Remarkable High Pressure Phase Line of Orientational Order in Solid Hydrogen Deuteride

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We have studied solid HD to pressures in excess of 100 GPa and to liquid helium temperatures. We have found the broken symmetry quantum phase transition of orientational order by means of Raman scattering. The pressure-temperature phase line has a very unusual reentrant behavior, different from the homonuclear isotopes when measured on the same time scale. The phase line is explained in terms of the rapid thermalization of rotational levels with changing temperature.

An understanding of the solid molecular hydrogens, H_2, D_2, and HD, at very high pressures requires a deep comprehension of orientational order (OO) in these substances. For example, orientational order and the insulator-metal (IM) transition are closely related [1]. A candidate phase for molecular metallic hydrogen is the new H-A phase at a pressure of 150 GPa investigated by Lorenzana, Silvera, and Goettel [2]. A transition at 150 GPa was first detected by Hemley and Mao [3] who misidentified it as an extension of the phase line for OO studied at low pressure, which we shall call quadrupolar ordering (QO). This misidentification was partially based on their extrapolation of the phase line for QO from 0.5 GPa where it is known, to 150 GPa. From our studies presented here on HD, bounds can be set on the phase line for QO for all of the isotopes of hydrogen at high density; this should prove very useful in identifying or excluding certain interpretations of high pressure phase transitions. At low pressure, OO in the hydrogens is fairly well understood, in particular for the pure ortho or para species. However, at higher pressures little is known about the OO, especially as a function of ortho-para (o-p) concentration, although OO phase transitions have been observed in pure para-H_2 and ortho-D_2. In our study of OO in HD we find a very unusual and unexpected phase line with reentrant behavior between phases of order and disorder. We explain the origin of this behavior and show how this phase line can be used to understand OO in high pressure H_2 and D_2. Our interpretation also leads to direct evidence that the electric quadrupole-quadrupole (EQQ) interaction is no longer the dominant anisotropic interaction at high pressures.

Before describing our experiment we briefly review the orientational behavior in the solid hydrogens [4]. At low pressure the free rotor quantum numbers J and M are good quantum numbers. The corresponding wave functions, the spherical harmonics, Y_{JM}, describe the single-molecule orientational distributions. Because of the identical particle nature of their nuclei and symmetry requirements of their wave functions, hydrogen and deuterium have two species, ortho and para, which interconvert very slowly in the solid (characteristic times of order hours to days). p-H_2 and o-D_2 correspond to even-J states, while o-H_2 and p-D_2 correspond to odd-J states. Metastable samples of almost pure ortho or para species can be prepared; at low temperatures only the $J=0$ or 1 states are occupied due to the splitting of several hundred K between rotational energy states. Since the $J=0$ state has a spherically symmetric spatial distribution there is no OO in p-H_2 or o-D_2 at low pressure and the lattice remains hcp to $T=0$ K, with essentially spherical distributions at the lattice sites. However, the $J=1$ state has a permanent electric quadrupole (EQ) moment and due to EQQ interactions, o-H_2 and p-D_2 orientationally order in the $Pa3$ structure, with a transition from an hcp to an fcc lattice for the molecular centers. A mixed o-p lattice of hydrogen has a critical percolation concentration ($C_{crit}=0.56$) of $J=1$ molecules for OO on the $Pa3$ lattice. Below the percolation concentration the lattice does not display long-range orientational order. This is understood from a picture in which ortho molecules bear EQ moments and the interactions are reduced when the solid is diluted with the spherical para molecules.

With increasing pressure the anisotropic interactions grow and eventually higher rotational levels are so strongly mixed into the ground state, even o-D_2 and p-H_2 have a transition to OO. This is called the broken symmetry phase (BSP) transition [5-8] which occurs at a critical pressure in the limit $T \rightarrow 0$ K, P_{co}, of 28 GPa in o-D_2 [9] and 110 GPa in p-H_2 [10]. In deuterium the critical temperature T_c for the BSP rises rapidly from 0 K with increasing pressure; the pressure dependence of T_c has not been studied in hydrogen. One more very interesting observation was made by Silvera and Jochemsen [11] on hydrogen under pressure. They found that C_{crit} decreased with increasing pressure, at very modest pressures. Clearly, this must be the case, since for the very high pressure BSP transition, $C_{crit}=0$. This also means that para molecules must participate in the anisotropic interactions, even at low density, and weakening of the EQQ interaction is only part of the effect of dilution of the ortho molecules. Harris [12] has shown that anisotropic interactions arise between ortho-para molecules in second order perturbation theory and vary as the 10/3 power of the density at low pressures.

