that characteristic behavior similar to that found here will also occur in a variety of other problems in plasma physics.[8]

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Raman Spectrum of Solid Orthodeuterium to 150 kbar at 5 K

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We have studied samples of 98.5% o-D_2 in a diamond anvil cell to pressures of 150 kbar at 5 K by means of Raman scattering. At 50–60 kbar the E_{2g} phonon and roton cross and hybridize. The coupling has been determined. The phase transition from the symmetric ground state at low pressure to an orientationally ordered ground state, predicted to occur between 31 and 73 kbar, does not take place. A predicted hcp-fcc structural phase transition is not observed.

In this Letter we present our results for the first low-temperature, ultrahigh-pressure measurements on one of the hydrogen isotopes, namely deuterium. Sharma, Mao, and Bell[1] have recently pressurized H_2 to 630 kbar (63 GPa); however, their work was at room temperature on normal hydrogen. Here we demonstrate the importance of low-temperature studies on a pure ortho-para species for obtaining detailed information of the properties of the solid molecular hydrogens (H_2,D_2, etc.). Our measurements provide new and unexpected results for the interactions, the excitation spectrum, and the structure of solid molecular deuterium.

At zero pressure the molecules in solid parahydrogen (p-H_2) and orthodeuterium (o-D_2) are in the spherically symmetric $J=0$ rotational state and the lattice is hcp (space group $I_{6h}{}^4$). The low-lying lattice excitations are phonons and $J=2$ rotons.[2] As the density is increased, anisotropic interactions lead to mixing of the higher rotational states into the ground state.[3] At a sufficiently high density the mixing of $J=2$ into the $J=0$ single-molecule states becomes so severe that the symmetry of the molecules will be broken and the ground state will be orientationally ordered.[4,5] In the broken-symmetry phase the excitations will be librons[6,7] and phonons with a characteristic spectrum. This phase has been predicted to occur at pressures of 31 (Ref. 5) and 73 (Ref. 4) kbar for o-D_2 and 86 (Ref. 5) and 270 (Ref. 4) kbar for p-H_2.[8] The differences in the predictions of the two theories evidently arise from the use of different anisotropic-potential parameters. From our Raman spectra we see no indication of the broken-symmetry phase transition up to 150 kbar. Since theories[7] which go beyond the mean-field theories of Refs. 4 and 5 do not predict substantially different critical densities for the same potentials, we interpret this to mean that the anisotropic interactions have a weaker radial dependence than had been thought

to be the case.

At pressures of 50–60 kbar a severe change occurs in the spectrum as seen in Fig. 1. We interpret this as a crossing and hybridization of E_{2g} roton and phonon modes. Except for this region the samples could always be prepared with the characteristic three roton lines and the single phonon line of the D_{6h}^4 space group (the spurious fourth roton branch in Fig. 1 is stress induced). Thus we conclude that at low temperatures up to 150 kbar the structure is hcp. Spectra at higher temperatures are very broad and more difficult to interpret. Our results provide strong evidence to settle recent controversies and speculations concerning structural hcp-fcc phase transitions in the hydrogens (H_2 and D_2).

