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Low-frequency Raman spectroscopy of deuterium to megabar pressures at 77-295 K

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Rotational and lattice phonon excitations in the Raman spectrum of solid molecular deuterium have been measured from 1.8 GPa to ~200 GPa at 77-295 K to study pressure-induced changes in structural and dynamical properties of the dense solid. Continuous and discontinuous changes in three distinct pressure ranges are observed. At lower pressures (< 30 GPa), there is a gradual increase in the linewidth of the $S_0(0)$ band, together with gradually decreasing resolution of the higher-energy $S_0(1)$ and $S_0(2)$ features. At intermediate pressures (60–100 GPa), a change in the pressure dependence and linewidth of $S_0(0)$, and a linewidth and intensity decrease in the E_{2g} phonon band occur. This is interpreted as evidence for a phase transformation in the molecular solid beginning at ~65 GPa (77 K). At the highest pressures (~160 GPa), abrupt changes in the low-frequency excitations suggest either an expansion of the molecular bond or a change in ordering at the vibron discontinuity. Evidence from the low-frequency spectra for interaction between the deuterium sample and diamond anvil is also examined.

I. INTRODUCTION

Identifying and detailing the high-pressure transformations in hydrogen and its isotopes are crucial for understanding its evolution to high-density semiconducting and metallic forms, including eventual nonmolecular ground states predicted at very high pressures.[1] Raman measurements of the high-frequency intramolecular vibrational mode (vibron) indicate that molecular hydrogen remains stable to at least ~250 GPa but undergoes a phase transition at 150 GPa (77 K).[2] At low pressures the hydrogen isotopes form insulating molecular solids with molecules in states of complete rotational disorder over a wide temperature range.[3] With increasing pressure, the rotational motion of the molecules is expected to become more restricted, ultimately leading to orientational ordering. In addition, crystallographic or structural transitions are possible, including both distortions of the low-density structures and discontinuous (first-order) transitions to new structures with large-scale changes in the underlying lattice symmetry. Theoretical calculations indicate that both the state of orientational order and the crystal structure of the high-pressure solids have a significant effect on the electronic properties, including the transition pressure of the predicted pressure-induced metallization within the molecular solid (e.g., by band-gap closure).[4–7] Thus, experimental structural information is essential for evaluating proposed mechanisms of metallization and related electronic transitions.[8]

The low-frequency Raman spectrum of the solid normal hydrogen is characterized by rotational bands [e.g., $S_0(J)$ corresponding to the $J+2\leftarrow J$ excitations in the free molecule for $v=0$], as well as lattice phonons characteristic of the rotationally disordered hexagonal close-packed structure.[3] The pressure dependence of these excitations provides information on phase transformations, in particular, on changes in rotational ordering and constraints on the crystal structure. Since high-pressure Raman studies are now possible well into the megabar range (> 100 GPa), these measurements complement direct structural studies possible at lower pressures using diffraction techniques.[9–14] Currently, x-ray-diffraction measurements have been carried out to 48 and 42 GPa for hydrogen and deuterium, respectively.[12–14] Previously, we reported measurements of the evolution of the low-frequency rotational bands and a lattice phonon of hydrogen to 162 GPa at 77–295 K.[15] Over this pressure interval the rotational bands broaden but persist and the lattice phonon, which correlates with the E_{2g} optical phonon of the hexagonal close-packed structure, shifts continuously. The continuity of the low-frequency bands as a function of pressure indicates that an underlying hexagonal structure persists above 150 GPa. However, new features in the low-frequency spectra are observed at higher pressures.[16]

Similar measurements for deuterium in the megabar range have not been reported. Measurements on this isotope have been limited to below 54 GPa for the rotational bands and to below 20 GPa for the lattice phonon.[17,18] Examination of these excitations in deuterium in the higher-pressure range is particularly important for furthering our understanding of isotope effects documented for hydrogen at high densities. Orientational ordering is energetically favored in the heavier isotope as a result of its smaller rotational constant [$B_{D_2}=29.9$ cm^{-1} versus $B_{H_2}=59.3$ cm^{-1} in the gas phase, where $B=h/(4\pi)^2cI$, and I is the rotational moment of inertia[19]], which results in stronger mixing of free-molecule rotational states in the condensed phases. Isotope effects are also observed in the pressure dependence of the molecular vibron; the pressure shift is significantly stronger in hydrogen than in deuterium.[20,21] In addition, a distinct isotope effect is observed in the pressure of the low-temperature 150-GPa

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phase transition (higher in deuterium).[21,22] It is of interest to determine whether or not these differences are associated with structural differences between the two isotopes.

We report here measurements of the rotational and lattice-phonon Raman excitations of solid molecular deuterium to pressures close to 200 GPa using diamond-anvil cells. Spectra are measured at both 77 and 295 K. We give close attention to evidence for structural transformations and information on the crystal structure of the solid under these conditions. We compare the results with data obtained from measurements of the vibron and optical spectra at these pressures, previous low-frequency Raman measurements on D_2 (at lower pressures and temperatures), and theoretical calculations.

II. EXPERIMENTAL PROCEDURES

Samples were loaded at room temperature in a modified Mao-Bell diamond-anvil cell with composite rhenium/T301 stainless-steel gaskets. Eight separate experiments were performed on deuterium carried out over different pressure ranges from 1.8 to 200 GPa and temperatures of 77-150 K and at 295 K. Experimental details for each run are listed in Table I. The basic design of the optical system has been described previously.[23,24] An argon-ion laser was focused with a 20-mm lens at 135–145° to the collection lens, which consisted of a 15-mm working distance Leitz UT-40 microscope objective. Low-temperature spectra were measured on samples cooled using two different cryostats. The highest-pressure studies were carried out using a windowless cryostat with the same optical system (experiments 1–4).[2,15] In this system the entire diamond cell is immersed in liquid nitrogen to the level of the samples. Because no window was placed above the upper diamond, the microscope objective could be located within the counter bore of the cooled diamond cell, as in room- (and higher) temperature measurements. The temperature was monitored with thermocouples mounted on both the upper and lower diamonds. In these experiments, the temperature was varied by adjusting the level of the liquid nitrogen or by resistance heating. This system was used for all experiments carried out above 40 GPa. Additional experiments were also carried out with diamond cells mounted in a custom-built liquid-nitrogen flow cryostat with a single window (experiments 5 and 6). Again, 135–145° excitation was used. The scattered light was collected with a longer working distance objective. Relative to the windowless cryostat, this system gives lower spatial resolution but higher mechanical and thermal stability. The latter was used in the present experiments on larger samples studied to maximum pressures of 40 GPa. Room-temperature measurements to 170 GPa were performed with a cell located outside of the cryostat (experiments 7 and 8).

