Isotope Effects in Dense Solid Hydrogen: Phase Transition in Deuterium at 190 ± 20 GPa

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Raman measurements of solid normal deuterium compressed in a diamond-anvil cell indicate that the material undergoes a structural phase transformation at 190 ± 20 GPa and 77 K. Spectroscopically, the transition appears analogous to that observed in hydrogen at 145 ± 5 GPa. The large isotope effect on the transition pressure suggests there is a significant vibrational contribution to the relative stability of the solid phases of hydrogen at very high densities.

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Once the exclusive domain of theoretical study, the behavior of hydrogen at ultrahigh pressures is now amenable to direct experimental investigation using ultrahigh-pressure diamond-anvil techniques.[1,2] The goal of this effort has been the characterization of hydrogen above 100 GPa, and in so doing, the testing of theoretical predictions of the insulator-metal transition pressure in this material, currently placed at 150 to 300 GPa.[3-6] We have demonstrated that solid hydrogen undergoes a phase transition at 145 GPa (77 K).[1] As discussed previously, the transition is structural and possibly associated with orientational ordering.[1] Recently, we have shown that on further increase in pressure the optical properties of the high-pressure phase change dramatically.[2] Above 200 GPa there is evidence found for ground-state electronic excitations at visible wavelengths, and at pressures in the 250-GPa range hydrogen samples are nearly opaque. These observations have led to the possibility that the transition at 145 GPa may be associated with band overlap.[2] If so, optical spectra, including both absorption and reflectivity measurements, indicate that the gap must be indirect. This interpretation is consistent with theoretical predictions that band overlap may occur below 200 GPa and that the gap is indirect (for the structures examined).[3-6]

An important constraint on the nature of phase transitions in solid hydrogen is provided by the study of isotope effects. There appears to be a significant isotope effect on the orientational-ordering transformation in the molecular solid, on the basis of phonon and roton measurements carried out below 100 GPa.[7,8] The ordering transformation occurs at significantly lower pressures in D_2 than in H_2 because of the lower rotational constant of the heavier isotope; this appears to be the case for both the pure $J=0$ solids and ortho-para mixtures.[7] There is also a pronounced isotope effect on the Raman-active vibron. In both hydrogen and deuterium, the frequency of the vibron increases with pressure but then decreases above a critical pressure. In H_2 the critical pressure is 30 GPa whereas in D_2 it is shifted to 50 GPa.[9,10] This weaker negative pressure shift of the D_2 vibron shift is magnified at higher pressures: at 125 GPa, for example, the vibron frequency in D_2 is about 40 cm^{-1} above, whereas in H_2 it is about 40 cm^{-1} below, the respective zero-pressure values. One explanation for these results is that the equations of state of the two solids are significantly different at very high densities; that is, if the vibron shift is strictly a function of volume, these results could indicate that hydrogen is significantly more compressible than deuterium at high pressures. Direct measurements at low pressures indicate, however, that the compressibility of the two solids are similar.[11] Alternatively, the difference in frequency shift with pressure may be associated with the higher anharmonicity of hydrogen due to its larger zero-point motion.[12]

In previous static compression work on deuterium, optical measurements to maximum pressures of 125 GPa (300 K) were performed.[10] In the present study we have pressurized deuterium in the 250-GPa range to examine possible transformations in the region of the major

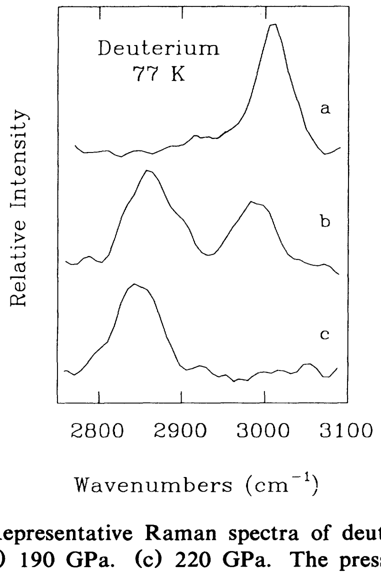

FIG. 1. Representative Raman spectra of deuterium. (a) 178 GPa. (b) 190 GPa. (c) 220 GPa. The pressures correspond to those determined from ruby located within 5 μm of the measured hydrogen volume.

structural change observed in hydrogen. Specifically, these measurements permit us to test the possibility that the transition in hydrogen is associated with orientational ordering. The experiments were performed using techniques described previously.[1,2] In these experiments, 20-50-μm-diam diamond-anvil tips are used; this produces a thin sample and sharp pressure gradients at the highest pressures. The Raman-active vibron was measured as a function of pressure using micro-optical techniques. The pressure was determined using the ruby-fluorescence method[13,14] to pressures of 240 GPa. Because of the use of low-fluorescence diamonds and the high sensitivity of the optical system, time-resolved techniques[15] were not needed to measure the ruby-fluorescence spectra to the maximum pressures.