HD does not have ortho-para species as the nuclei are distinguishable; all rotational states are rapidly populated according to a Boltzmann distribution as temperature is

varied. At low pressure HD has essentially spherically symmetric molecules on an hcp lattice as T approaches zero; OO at low temperature has never been reported.

We have studied HD to pressures of 120 GPa and temperatures as low as 3.5 K by Raman scattering in a diamond anvil cell (DAC). The DAC was placed in a cryostat and HD [13] was cryogenically loaded in the liquid state and pressurized. The DAC, cryostat, and cryogenic loading technique are described elsewhere [14]. Pressures were determined from the fluorescence spectrum of a few micron-sized ruby grains scattered in the sample. A Spectra Physics model 2030 argon ion laser was used to excite the ruby. Various lines of the laser were used, following the pumping scheme outlined by Eggert et al. [15]. The laser spot was focused to a diameter of 5 μm at the sample with a Nikon microscope and a pair of imaging lenses. The fluorescence signal was collected and analyzed using a Spex triple monochromator and a Tracor Northern intensified diode array. The ruby remained quasihydrostatic throughout the experiment as evidenced by the R_1 linewidth and shape. Thus, the quasihydrostatic pressure scale [16] was used for pressure determination. Pressure variations in the sample of only a few percent were observed at the highest pressures.

Our initial experimental objective was to find P_{co} for the BSP transition in HD. We studied both the Raman active rotons and vibrons shown in Fig. 1. In earlier studies on D_2 [9] it was shown that the three Raman active rotons first broaden as pressure increases and then transform into a new spectrum at the BSP phase line, as the spectrum of elementary orientational excitations in this phase are librons rather than rotons; the vibron has a discontinuity in frequency at the phase line. Similar behavior is found for HD. Although the HD vibron frequency shifts substantially with changing pressure [17], at the phase line it has a small discontinuity of about 7 cm^{-1}. Because of the sharpness of the vibron, detection of the discontinuity is the more accurate method of determining the phase line, and has been used in this work. In Fig. 1 the discontinuity is seen on the 64 GPa curve. The intensity is seen to shift from one vibron peak to the other as the phase line is crossed. It is not clear if the coexistence of the two peaks at the phase line is simply due to the small pressure variations in the sample so that both phases coexist or if it is intrinsic due to a first order nature of the transition. We examined the transition line for hysteresis up to about 70 GPa and found no evidence of this. Since it is difficult to vary the pressure by small increments, most of our scans were performed by continuously varying the temperature at a fixed pressure, to locate the phase line [18].

The BSP transition in HD was found at a critical pressure of 68.3 GPa at 3 K and extrapolated to $P_{co}=69.0 \pm 2$ GPa, in the limit that T approaches 0 K. The BSP transition takes place when a parameter which characterizes the admixture of rotational states, $\eta = \langle V_{anis} \rangle / B$, exceeds a certain value. Here, $\langle V_{anis} \rangle$ is an expectation
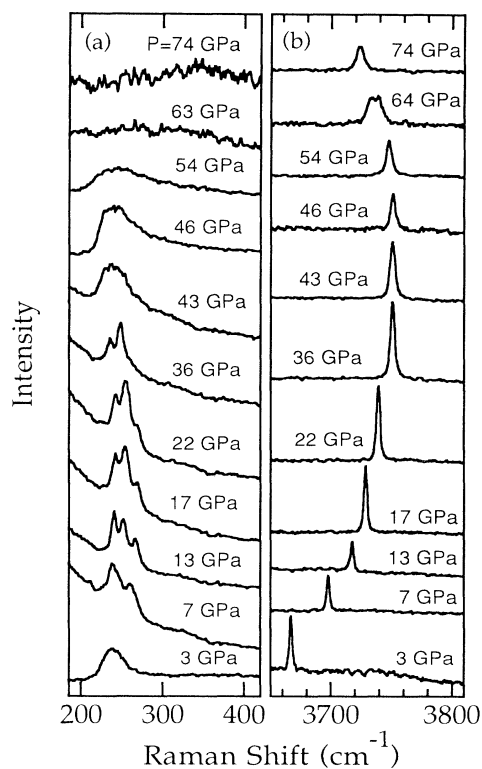

FIG. 1. Raman spectra of HD for several pressures with temperature 5–7 K. Intensities are not normalized to each other. (a) Rotational spectra, (b) vibron spectra.

value of the anisotropic interaction and B is the rotational constant. Since $\langle V_{anis} \rangle$ is believed to increase rapidly with density, whereas B is almost constant, the value of $\langle V_{anis} \rangle$ will determine the critical density or pressure for OO. When considering isotopes we note that B is proportional to the reciprocal of the reduced molecular mass μ, so the larger μ, the lower P_{co}. As expected, P_{co} for HD falls between the values for hydrogen and deuterium.