All Raman spectra were collected using a triple spectrograph (Spex Triplemate, model 1877). For the higher-pressure measurements, a 1024-channel (25 mm) intensified diode-array detector (Princeton Instruments IRY) was used.[23] Both 1152×298 pixel and 1024×1024 l-N_2 cooled CCD's (Princeton Instruments) were employed as detectors in the later experiments with the flow cryostat. In both systems the optical system was configured so that the signal from the sample could be directed with kinematically mounted mirrors to addition-

TABLE I. Summary of experiments on deuterium.

			Cylinder anvil[b]			Piston anvil[b]			
Exp. no.	T (K)[a]	P_{max} (GPa)	A (μm)	B (μm)	θ (deg)	A (μm)	B (μm)	θ (deg)	Sample diameter (μm)[c]
1	77–150	120	559	146	4	564	144	4	60–40
2	77–150	200	508	52	9	498	103	8	40–30
3	77–150	120	497	74	8	492	54	9	35–25
4	77–150	150	484	69	9	495	49	8	30–20
5	77	36	600			600			300–200
6	77	33	480			665			300–200
7	295	155	495	102	10	490	50	7	30–20
8	295	129	287	50	8	270	48	10	30–20

[a] Samples were loaded at room temperature (295 K). In each case, Raman spectra were measured prior to cooling.

[b] Dimensions for the tips of beveled anvils (e.g., Ref. 24): A = culet diameter, B = diameter of the central flat, θ = bevel angle. Flat culet (unbeveled) diamonds were used in experiments 5 and 6. In the latter experiments the culets had a slight elliptical shape (by up to 10%), and the mean value of the diameter is listed.

[c] Approximate sample diameter during the coarse of the experiment. The first number for the diameter is the size of the hole drilled in the gasket, the second is the approximate diameter of the sample at high pressure. In the experiments carried out with beveled diamonds (experiments 1–4, 7, and 8) the sample thickness varied approximately from 5 to 2 μm. In contrast, in the experiments carried out with flat culet diamonds (experiments 5 and 6) the thickness changed from 35 to 25 μm. The sample thickness was estimated from white-light interference fringes.

al spectrographs for other measurements. This facilitated rapid measurements without changing position of the sample, laser, or moving the gratings and optics of the triple spectrograph. The pressure was determined using a 0.18-m spectrograph (Jarrell-Ash) also equipped with an intensified diode-array detector (17-mm, 700-channel Princeton Instruments). In some experiments, a third spectrograph (0.64-m Jobin Yvon) with a diode array was employed for measurements on the higher-frequency vibron. All of the reported spectra were periodically checked using a different laser-excitation frequency to ensure that they were true Raman spectra.

III. RESULTS

The evolution of the low-frequency Raman spectrum of deuterium from 1.8 to 177 GPa at 77 K is shown in Fig. 1. A gradual broadening of the low-frequency $S_0(0)$, $S_0(1)$, and $S_0(2)$ bands is observed below 30 GPa. The spectra are dominated by the relatively strong $S_0(0)$ transition, which persists to very high pressures. In addition, a weaker, sharper, and strongly pressure-dependent band is observed up to ~100 GPa. This band, which is continuous with earlier measurements of the E_{2g} lattice phonon, weakens [with respect to the $S_0(0)$ signal] gradually with increasing pressure above 100 GPa, and diamond fluorescence tends to increase at these pressures. The phonon could not be measured above 100 GPa, although the low-frequency extension of the $S_0(0)$ band is readily apparent. With increasing pressures above ~140 GPa at 77 K the low-frequency band is obscured somewhat by increasing diamond fluorescence but is observed up to and through the high-pressure phase transition at ~165 GPa.

The pressure dependence of the mode frequencies measured at 77 K is given in Fig. 2. The results of the six different experiments carried out at this temperature are denoted by different symbols to underscore the reproducibility of the results. We also compare the pressure shift of the high-frequency Raman-active vibron, including the discontinuity associated with the phase transition at 160–170 GPa.[21,25] The $S_0(0)$ band has a frequency $\nu = 180$ cm^{-1} for the isolated molecule in the gas phase, increasing at 200 cm^{-1} at 10 GPa. At pressures where the $S_0(1)$ and $S_0(2)$ frequencies are not plotted in the figure, the peaks had broadened to form a diffuse tail on the lower-frequency bands and no unique fit for the peak position was possible. The frequency of the band correlating with $S_0(0)$ at low pressure increases nearly monotonically with pressure to ~160 GPa. A discontinuous change in the Raman shift of the low-frequency mode is observed at pressures near the vibron discontinuity. In addition, a break in the slope of the pressure shift is observed near 65 GPa. The large pressure shift of the E_{2g} phonon is clearly evident. The phonon frequency increases strongly with pressure with no observable discontinuities to 100 GPa, other than the previously documented mixing with the E_{2g} component of $S_0(0)$.[18] Above ~100 GPa, the phonon could not be measured.

The results of the chi-squared analysis[26] for the frequency shifts and linewidths shown in Fig. 1 are given as a function of pressure in Fig. 3. There appears to be a break in the pressure shift of the $S_0(0)$ band frequency at 65 GPa [Fig. 3(a)]. The half-width increases monotonically with pressure (from 30 cm^{-1} at 10 GPa to ~100 cm^{-1} at 65 GPa) but then decreases to about 50 cm^{-1} at 100 GPa [Fig. 3(b)]. The half-width of the E_{2g} phonon increases from <5 to ~20 cm^{-1} at 65 GPa and then decreases [Fig. 3(c)]. At pressures from 100 to 160 GPa, the linewidth of the low-frequency band remained nearly constant (half-width ~50 cm^{-1} at 77 K). In addition, we note that the intensity of the phonon decreases markedly between 65 and ~100 GPa [Fig. 3(d)]. All of these