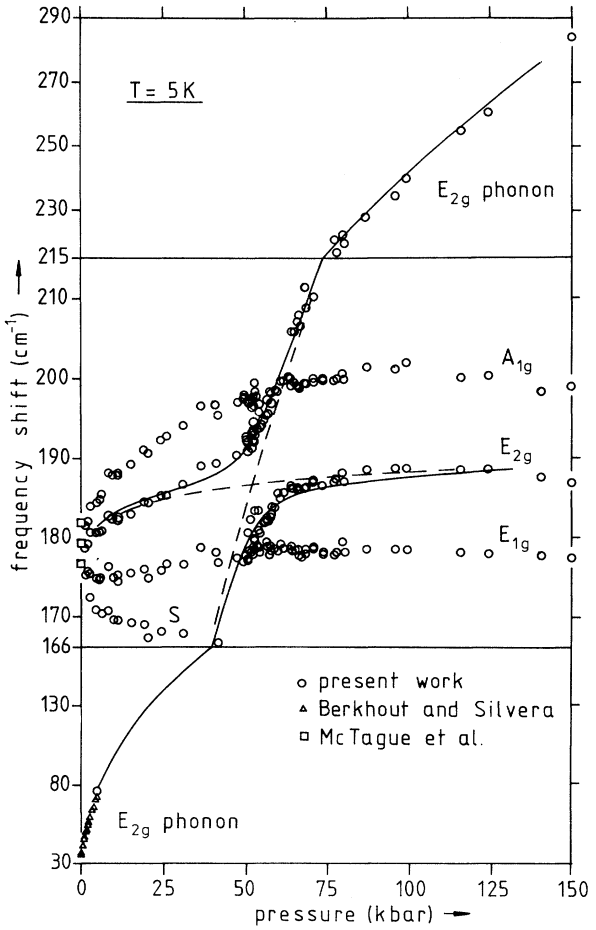

FIG. 1. Pressure dependence of lattice excitations in 98.5% o-D_2. The dashed lines represent a fit to the E_{2g} roton and phonon modes without interaction. The solid line is a fit to Eq. (2) with $c_0^{E_{2g}} = 6$ cm^{-1}. The accuracy in the frequency determination of the modes is ± 1 cm^{-1}. Note the scale changes on the vertical axis.

Some years ago Cook *et al.*[9] observed an anomaly in isobars of solid H_2 near the melting line. This led Roder[10] to speculate that a phase transition had taken place. Manzelli, Udovidchenko, and Esel'son[11] studied the premelting region and observed an anomaly in the compressibility and claimed in this and later work that an hcp-fcc phase transition had taken place. Mills[12] speculated on the (p-T) phase diagram suggesting that the hcp-fcc phase line would intersect the pressure axis at $p \sim 1$ kbar. Theoretically Brodyanskii, Freimand, and Krupskii[13] had predicted such a phase transition; Holian[14] predicted, in analogy with his work on helium, that for D_2 the hcp-fcc phase line intersects the p axis at about 9 kbar. Experimentally, Silvera, Driessen, and de Waal[15] could not reproduce any of the thermodynamic anomalies and suggested that earlier measurements may have suffered experimental difficulties or were nonequilibrium phenomena and that all of the speculations in the literature were premature. Vindryaevskyi *et al.*[16] have recently used elastic-neutron-scattering techniques to show that up to 5 kbar p-H_2 only exists in the hcp structure. Our results show that at low temperature up to pressures of 150 kbar solid o-D_2 has the hcp structure.

Finally we address ourselves to the low-temperature hcp-fcc phase transition of Durana and McTague.[17] This transition was proposed to interpret the $J = 2$ roton spectrum which developed an extra line for $p \gtrsim 1$ kbar. Although subsequently it has been believed to be a strain effect, this has never been definitively established. We have been able to obtain spectra with this extra line (the low-frequency, low-pressure roton branch labeled S in Fig. 1). By annealing of such a sample at high temperatures the extra line disappears and a three-line roton spectrum is obtained as in Fig. 2. We believe this to be the true equilibrium state characteristic of an unstrained crystal. We note that above $p \simeq 10$ kbar, the frequencies of the hcp rotons were almost unchanged when the fourth line was present. The remainder of this Letter will be devoted to a description of our experimental technique and the roton-phonon crossing.