Since T_c depends on a thermal average of V_{anis} and theory indicates that V_{anis} increases rapidly with pressure, we expect T_c for the BSP to increase rapidly with pressure as was observed for o-D_2. Surprisingly we observed the opposite effect, that T_c actually decreases with temperature for P in the region of P_{co}, as shown in Fig. 2, which maps out the phase line. This boomerang shaped phase line shows that the disordered phase is reentrant between P_{co} and P_{cm}, the minimum pressure for which the transition occurs. In this pressure range at $T=0$ K the solid is in the symmetric state [7,19]. For fixed pressure, as temperature is increased, the solid goes from a disordered to an ordered to a disordered phase.

This phase line can be understood by considering a series of phase lines for fixed concentration C of odd-J rotational levels (i.e., the ortho concentration for hydrogen), as shown in Fig. 3. These lines are fictitious, since they have not been determined theoretically or experimentally at high pressure; however, they are intelligent
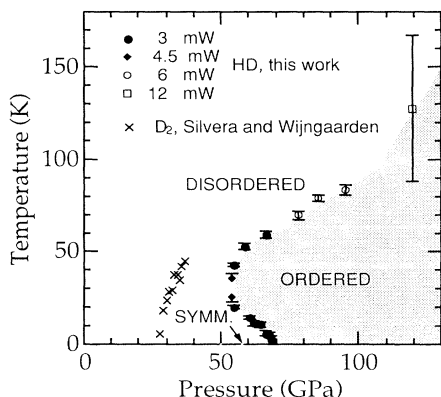
FIG. 2. The phase line for orientational order in HD; we also show the line for the BSP phase in o-D_2, for comparison. Laser powers were kept low to minimize heating.

FIG. 3. The phase line of HD, along with a number of fictitious lines for constant C.

guesses, inspired by behavior found in the regions which have been investigated. For $C=1$ at low pressure the behavior V_{anis} is due to EQQ interactions and T_c increases as $\rho^{5/3}$, where ρ is the molecular density [11]. The line for pure EQQ interactions for $C=1$ is shown. The theoretical phase line for $C=1$ should not cross the experimental line, as we shall see below, so we draw in a more appropriate line which does not cross the phase line. At the other extreme, $C=0$, we know that for o-D_2, T_c rises rapidly with density, and we create an analogous curve. At very high density we expect these two lines to merge together as the molecules will be orientationally well localized and the differences between anisotropic interactions for odd and even orientational states should be small. We can also draw in a curve for the critical percolation concentration which has $T_c=0$ at $P=0$. A few additional lines will be identified shortly.

We now realize that for HD, in contrast to the homonuclear isotopes, C is determined by the Boltzmann probability with inclusion of both even and odd rotational states. Since any molecule with $J\neq0$ can dramatically affect the ordering it is appropriate to take $C=1-C_{J=0}$, rather than $C=1-C_{even-J}$; thus,

$$C = \frac{\sum_{J=0}^{\infty}(2J+1)e^{-E_J/k_BT} - 1}{\sum_{J=0}^{\infty}(2J+1)e^{-E_J/k_BT}}, \quad (1)$$

where $E_J = B_{HD}J(J+1)$ and $B_{HD}/k_B = 64.27$ K [20]. A plot of C vs T is shown in Fig. 4(a).