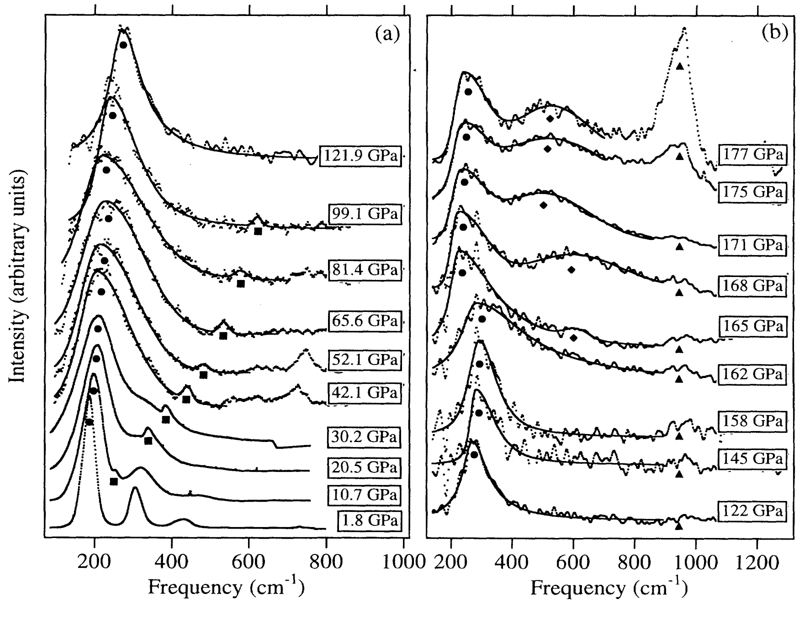

FIG. 1. Representative low-frequency Raman spectra of deuterium from 1.8 to 177 GPa at ~77 K. Low-pressure spectra were measured with an l-N$_2$ cooled CCD detector (experiments 5 and 6); higher-pressure spectra were recorded using an intensified diode array (experiments 1 and 2). Laser excitation at 514.5 nm was used. The solid lines are fits to the spectra (Ref. 26). The circles and squares denote the $S_0(0)$ and E_{2g} phonon bands. Note the abrupt shift in the lowest frequency peak between 162 and 165 GPa (experiment 1). In other experiments the shift occurred at lower pressures [$\lesssim 150$ GPa, i.e., below the pressure of the vibron discontinuity (Ref. 16)], as indicated in Fig. 2 (experiments 4 and 5). A broad feature that appears once the material has transformed to the high-pressure phase is marked with the solid diamond. The peak identified with the triangle is associated with the diamond anvil.

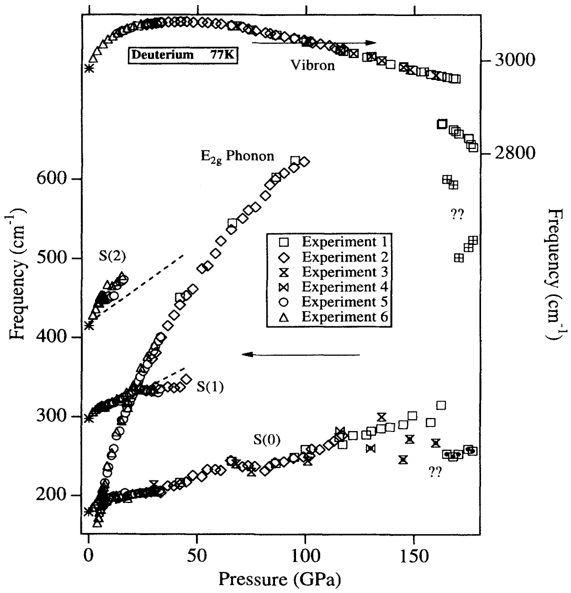

FIG. 2. Pressure dependence of the principal Raman excitations of deuterium at 77 K. The vibron data are from Refs. 21 and 25. The dashed lines show the $S_0(1)$ and $S_0(2)$ positions calculated from the pressure shift of $S_0(0)$ assuming free rotation. The square-dot symbols for the data above 160 GPa correspond to the lowest-frequency peaks shown in Fig. 1. The positions of the additional higher-frequency bands at these pressures are indicated by the plus-squares.

trends were observed in at least two different experiments, as indicated in the figure.

Selected spectra measured as a function of pressure at 295 K are shown in Fig. 4. These spectra are weak, with multiple peaks associated with the $S_0(0)$, $S_0(1)$, $S_0(2)$, $S_0(3)$, and $S_0(4)$ transitions. The intensity is distributed over a wider manifold of rotational bands relative to hydrogen as a result of the lower rotational constant (and hence greater population of higher J states) in the lighter isotope. Figure 4 also compares spectra measured near 135 GPa at 77 and 295 K. Both the 77- and 295-K spectra exhibit a low-frequency band at ~ 300 cm^{-1}. The band has a significantly larger linewidth at room temperature.

Significant spectral changes are observed at 150–160 GPa and 77 K. A discontinuous decrease in frequency is observed near the low-frequency band near the pressure interval of the vibron discontinuity (Figs. 1 and 2). In addition, new peaks develop at higher pressure. The spatial dependence of the spectrum within the sample at ~ 170 GPa is shown in Fig. 5. The shape of the low-frequency band does not depend strongly on position, even when the excitation is largely on the gasket area; this suggests that the band is diamond related, although deuterium trapped at the gasket-diamond interface or diffused into the diamond may be required. The increased intensity at $\Delta\nu > 600$ cm^{-1} (relative to the laser line, $\nu_L = 19\,435$ cm^{-1}) arises from fluorescence and Raman scattering from the stressed diamond.[27] The band at ~ 1400 cm^{-1} is a Raman feature of the diamond following either structural transformation or plastic deformation of the anvil.[27] Both of these transitions have been observed in high-pressure control experiments not involving hydrogen or deuterium.

IV. DISCUSSION

These results provide evidence for both continuous and discontinuous changes in structural and dynamical properties of deuterium with increasing pressure from 1.8 to ~ 200 GPa. In common with our previous reports on dense hydrogen, each of these changes was observed in measurements performed in separate samples and pairs of diamonds (e.g., Ref. 14). We now discuss these changes in further detail. In particular, we examine the evidence these data provide for a new transition in dense deuterium. We compare the results with previous low-pressure data for deuterium, high-pressure spectra for hydrogen, and relevant theoretical calculations.