Representative spectra of solid molecular deuterium at 77 K in the region of the Raman-active vibron are shown in Fig. 1, and the pressure dependence of the vibron frequency to pressures above 200 GPa is summarized in Fig. 2. A single, well-resolved band which decreases in frequency with pressure above 50 GPa was observed initially, as in previous studies.[9,10] Above 100 GPa, the negative pressure shift of the vibron, measured here at 77 K, converged with that measured previously at room temperature to 125 GPa, and continued to higher pressures. At 190 ± 20 GPa, however, a second, broader peak appeared 130 ± 5 cm^{-1} below that of the first. The two peaks coexisted over a small pressure interval with the intensity of the new peak growing at the expense of the first with increasing pressure. With further increase in pressure, the higher-frequency peak completely disappeared. The second peak continued to decrease in frequency with increasing pressure; at the highest pressures attained the frequency of the peak was 2793 cm^{-1}. The pressures could not be determined reliably above 240 GPa as a result of the decrease in the ruby-fluorescence intensity. We estimate a maximum pressure on the deuterium of 240-280 GPa was reached.[2,16]

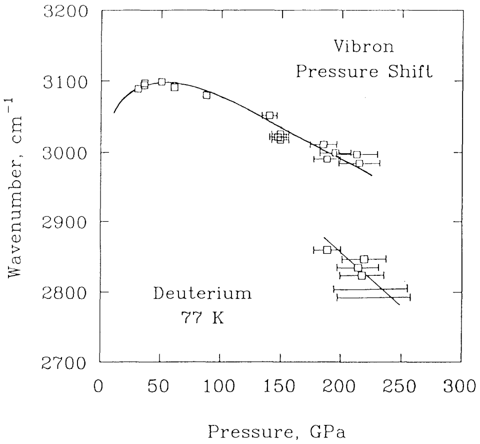

FIG. 2. Pressure shift of the Raman-active vibron of molecular deuterium to ultrahigh pressures. The second, lower-frequency vibron first appeared at a ruby pressure of 190 ± 20 GPa. The two peaks coexisted over a pressure interval of approximately 20 GPa, with an average separation of 130 cm^{-1} between them. The width of the mixed-phase region is likely to reflect the magnitude of pressure gradients in the sample across the ~5-μm laser spot (i.e., separate hydrogen-containing regions at slightly different pressures may be probed by the laser in a single measurement). The mixed-phase behavior could also represent sluggish transformation kinetics. A similar two-phase region was observed in the transition in hydrogen (Ref. 1). The error bars for the higher-pressure points include the uncertainties arising from the broadness of the ruby R_1 peaks and the effects of the estimated pressure gradients. The pressure could not be measured directly for the highest-pressure spectra. At these pressures, the sample had completely transformed to the high-pressure phase, as in Fig. 1.

The appearance of the second, broader vibron and the coexistence of the two peaks over a small pressure interval strongly resemble what was recently observed in hydrogen.[1] The phase diagram for hydrogen presented by Silvera[7] indicated that the orientational-ordering transformation should occur near the pressure-temperature conditions of the transition observed previously for hydrogen.[1] Since the orientational ordering in deuterium is reported to occur at lower pressures, the present results indicate the transitions observed for the two isotopes at ultrahigh pressures are not associated with a simple ordering mechanism (i.e., of the type documented for the low-density solid). Hence the previously proposed phase diagram[7] is incorrect, and the phase relations in hydrogen at high densities are likely to be more complicated than previously thought. This conclusion is consistent with recent experiments reported by Lorenzano, Silvera, and Goettel.[17] The present measurements do not preclude the possibility that minor structural changes occur below the major transition at 190 GPa, if such transitions give rise to smaller (< 15 cm^{-1}) discontinuities in the vibron frequency.

Despite the uncertainties in pressure, the present data clearly indicate that the transition in deuterium occurs at a higher pressure than that in hydrogen (190 vs 145 GPa). In addition, the vibron discontinuity is larger in the heavier isotope (130 vs 100 cm^{-1}).[18] At present we cannot rule out the possibility that the difference in transition pressure may be associated in part with kinetic effects, in which case the higher transition pressure in deuterium could arise from sluggish kinetics associated with its heavier mass. Possible differences in transition kinetics for the two isotopes can be checked by reversing the transition; however, it is typically difficult to decompress samples at these high pressures in a controlled fashion without loss of the sample. Alternatively, the different transition pressures represent differences in phase stabilities for the two isotopes. If so, the difference implies a significant vibrational contribution to the phase stability in hydrogen at very high densities.

Such a difference is in fact consistent with previous observations of isotope effects on the vibrational dynamics of dense molecular hydrogen. The weaker pressure dependence of the vibron in deuterium relative to hydrogen at high pressures was noted above.[10] The transition in deuterium occurred when the vibron reached a value of 2990 cm^{-1}, which is close to its zero-pressure value; in contrast, the hydrogen transition occurred when the vibron was approximately 100 cm^{-1} below its zero-pressure value. The more pronounced pressure dependence of the vibron frequency for hydrogen indicates that the molecules in this solid are significantly more anharmonic than in deuterium at a given pressure (density). Ashcroft[12,19] has shown that the different pressure dependences of the vibron frequencies may arise from large differences in zero-point energy for the two isotopes. If the phase transitions in the two isotopes involve the same crystal structures, it is possible that the differences in zero-point energy may also be responsible for the higher phase-transition pressures for the heavier isotope. Moreover, since the difference in zero-point energy for the two isotopes is expected to be comparable to the energy differences between different structures,[12,19] it is also possible that the two isotopes crystallize in different structures at high pressures and have a different series of phase transitions in the molecular solid prior to metallization (and perhaps into the metallic regime). The insulator-metal transition itself remains a possibility for the structural transition.[2] In fact, recent theoretical calculations indicate that band overlap could occur in the molecular phase as low as 150 GPa.[6,19] Measurements of absorption and reflection spectra of deuterium to examine this question will be presented elsewhere. At the point of band overlap, electron density will be removed from the molecular bonds to conduction states, causing a decrease in frequency of the molecular vibron. The magnitude of this frequency shift could therefore provide useful constraints on the mechanism of band overlap in the molecular phase.

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