For the real HD sample at P_{co} (i.e., $C=0$), when the sample temperature is raised from 0 K, equilibrium is rapidly established and C increases. The transition is now determined by a curve appropriate to the concentration C at the new temperature, so the critical pressure shifts down. This continues until P_{cm} is reached, where the concentration is insufficient for the transition to occur at the elevated T and the phase line loops up. To understand the upper part of the phase line, consider a fixed pressure between P_{co} and P_{cm}. As the crystal is warmed, levels with $J>0$ are populated, but the system remains
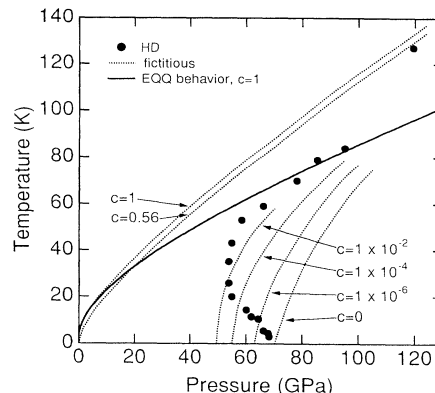
unordered until a critical concentration is reached; this locates the lower T_c of the phase line. With increasing temperature, the $J=1$ concentration increases and the order parameter increases (T/T_c becomes less than 1). With still increasing temperature the tendency to disorder due to thermal agitation, characteristic of all phase transitions, wins over the increase of T_c due to increasing C; molecules disorder and the solid enters the disordered phase. Thus, the transition is reentrant. At $T=0$ K the solid is symmetric; for $T\neq0$ K, but below the phase line the solid contains unordered molecules with $J\neq0$; it then goes to the ordered phase and finally becomes disordered. The curves in Fig. 3 for low C have been assigned a concentration corresponding to the temperature where the
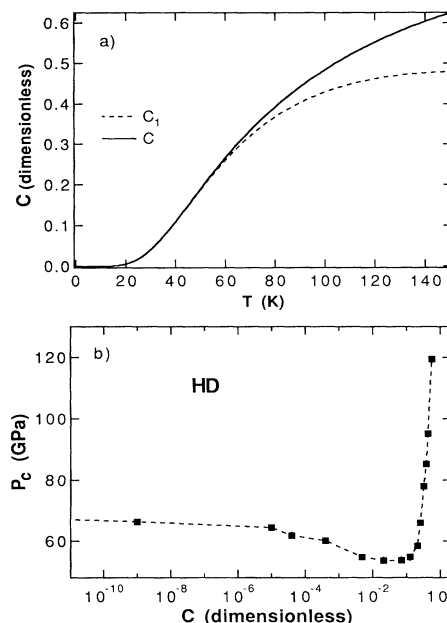

FIG. 4. (a) The non $J=0$ concentration C as a function of temperature in HD, based on zero pressure energy levels. The dotted line shows the concentration of $J=1$ molecules. (b) The critical pressure as a function of C; the dashed line is a guide to the eye.
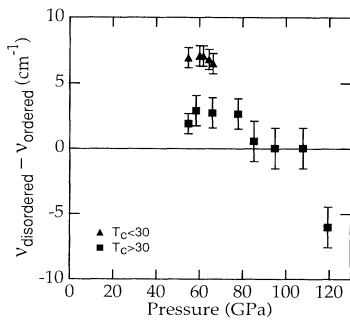
FIG. 5. The shift of vibron frequency at the HD phase line.

phase line is crossed. We see that near P_{co} where $J=0$ molecules are on the verge of ordering, extremely small concentrations of $J=1$ molecules have an enormous affect on the lower T_c. A possible explanation is that near P_{co} the solid is highly polarizable and a small "impurity" concentration of molecules with permanent EQ moments EQ polarizes an enormous cluster around it, strongly influencing P_c. In Fig. 4(b), we plot P_c vs C, where we have determined C by using the results of Fig. 4(a), evaluated at $T=T_c$.

An additional interesting observation is the shift in the vibron frequency at the phase line, shown in Fig. 5. At P_{co} the frequency decreases upon entering the BSP phase by 6.5 ± 0.5 cm^{-1}. This is in reasonable agreement with the mean field theory of Igarishi [8]. He calculates the frequency difference for the admixture of the $J,M=2,0$ state into the 0,0 ground state. Using Stoicheff's [21] data on Raman scattering in hydrogen and its isotopes we find that the shift should be about twice as large in HD as in D_2, which had a measured shift of 3 cm^{-1} [9]. However, with increasing pressure the sign of the shift changes, an observation for which we have no explanation. With increasing pressure, higher rotational states will be mixed into the ground state, but in a mean field theory these should not change the sign of the shift.

The results for HD have implications for H_2 and D_2. These solids can be in metastable states far from equilibrium, as C changes very slowly with time. Thus, hydrogen and deuterium probably have phase lines for each C similar to the fictitious ones of Fig. 3. Interactions are expected to be similar for all isotopes at a given density. The HD results imply that anisotropic interactions and T_c rise rapidly with increasing pressure. The validity of the use of EQQ as the dominant anisotropic interaction at high pressure has often been questioned. Our results show that a theoretical phase line based on such an interaction for $C=1$ crosses the experimental phase line for $C<1$. We conclude that anisotropic interactions at high density are stronger than EQQ.

Another possible modification of the interaction is the pressure dependence of the EQ moment. The most important effect on the EQ moment would be due to the change of the internucleon distance with pressure. This has been studied by Loubeyre et al. [22] who found a

small decrease in the bond length which would result in a small weakening of the EQQ interaction; this would not explain the observed behavior.

Finally, we mention that due to the lack of inversion symmetry HD has a small electric dipole moment, about 6×10^{-5} D [23]. Since we do not expect this to change much in our pressure regime, the dipolar interactions will be too small to have a significant effect on the OO at the temperatures in this experiment. At very low temperature this interaction may vectorially align the HD molecules.

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