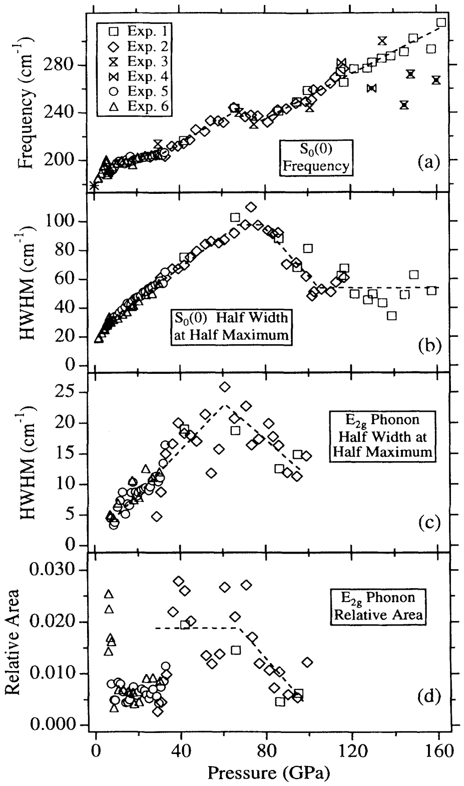

FIG. 3. Pressure dependence of the (a) $S_0(0)$ frequency, (b) $S_0(0)$ half-width (HWHM), (c) lattice-phonon half-width, (d) relative area of the lattice phonon. The drawn lines are intended to serve as a guide to the eye. The initial decrease in the intensity of the phonon shown in (d) arises from mixing with the $S_0(0)$ (Refs. 18 and 31). The subsequent increase at 30 GPa was reproducible but is not understood. Above 100 GPa, the relative area was estimated to be < 0.002.

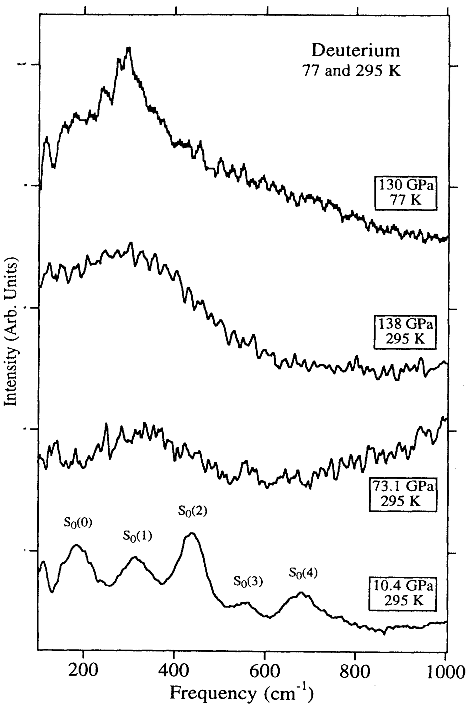

FIG. 4. Selected Raman spectra of deuterium as a function of pressure from 10.4 to 138 GPa at 295 K. A spectrum at 130 GPa and 77 K is also compared.

A. Lower-pressure spectra

The key change at low pressures (to 30 GPa) is the broadening and pressure shift of the low-frequency bands. The frequencies of the $S_0(0)$, $S_0(1)$, and $S_0(2)$ bands assuming a free-rotation model are $6B$, $10B$, and $14B$, respectively (ignoring crystal-field effects). The frequency of the $S_0(0)$ band increases from 180 to ~ 300 cm^{-1}; if this were due to a drop in I driven by a contracting intramolecular bond then the $S_0(1)$ and $S_0(2)$ frequencies would shift as shown in Fig. 2. Indeed, the pressure dependence of the higher bands predicted from this analysis fits the data reasonably well [to ~ 50 GPa for $S_0(1)$ and to ~ 30 GPa for $S_0(2)$]. Assuming $r \sim \nu^{-1/2}$ for the bond length and rotational band frequency, the measured pressure shift implies a contraction of the bond by 6% to 30 GPa and by 11% to 50 GPa. This may be compared with a bond compression of 3% in solid H_2 calculated by Loubeyre, Jean-Louis, and Silvera[28] from lower-pressure roton data for this isotope.

The above analysis, however, ignores the effect of a growing crystal field, which should increase with increasing density even if J remains a good quantum number. Indeed, the gradual broadening of the $S_0(0)$ band could reflect a growing crystal-field interaction which causes the magnetic sublevels of the $S_0(J)$ band $(-J \le m_J \le J)$ to be split by the hcp crystal field. Detailed calculations of the crystal-field contribution to the spectrum are in progress and will be presented elsewhere. A gradual molecular orientational ordering could also give rise to these changes; the rotational bands must then be associated with increasingly restricted motion. The shift may be due to either crystal-field perturbations or a gradual structural or rotational ordering transformation in the molecular solid.[29] Unfortunately, the current data do not provide a way to distinguish further between these two (possibly related) effects. Despite this uncertainty, it is important to note that the phonon remains clearly identified. The presence of the optical phonon, and its continuity over this pressure range, indicates that the solid maintains an underlying lattice structure close to hexagonal close packed. For example, this rules out a complete transition to an fcc-based structure (at least to ~ 100 GPa), in which case symmetry considerations preclude a Raman-active phonon.

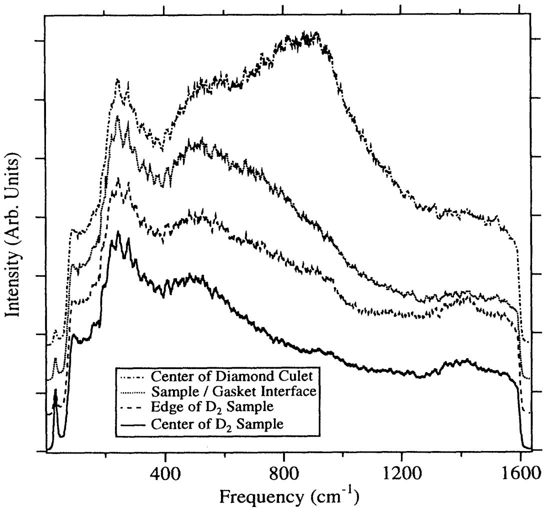

FIG. 5. Spatial dependence of the spectra within a sample at >170 GPa. An intense feature at a Raman shift of 800 cm^{-1} appears at the center of the diamond culet. This is the region of the highest pressure (stress) of the anvil.

B. Phase transition at 65 GPa

The changes in the spectra between 60 and 100 GPa described above, a kink in the $S_0(0)$ frequency, a decrease in the half-width of the $S_0(0)$ and the phonon bands, and the gradual weakening and disappearance of the phonon, suggest a phase transition in this pressure range. The breadth of the transition, ~ 35 GPa, is significantly larger than pressure gradients in the cell. Moreover, similar results were obtained in different runs (e.g., experiments 1 and 2).

