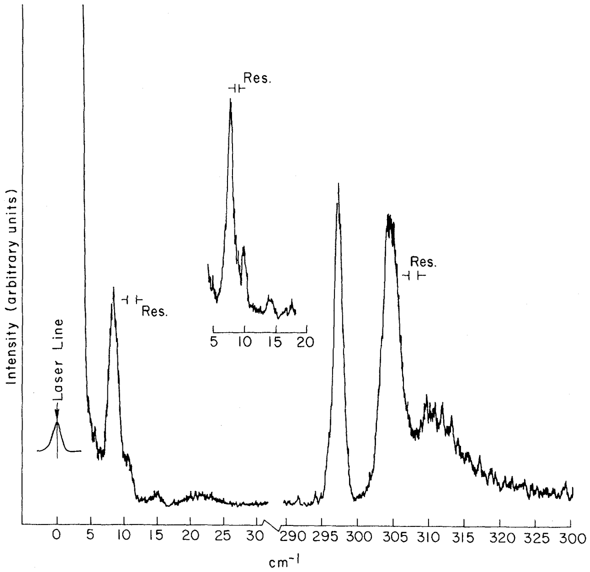

FIG. 2. Raman spectrum of solid p-D_2 at 1.6°K (para purity ≈ 98%). The absolute scale for high frequency shifts is accurate to ~1 cm^{-1}.

The second approach is to assume a structure having symmetry lower than $Pa3$. Such an assumption is not inconsistent with the neutron-diffraction data which have low signal-to-noise ratio and which were taken at small angles. In addition, the theoretical treatments predicting the $Pa3$ structure neglect dynamical effects and all intermolecular interactions other than electric quadrupole-quadrupole. We have therefore looked for the simplest distortion of the $Pa3$ structure that could explain the experimental data. The absence of librational excitations in far-infrared spectra,[18] the absence of optical phonon lines in the present Raman study, and other evidence[19] suggest that the molecular sites have inversion symmetry. The space group C_{3i}^2 satisfies the requirements.[20]

For this structure, the degeneracy of the T_g modes of the $Pa3$ structure is partially lifted, being split into a twofold E_g and a nondegenerate A_g mode, both of which are Raman active. The approximate ratio of the intensities is 2:1, and thus we can identify the second and third highest frequency lines with the E_g and A_g modes, respectively. The absence of an observable splitting of the highest frequency line for both H_2 and D_2 is perhaps due to the linewidth being greater than the expected splitting of the upper T_g mode. We note that the much greater width of the upper line is consistent with the observation that, because of energy conservation, only the highest modes can decay via conversion into two excitations within the band.

Assigning a single frequency to the center of gravity of the second and third lines (8.3 cm^{-1} for H_2 and 11.7 cm^{-1} for D_2), we get a remarkably good frequency fit to the nonlinear libron theory[3,4] with the following values[21] of the effective nearest-neighbor quadrupole coupling constant $(\Gamma_{\text{eff}}/\Gamma_0)_{H_2}=0.85$ and $(\Gamma_{\text{eff}}/\Gamma_0)_{D_2}=0.96$. Here $\Gamma_0=6e^2Q^2/25R^5$ is 0.68^{-1} for H_2 and 0.84 cm^{-1} for D_2. The experimental intensity of the upper line, which has a large uncertainty, is in poor agreement with theory for the undistorted structure.

A further point of appeal for the proposed $C_{3i}{}^2$ structure is in the interpretation of the earlier reported[18] far-infrared data in which the number of observed optical-phonon absorption lines could not be explained. In the $C_{3i}{}^2$ space group, the phonon modes of symmetry E_u and A_u which were inactive in the $Pa3$ structure become active. The two T_u modes split into E_u+A_u, but this splitting might be small for a $C_{3i}{}^2$ space group on a fcc lattice, since the quadrupolar interactions have very little effect on the phonon frequencies in H_2 and D_2.

A new structure has been proposed for the ordered state of H_2 and D_2 based mainly on a frequency fit of the present data. Work is in progress to improve the quality of the experimental observations, and to ascertain whether the distortion required to fit the frequencies is compatible with intensity ratios.

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