Gas samples of 98.5% o-D_2 were made by catalyitc conversion on Apaché nickel silica at $T \simeq 19$ K. This concentration was determined from the intensity ratios of the $J = 0 \rightarrow 2$ and $J = 1 \rightarrow 3$ transitions.[6] High pressures were achieved with a diamond anvil cell (DAC). The DAC is mounted in a helium cryostat with optical windows and can

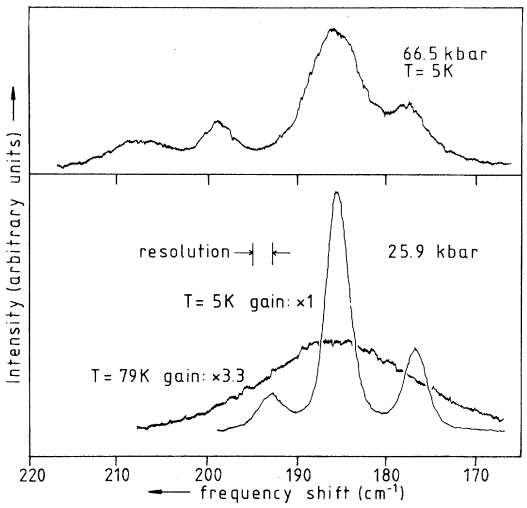

FIG. 2. Typical Raman spectra for a laser power of 300 mW. The importance of low temperature is demonstrated by the two spectra at 25.9 kbar.

be cooled by exchange gas or by direct immersion in liquid helium. Most measurements were made at $T \simeq 5$ K. The sample chamber was a cylindrical hole in an Inconel X750 gasket; the initial diameter was ~100 μm and thickness ~150 μm. The sample was compressed in this chamber between two diamonds, along with a small ruby crystal which serves for pressure measurement.[18] Pressure could be varied with a resolution of ~100 bars with a similar measuring accuracy. Maximum pressures were determined by the sudden disappearance of the gasket hole while increasing the pressure. The pressure was reasonably hydrostatic in nature as determined by the ruby linewidth. Raman spectra were obtained using a backscattering geometry. Excitation was from the 5145-Å line of an argon-ion laser operated at about 300 MW. Spectra were measured with a Spex 1402 double monochromator. At low temperatures typical peak counting rates were 6×10^3 Hz with a resolution of ~2.5 cm^{-1}. About 120 spectra with frequency shifts up to 400 cm^{-1} were measured at about 100 pressures and several temperatures in three samples. Typical spectra are shown in Fig. 2; a summary of our observations is shown in Fig. 1.

To understand the excitation spectrum we begin with the Hamiltonian (suppressing internal vibration coordinates)

$$\overline{H} = \left[\sum_i \frac{P_i^2}{2M} + \tfrac{1}{2}\sum_{i,j} V_I(i,j)\right] + \left[\sum_i B\vec{J}_i^2 + \tfrac{1}{2}\sum_{i,j} V_A(i,j)\right], \tag{1}$$

where the first and third terms are the molecular translational and rotational kinetic energy, respectively, and the second and fourth terms the isotropic and anisotropic parts of the intermolecular interactions, with

$$V_A(1,2) = \left(\frac{16\pi}{5}\right)^{1/2} B(R_{12})[Y_2^0(\omega_1) + Y_2^0(\omega_2)] + 4\pi \sum_{j=0,2,4} \epsilon_j(R_{12})\alpha_j \sum_\mu C(22j;\mu-\mu) Y_2^{-\mu}(\omega_2). \tag{2}$$

Here $C(22j;\mu-\mu)$ is a Clebsch-Gordan coefficient, $B(R)$ and $\epsilon(R)$ are radial dependences, and α_j are numerical coefficients which can be found in Ref. 6.