The changes in the low-frequency rotational band could be caused by a change in the orientational order and/or a change in the crystal structure. Although there is a break in the pressure shift of the low-frequency mode, the continuity of the band at both low and high pressure indicates that the change is not an abrupt transition. It is possible that the molecules gradually order over a wide pressure range, possibly associated with lattice disorder due to ortho-para states of deuterium (70–30 % mixture at 77 K at equilibrium). Alternatively, the transition may represent sluggish structural transition (e.g., hcp to fcc) with or without orientational ordering. If so, the breadth of the transition could represent the formation of mixed or intermediate hexagonal-cubic close packing, similar to what has been observed in the fcc-hcp transition in xenon (in the latter, hcp is the high-pressure phase).[30]

The measured changes in the phonon band allow the possibility of a change of crystal symmetry above 100 GPa. A crystal structure with the molecular center of mass located in sites with inversion symmetry (e.g., fcc or bcc) lacks a Raman-active phonon. The decreasing intensity of the phonon band above 60 GPa would thus be consistent with a gradual transition to such a structure (from hcp). The structure observed for ordered hydrogen isotopes with high $J=1$ content at low densities,[19] which is based on an fcc lattice with molecular axes aligned along body diagonals and the space group $Pa3$, is such a structure. The loss of the phonon signal offers no constraints on the state of orientational order, but does suggest that a structural transition may be involved. It is clear that loss of a weak signal is not sufficient criterion for establishing evidence for a phase transition; however, as shown in Fig. 3(c), the phonon becomes sharper above ~ 60 GPa and hence should have been easier to detect. Likewise the diamond fluorescence at 100 GPa is sufficiently low that the signal-to-noise ratio is still fairly high. We believe that the correspondence between the changes in the rotational and the phonon bands (Fig. 3), coupled with the excellent reproducibility in the two high-pressure runs in which the highest signal-to-noise ratio was obtained (experiments 1 and 2), lend credence to the hypothesis that the loss of phonon signal is due to a structural phase transition.

It is now useful to consider the relationship between the phase transition identified here at 65–100 GPa and 77 K to that reported previously at lower pressure and temperatures for ortho-D_2.[17] Silvera and Wijngaarden[17] studied the Raman spectrum of orthodeuterium (pure $J=0$) at 5 K to 54 GPa. They reported the observation above 28 GPa of a broadened low-frequency doublet at about 170 and 230 cm^{-1}, which they interpreted as arising from an ordering-type transition (broken-symmetry transition) in the $J=0$ molecules. It is possible that the 65-GPa transition at 77 K represents a continuation of a similar phase line. The gradual narrowing of our rotational band is qualitatively similar to the splitting (and narrowing) of one of the branches of the doublet observed by Silvera and Wijngaarden. This interpretation implies that crystal-field or other effects have shifted the low-frequency branch of the doublet out of our field of view. Preliminary crystal-field calculations suggest that this may be consistent with our data. We note that due to differences in the ortho-para content of our samples and that of Silvera and Wijngaarden ($c_0=0.7$ and 1.0, respectively) the phase transitions are not rigorously connected but rather may be members of a family of similar transitions (including the ambient-pressure ordering transitions for high $J=1$ concentrations) for each ortho-para concentration. As mentioned above, the existence of $J=0$ and 1 molecules in samples at 77 K may contribute to the gradual nature of the transition.

Silvera and Wijngaarden[17] were unable to measure the optical phonon above the transition, and they proposed that the high-pressure phase had cubic $Pa3$ structure. This would also be consistent with our lack of a measurable phonon above 100 GPa. Silvera and Wijngaarden also observed a discontinuity in the Raman vibron with increasing pressure (at 3 cm^{-1} at 10 K, decreasing to ~ 1 cm^{-1} at 50 K). No such vibron discontinuity ($>1-2$ cm^{-1}) has yet been observed over the temperature range of this study (77-295 K) below the major phase transition at 165 GPa.[21,22] The gradual nature of our spectral changes, however, may preclude such an observation. The room-temperature spectra, in principle, provide an additional point on the proposed phase lines. Indeed, the low-frequency band in the 295-K spectra becomes better resolved at ~ 100 GPa, but the change is relatively small and we cannot make an unambiguous identification of spectral changes. We attribute the broadening of the low-frequency band at higher temperature to increased rotational disorder and the effects of rotational averaging and will be examined in detail elsewhere.[31]

C. Comparison with hydrogen

A representative low-frequency Raman spectrum of deuterium at 99 GPa is compared with that measured for hydrogen at a similar pressure in Fig. 6. The persistence of the $S_0(0)$ and $S_0(1)$ bands to 100 GPa in hydrogen was interpreted as an indication of free (or nearly free) rota-

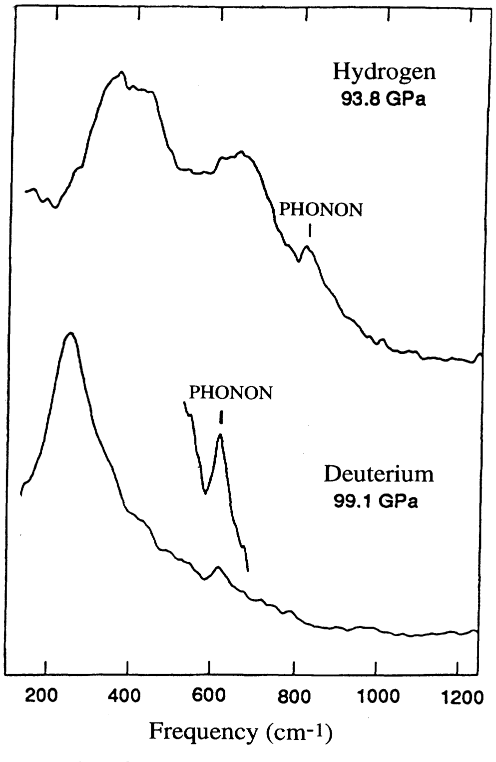

FIG. 6. Examples of low-frequency Raman spectra of hydrogen and deuterium at 77 K. The two broadened low-frequency bands observed in H_2 correlate with the $S_0(0)$ and $S_0(1)$ rotational transitions (Ref. 15). The optical phonons observed in both isotopes are indicated.

tion of the molecules to these pressures.[15] Notably, there is also a splitting of the $S_0(0)$ band in hydrogen, which was observed to begin at about 30 GPa (77 K).[15] In contrast, the first peak in the deuterium shows no obvious substructure.

Further evidence for different behavior of the two isotopes under these conditions is obtained by comparison of the phonon frequencies. The volume dependence of the optical phonon frequency for the two isotopes, from ambient pressure to our highest pressures at 77 K, is shown in Fig. 7. We use the x-ray-diffraction equation of state[11] for the high-pressure data ($V < 9$ cm^3/mol) and the tabulated volumes for the low-pressure data ($V > 10$ cm^3/mol).[32] The D_2 curve reproduces the results obtained by Wijngaarden, Goldman, and Silvera[18] (using the new equation of state) and Berkhout and Silvera[32] at lower pressures, as noted previously for H_2.[15] The log-log plot of phonon frequencies shown in Fig. 7(a) clearly shows that $\ln(\nu)$-$\ln(V)$ is supralinear. We fit all of the data, without weighting, to the quadratic functions

$$H_2\text{:}\quad \ln(\nu)=7.457-0.350\ln(V)-0.285\ln(V)^2\ ,$$

$$D_2\text{:}\quad \ln(\nu)=7.301-0.489\ln(V)-0.258\ln(V)^2\ ,$$

shown by the solid lines in Fig. 7(a). Using a cubic polynomial did not improve the fit. The mode-Grüneisen parameter, $\gamma=-\partial\ln(\nu)/\partial\ln(V)$ shown for both hydrogen and deuterium in the inset of Fig. 7(a), drops by a factor of 2 for both isotopes.

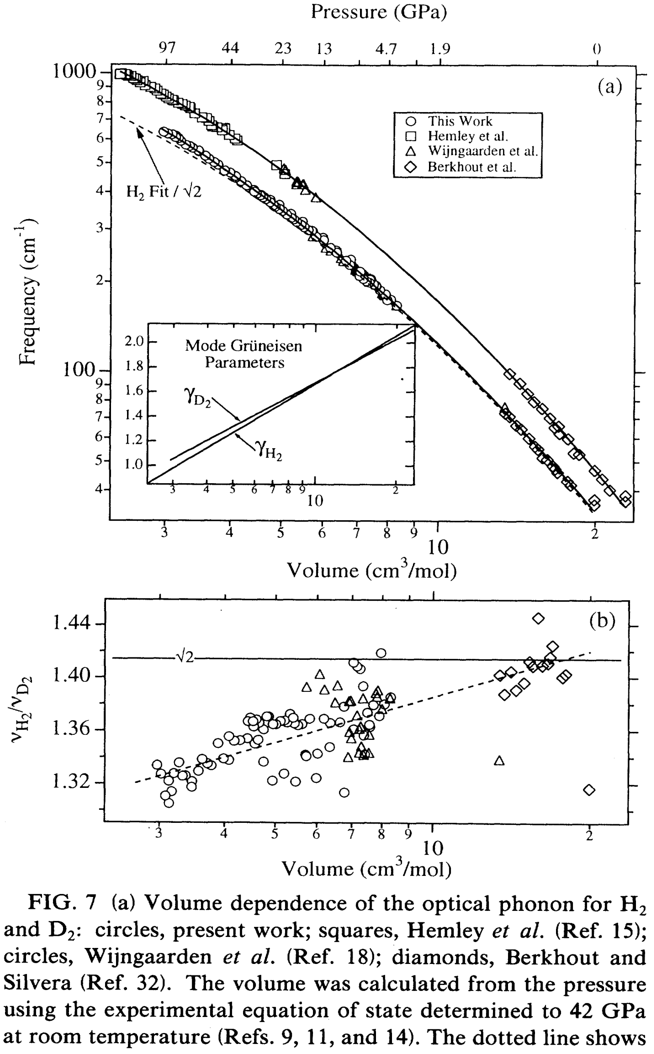

FIG. 7 (a) Volume dependence of the optical phonon for H_2 and D_2: circles, present work; squares, Hemley *et al.* (Ref. 15); circles, Wijngaarden *et al.* (Ref. 18); diamonds, Berkhout and Silvera (Ref. 32). The volume was calculated from the pressure using the experimental equation of state determined to 42 GPa at room temperature (Refs. 9, 11, and 14). The dotted line shows the frequencies expected for D_2 on the basis of the measurements for H_2 in the harmonic approximation. The data of Wijngaarden *et al.* (Ref. 18) have been corrected using the newer equation of state (Refs. 11 and 14). (b) The ratio of the frequencies as a function of volume.

At low compression, the frequencies of the modes differ by a factor of $2^{-1/2}$ as a result of the differences in masses [i.e., $(m_{H_2}/m_{D_2})^{1/2}$], as expected if the modes are harmonic and the crystal structure and volume are identical for the two isotopes. In Fig. 7(a), we have plotted the fit to hydrogen divided by $2^{1/2}$ as a dashed line. It is evident that this relationship does not hold at high compression: the D_2 curve is higher than that expected on the basis of the measurements for H_2. Figure 7(b) shows the ratio ν_{H_2}/ν_{D_2}, where ν_{H_2} is interpolated from the above fit to all data. The frequency ratio falls from the harmonic value of 1.41 at 18 cm^3/mol to about 1.32 at 3 cm^3/mol. This decrease may be due to an anharmonic perturbation in the intermolecular potential which would affect the frequency ratio more strongly as the frequencies increase, sampling higher-energy regions of the potential.

Alternatively, if we assume harmonic potentials, the frequency ratio may reflect a structural difference or difference in ordering between hydrogen and deuterium, since orientational ordering should result in a more efficient packing of the molecules relative to the rotationally disordered state. Since the frequency of the phonon is a strong function of volume, the offset indicates that the molar volume of deuterium (which might be partially ordered) is lower than that of hydrogen (which might not be ordered) at the same pressures. It is important to note that the low-pressure data of Berkhout and Silvera[32] were measured at 4.2 K, the intermediate-pressure data of Wijngaarden, Goldman, and Silvera[18] were taken at 5 K, and all of our data used in this analysis were measured at 77 K. Our data were taken for D_2 in a nominally disordered state. The available diffraction data provide some evidence for a lower volume in D_2 even at room temperature ($\sim 2\%$ at 30 GPa),[14] so it is possible that effects of partial rotational ordering or small structural distortions from hcp are present at room temperature. If the volume difference at 77 K persists to higher pressure (> 150 GPa), it may contribute to the isotope effect on the pressure of the high-pressure phase transition (i.e., the low-pressure phase is stabilized to higher pressures in the heavier isotope).