The Hamiltonian for the roton-phonon problem can be written in the occupation number representation as $H_{\text{phonon}} + H_{\text{roton}} + H_{rp}$, where H_{rp} is the roton-phonon coupling. From the first part of Eq. (1), one finds

$$H_p = \sum_{\vec{k},\lambda} \hbar\omega_{p\vec{k}}{}^{\lambda}(a_{\vec{k}}{}^{\lambda\dagger} a_{\vec{k}}{}^{\lambda} + \tfrac{1}{2}) \tag{3}$$

which represents the phonons with construction operators $a_{\vec{k}}{}^{\lambda}$ of branch λ, energy $\hbar\omega_{p\vec{k}}{}^{\lambda}$, and wave vector $\vec{k}$. In the hcp structure at $\vec{k}=0$ the optical phonons can be labeled by their irreducible representation E_{2g} for the Raman-active transverse optical (TO) mode and B_{2g} for the longitudinal optical (LO) mode. From the second part of Eq. (1), the roton Hamiltonian can be written[7] as

$$H_r = \sum_{\vec{k},\lambda} \hbar\omega_{r\vec{k}}{}^{\lambda} b_{\vec{k}}{}^{\lambda\dagger} b_{\vec{k}}{}^{\lambda}. \tag{4}$$

At $\vec{k}=0$ there are ten $J=2$ roton modes with a mean energy of ~$6B$ and split by V_A (Ref. 2). Five of these are Raman active and are usually labeled by the projection quantum number $m=0$, ±1, and ±2 (the energy is degenerate in $\pm m$, so that only three distinct lines are observed[19]); we shall label the modes by their corresponding irreducible representation A_{1g}, E_{1g}, and E_{2g}. A linear coupling term of the form

$$H_{rp} = \sum_{\vec{k},\lambda} c_{\vec{k}}{}^{\lambda}(a_{\vec{k}}{}^{\lambda\dagger} b_{\vec{k}}{}^{\lambda} + a_{\vec{k}}{}^{\lambda} b_{\vec{k}}{}^{\lambda\dagger}) \tag{5}$$

can be found by expanding V_A [Eq. (2)] in a Taylor

series about the lattice displacement $\vec{R}_{12}$. At zero pressure the electric quadrupole-quadrupole (EQQ) interaction, corresponding to $j=4$ in V_A, is dominant and mainly responsible for the roton splittings. However, in the Taylor expansion this term is less important as it yields a roton-phonon coupling which is nonlinear in the $b_k{}^\lambda$'s [from perturbation theory one can then derive an effective linear coupling, with $c_k{}^\lambda \sim \Gamma^2/B$, where Γ ($\ll B$) is the EQQ coupling parameter]. The first term in Eq. (2) is smaller than the EQQ term; however, it grows rapidly with pressure and gives rise directly to a linear coupling as in Eq. (5). In this Letter we shall not evaluate $c_k{}^\lambda$ theoretically, but rather provide an experimental value.

At $\vec{k}=0$ the only modes which will interact are those of the same symmetry, the E_{2g} phonon and roton, as is also seen experimentally. The coupled Hamiltonian can be diagonalized by means of Bogoliubov transformation to yield energies for the E_{2g} modes at $\vec{k}=0$ with the density dependence of the uncoupled frequencies as variable. We find

$$\frac{E}{\hbar}=\frac{\omega_{r0}{}^{E_{2g}}+\omega_{p0}{}^{E_{2g}}}{2} \pm \tfrac{1}{2}[(\omega_{r0}{}^{E_{2g}}-\omega_{p0}{}^{E_{2g}})^2+(2c_0{}^{E_{2g}})^2]^{1/2}. \quad (6)$$

We determine $c_0{}^{E_{2g}}$ as follows. An expression for the E_{2g} phonon was fitted to the low-[20] and high-pressure data without use of points in the crossing region to provide $\omega_{p0}{}^{E_{2g}}$ versus pressure. This is represented by a broken line in Fig. 1. Similarly, an expression for $\omega_{r0}{}^{E_{2g}}$ versus pressure was fitted to the E_{2g} roton mode. $c_0{}^{E_{2g}}$ was taken to be density independent and varied in Eq. (6) to provide the best fit to experiment, yielding $c_0{}^{E_{2g}}=6.0\pm1.0$ cm^{-1} at the crossing. The corresponding solutions to Eq. (6) are plotted as the solid lines in Fig. 1.

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