In hydrogen a sharp Raman band continuous with the E_{2g} phonon at lower pressure was tracked to pressures above 150 GPa.[15] This observation suggests that the underlying hexagonal structure persists into this pressure range (at ~ 77 K) for this isotope (and ortho-para state). However, the intensity of the E_{2g} phonon for hydrogen also decreases at a pressure of 100 GPa (though it could be measured). Evidence for additional phonon structure in the low-frequency spectra of hydrogen above 100 GPa was also reported, though the signal-to-noise ratio for these features was low because the bands are weak and because of stress-induced diamond fluorescence.[15] We emphasize that loss of spectral bands above 100 GPa alone should not, in general, be taken as evidence for a transition because these Raman bands become increasingly difficult to measure as a result of the diamond fluorescence (see Ref. 33); positive evidence is required to establish the existence of a phase transformation. Notably, infrared spectra of hydrogen show continuity of the phonon-vibron combination bands over these pressure ranges at both 295 K (Ref. 34) and liquid-nitrogen temperature.[35] However, a new vibron infrared absorption band has been observed near 110 GPa (77 K),[35] which has been identified as a new phase transition in this isotope. It would be useful to extend these infrared measurements to deuterium to examine the infrared signature of the transition observed in the present study of deuterium.

D. Comparison with theoretical calculations

A number of calculations of the transition pressure for orientational ordering in the hydrogen isotopes have been performed, particularly for the pure systems ($J=0$ and 1 solids at zero temperature). The early calculations were performed assuming the ordered phase has cubic $Pa3$ structure (e.g., Refs. 36–39). The persistence of the hcp structure to pressures of at least ~100 GPa for both isotopes is consistent with the results of recent theoretical calculations which indicate that structures based on hcp are stable relative to cubic (e.g, $Pa3$) at high densities.[4,7,40–42] Kaxiras, Broughton, and Hemley[7] have performed an extensive series of calculations of different molecular ordering schemes within hcp. A new class of oriented hexagonal structures based on a herringbone-type configuration has been found to be energetically favored and to have larger band gaps than those of the structures assumed in previous work. Whether or not the 65–100 GPa transition identified here may be similar to such a structure remains to be investigated. This assignment is consistent with the experimental evidence for a band gap (insulating state) to high pressures (i.e., to at least ~150 GPa), which is one of the key problems with previously proposed ordered hexagonal structures (see Refs. 4 and 7). Recent theoretical work by Surh, Barbee, and Mailhiot[43] also points to the possibility of a transition of this general type in D_2 occurring at these pressures.

Runge *et al.*[44] have suggested on the basis of path-integral Monte Carlo calculations that ortho-D_2 orders into the fcc lattice (whereas para-H_2 orders in hcp), with a transition to hcp at some higher pressures. Our results demonstrate that ordering in D_2 does not occur on the fcc lattice over the temperature interval of 77–295 K and at 10 to at least 100 GPa. Further work is required to determine the P-T stability field of the phases as function of pressure, temperature, and ortho-para concentration. Specifically, the phase relations at both low temperatures (<77 K) and low pressures (down to 0.5 GPa) and at very high pressures (above 50 GPa) need to be studied in more detail. Determination of the crystal structures of the phases should be possible by low-temperature single-crystal x-ray-diffraction techniques.[45]

E. 150-GPa phase transition

The high-pressure phase transition associated with the high-frequency vibron discontinuity is now well established in both hydrogen and deuterium at 150–165 GPa.[2,8,22,46] A notable feature of the present study is the coincidence between the frequency shift of the low-frequency band at the pressure of this transformation (most accurately determined in experiment 1). We first consider the hypothesis that this feature arises from an excitation in bulk deuterium. If one assumes that the band is continuous with a low-pressure $S_0(0)$ peak and is thus indicative of the persistence of rotational disorder in the high-pressure phase, the frequency drop suggests an expansion of the bond of ~10%. This shift may be compared with the decrease in vibron frequency across the transition (3.5% for D_2),[21,22] both of which are consistent with bond weakening at the phase transition.[1,2,35] Additional features appear in the spectra above 160 GPa (Figs. 1 and 2). It is compelling to ascribe these peaks to new Raman bands associated with structural or ordering transitions at higher pressures (i.e., phonon or librational excitations).

If the spectral features described above are associated with the high-pressure phase of deuterium, however, we must postulate that the additional low-frequency bands at 200–300 cm^{-1} that appear *below* the phase transformation (Fig. 2) are associated with other phenomena. Recently, we showed that an intense band at 250 cm^{-1} appears in samples of H_2 and D_2 at pressures above 150 GPa but in some cases below the vibron discontinuity.[16] This band may be attributed to a pressure-induced diamond-hydrogen interaction,[33] a new phase of carbon (perhaps also induced by the presence of hydrogen), or to a new nonvibrational excitation.[16] Examination of the spectra measured to date suggests that there could be two distinct bands in this region, one associated with a rotational (or librational) excitation in bulk D_2 and the stronger feature associated with other phenomena and appearing before the vibron discontinuity.[16] The latter appears to be a precursor to diamond fluorescence and eventual anvil failure at higher pressures. Indeed, an additional complication to arriving at a unique interpretation of these results is both the broadband and sharp fluorescence features in the spectra that appear at the highest pressures (e.g., Figs. 1 and 5).[16] The measurements of the Raman spectra as a function of spatial position on the sample and gasket at the highest pressures (170–200 GPa; e.g., Fig. 5) indicate that additional excitations that do not arise from bulk D_2 contribute to the spectra.[16] Further characterization of these features is essential for interpreting the spectra of hydrogen and deuterium at these pressures and for examining additional pressure-induced transformations above 150 GPa.

V. CONCLUSIONS

Low-frequency Raman measurements of molecular deuterium provide evidence for changes in the solid in three distinct pressure ranges (at 77 K). At low pressures (< 30 GPa), the width of the $S_0(0)$ band increases together with a decrease in the intensity of the $S_0(1)$ and $S_0(2)$ bands. At intermediate high pressures (60–100 GPa) we observed a cusp in the pressure dependence of the $S_0(0)$ frequency, a decrease in the width of the $S_0(0)$ and E_{2g} phonon bands, and a decrease in the intensity of the E_{2g} phonon. This is interpreted as evidence for a structural and/or orientational phase transition in the molecular solid. The behavior of H_2 and D_2 at megabar pressures and comparable temperatures differs: the two systems may exhibit different states of order under these conditions, an effect that could be associated with differences in the effective ortho-para state of the samples. At the highest pressures in the vicinity of the vibron discontinuity (> 160 GPa), abrupt changes in the low-frequency band are also documented. These may be interpreted as arising from expansion of the molecular bond, consistent with the drop in the vibron frequency, or a change in orientational order, across the transition. There is also evidence for other transformations, including pressure-induced interactions between diamond and the deuterium samples in the high-pressure phase.

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[1] H. K. Mao and R. J. Hemley, Am. Sci. **80**, 234 (1992).

[2] R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **61**, 857 (1988).

[3] J. van Kranendonk, *Solid Hydrogen* (Plenum, New York, 1983), p. 306.

[4] N. W. Ashcroft, in *Molecular Solids Under High Pressure,* edited by R. Pucci and G. Piccitto (Elsevier, Amsterdam, 1991), p. 201.

[5] A. Garcia, T. W. Barbee, M. L. Cohen, and I. F. Silvera, Europhys. Lett. **13**, 355 (1990).

[6] H Chacham and S. G. Louie, Phys. Rev. Lett. **66**, 64 (1991).

[7] E. Kaxiras, J. Broughton, and R. J. Hemley, Phys. Rev. Lett. **67**, 1138 (1991).

[8] R. J. Hemley and H. K. Mao, Science **249**, 391 (1990).

[9] H. K. Mao, A. P. Jephcoat, R. J. Hemley, L. W. Finger, C. S. Zha, R. M. Hazen, and D. E. Cox, Science **239**, 1131 (1988).

[10] V. P. Glazkov, S. P. Besedin, I. N. Goncharenko, A. V. Irodova, I. N. Makarenko, V. A. Somenkov, S. M. Stishov, and S. S. Shilsteyn, Pis'ma Zh. Eksp. Teor. Fiz. **47**, 569 (1988) [JETP Lett. **47**, 661 (1988)].

[11] R. J. Hemley, H. K. Mao, L. W. Finger, A. P. Jephcoat, R. M. Hazen, and C. S. Zha, Phys. Rev. B **42**, 6458 (1990).

[12] R. J. Hemley, H. K. Mao, J. Z. Hu, and L. W. Finger, Eos Trans. Am. Geophys. Union **71**, 1620 (1990).

[13] L. W. Finger, H. K. Mao, R. J. Hemley, and J. Z. Hu, Bull. Am. Phys. Soc. **36**, 529 (1991).

[14] R. J. Hemley and H. K. Mao, in *Shock Compression of Condensed Matter-1991,* edited by S. C. Schmidt, R. D. Dick, J. W. Forbes, and D. G. Tasker (Elsevier, New York, 1992), p. 27.

[15] R. J. Hemley, H. K. Mao, and J. F. Shu, Phys. Rev. Lett. **65**, 2670 (1990).

[16] R. J. Hemley and H. K. Mao, Phys. Lett. A **163**, 429 (1992).

[17] I. F. Silvera and R. J. Wijngaarden, Phys. Rev. Lett. **47**, 39 (1981).

[18] R. J. Wijngaarden, V. V. Goldman, and I. F. Silvera, Phys. Rev. B **27**, 5084 (1983).

[19] I. F. Silvera, Rev. Mod. Phys. **52**, 393 (1980).

[20] H. K. Mao, P. M. Bell, and R. J. Hemley, Phys. Rev. Lett. **55**, 99 (1985).

[21] R. J. Hemley, H. K. Mao, and M. Hanfland, in *Molecular Systems Under High Pressure,* edited by R. Pucci and G. Piccitto (Elsevier, Amsterdam, 1991), p. 223.

[22] R. J. Hemley and H. K. Mao, Phys. Rev. Lett. **63**, 1393 (1989).

[23] R. J. Hemley, P. M. Bell, and H. K. Mao, Science **237**, 605 (1987).

[24] H. K. Mao, in *Simple Molecular Systems at Very High Density,* edited by A. Polian, P. Loubeyre, and N. Boccara (Plenum, New York, 1989), p. 221.

[25] R. J. Hemley, M. Hanfland, and H. K. Mao (unpublished).

[26] For this analysis, we used a summation of pseudo-Voight functions (Lorentzian and Gaussian peaks of variable area) for the rotational bands and a Gaussian for the phonon. When the $S_0(1)$ band evolved to form a broad shoulder on the stronger $S_0(0)$, we then replaced the sum of Voight functions with a single asymmetric Voight function with different widths above and below ν_0.

[27] H. K. Mao and R. J. Hemley, Nature **351**, 721 (1991).

[28] P. Loubeyre, M. Jean-Louis, and I. F. Silvera, Phys. Rev. B **43**, 10 191 (1991).

[29] R. J. Hemley and H. K. Mao, Annu. Rep. Dir. Geophys. Lab. **1990**, 141 (1991).

[30] A. P. Jephcoat, H. K. Mao, L. W. Finger, D. E. Cox, R. J. Hemley, and C. S. Zha, Phys. Rev. Lett. **59**, 2670 (1987).

[31] J. H. Eggert, R. J. Hemley, and H. K. Mao (unpublished).

[32] P. J. Berkhout and I. F. Silvera, J. Low Temp. Phys. **36**, 231 (1979).

[33] H. K. Mao and R. J. Hemley, Science **244**, 1462 (1989).

[34] H. Hanfland, R. J. Hemley, H. K. Mao, and G. P. Williams, Phys. Rev. Lett. **69**, 1129 (1992).

[35] M. Hanfland, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. **70**, 3760 (1993).

[36] J. Felsteiner and Z. Friedman, Phys. Rev. B **8**, 3996 (1973).

[37] W. England, J. C. Raich, and R. D. Etters, J. Low Temp. Phys. **22**, 213 (1976).

[38] A. Lagendijk and I. F. Silvera, Phys. Lett. **84A**, 28 (1981).

[39] W. B. L. M. Janssen and A. van der Avoird, Phys. Rev. B **42**, 838 (1990).

[40] S. Raynor, J. Chem. Phys. **87**, 2795 (1987).

[41] T. W. Barbee, A. Garcia, M. L. Cohen, and J. L. Martins, Phys. Rev. Lett. **62**, 1150 (1989).

[42] H. Nagara and T. Nakamura, Phys. Rev. Lett. **68**, 2468 (1992).

[43] M. P. Surh, T. W. Barbee, and C. Mailhiot, Phys. Rev. Lett. **70**, 4090 (1993).

[44] K. J. Runge, M. P. Surh, C. Mailhiot, and E. L. Pollock, Phys. Rev. Lett. **69**, 3527 (1993); **70**, 2974(E) (1993).

[45] P. Loubeyre, R. LeToullec, J. P. Pinceaux, H. K. Mao, J. Hu, and R. J. Hemley (unpublished).

[46] H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, Phys. Rev. Lett. **63**, 2080 (1989).