Invariant Points and Phase Transitions in Deuterium at Megabar Pressures

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An extensive and detailed study of deuterium to 200 GPa and 20–300 K reveals a number of new features of its phase diagram. A well-defined Raman vibron discontinuity is observed across the I-III phase line above the I-II-III triple point at 167 GPa and 130 K. Evidence for additional invariant points is found, including one at 182($\pm$3) GPa and 235($\pm$15) K where the discontinuity disappears. Measurements of the phase III vibron reveal a new functional dependence of the order parameter with temperature and a previously undisclosed parallel to classical orientational phase transitions.

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Study of the phase transitions of hydrogen at megabar pressures ($>$100 GPa) is essential for understanding the evolution of the solid from a system of weakly interacting molecules at low density to theoretically predicted monatomic states at high compressions [1]. Recent work demonstrates that at least three distinct molecular phases persist to these pressures [1]: phase I, the rotationally disordered lower pressure phase with the hcp structure [2,3]; phase II, the low-temperature symmetry-breaking phase [4–7]; and phase III, which is stable above 150 GPa. The latter is characterized by a large discontinuity in the Raman and IR vibrons [6–10], a sharp decrease of the vibron discontinuity which disappears above a critical [11] or tricritical [12] point, and a dramatic increase of the infrared vibron oscillator strength [6,13]. These results have recently inspired a large number of theoretical studies [13–24], some of which indicate the possibility of new phenomena (e.g., Refs. [14,15]).

Despite these recent experimental and theoretical advances, there remain fundamental questions, if not considerable confusion concerning the high-pressure transformations and phase diagram of hydrogen. Mao and Hemley [1] reported the basic configuration of the phase diagram in which three phase boundaries (I-II, II-III, and I-III) meet at an invariant (triple) point above which the I-III transition is discontinuous but the discontinuity diminishes with temperature. On the other hand, Cui et al. [7] presented a similar phase diagram for deuterium but reported no discontinuity in either Raman or IR vibron at the I-III transition. Consequently, they concluded that the proposed critical point in hydrogen [11] is actually a triple point (see also Ref. [17]). The existence of a critical versus a triple point defines the symmetry differences between phases I and III and thus has fundamental implications for the crystal structure, which is currently unknown at these pressures. Moreover, the nature and extent of the orientational ordering in phase III has not been established [4,8,25]. These uncertainties present major obstacles to further theoretical understanding of the electronic properties of the dense solid [13–24].

The present study resolves several of these questions but raises new issues. We report major improvements in experimental resolution and a comprehensive mapping in *P-T* space. We show that the triple point in deuterium is, in fact, distinct from the higher temperature critical or tricritical point. Moreover, we have discovered a number of new features of the phase diagram, including evidence for additional transitions. We performed accurate measurements of the vibron frequency as a function of temperature and pressure to determine the nature and extent of molecular ordering. The results reveal a new functional form for an order parameter derived from the vibron frequency shift, a result which parallels the behavior of classical orientational transitions.

To improve the resolution over previous work, a high-dispersion, high-throughput, 1.33-m MacPherson spectrograph equipped with a charge-coupled-device detector was used for measuring Raman spectra. We overcome the problem of pressure-induced anvil fluorescence [7] by careful selection of the diamond anvils and use of variable laser excitation wavelengths with both Ar and Kr ion lasers (488.0–647.1 nm excitation). High-purity normal deuterium was loaded at room temperature into a multimegabar Mao-Bell diamond-anvil cell modified with a helium diaphragm drive [26]. Pressure variations in the sample were minimized ($<$4 GPa at the highest pressures) by the use of a small sample diameter ($\sim$10 μm). The diamond cell was mounted in a custom-built continuous-flow optical cryostat, which provided excellent temperature control and stability, critical factors in the present study. Pressures were determined from the vibron frequency which was previously calibrated against the ruby gauge [5,12]. For every diaphragm pressure (load on the sample), several temperature cycles were made, and the vibron carefully monitored to ascertain possible sample pressure shifts. After pressure stability and reproducibility were assured (usually on the second cycle), spectra were measured as a function of temperature. More than 800 Raman spectra were measured at pressures up to 200 GPa and at temperatures ranging from 20 to 300 K,

mostly concentrated near phase boundaries where data were taken at 1–2 K per step. This exhaustive effort contrasts to previous work, where only a few P-T points obtained from limited temperature scans were reported.

The I-II transition is characterized by a pressure-dependent change in vibron frequency of $|\Delta\nu| < 10$ cm^{-1}. In contrast, the II-III transition is associated with a large vibron frequency decrease ($\Delta\nu \sim 100$ cm^{-1}), and the I-III transition has a comparable discontinuity which decreases with temperature. Numerous temperature cyclings were performed to examine possible hysteresis of the transitions. The transitions were found to be reversible with no detectable hysteresis. When two coexisting phases were observed, the P-T range of coexistence and the relative intensity of the two phases were entirely consistent with the small residual pressure gradient (2–4 GPa) in the sample. The P-T phase diagram is shown in Fig. 1 [27].

At the I-III phase boundary above the triple point, the separation of the vibrons of the two coexisting phases is 40 cm^{-1}; this is significantly larger than the widths of the individual peaks of phases I and III (FWHM = 15 and 20 cm^{-1}, respectively), clearly indicating a discontinuity in the Raman vibron (Fig. 2). However, the discontinuity decreases rapidly with increasing P-T along the I-III boundary, and eventually the two peaks merge into an overlapping doublet. Meanwhile, the temperature dependence of the vibron frequencies $\nu(T)$ changes sharply at the I-III transition, from being nearly temperature independent in phase I to having a steep increase with temperature in phase III. This sharp change, combined with a small yet finite pressure gradient in the sample, can also produce the apparent overlapping doublet or a peak with a shoulder even without a vibron discontinuity.

In order to determine the limits for detecting a small first-order discontinuity, we utilized the improved resolu-

FIG. 2. Representative Raman spectra of the vibrons as a function of temperature at 168 GPa. The solid lines are fits to the data [28].

tion of the spectra and deconvoluted the contribution to the two peaks by taking into account the presence of a pressure gradient [28]. The latter one needs a simple analytical approximation for $\nu(T)$ in phase III. We found a formula that describes the experimental data very well: $\nu(\tau < 1) = \nu_0 - (A/a)\{1 - \exp[-a(1 - \tau)^b]\}$, where $\tau = T/T_c$. We were able to fit all measured spectra with $b = 0.75$ and weakly pressure dependent $a = 2.3$ to 2.9. Figure 3 shows a detail of a spectrum obtained at 178 GPa
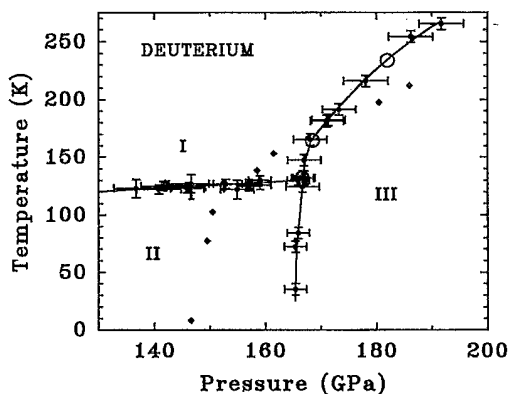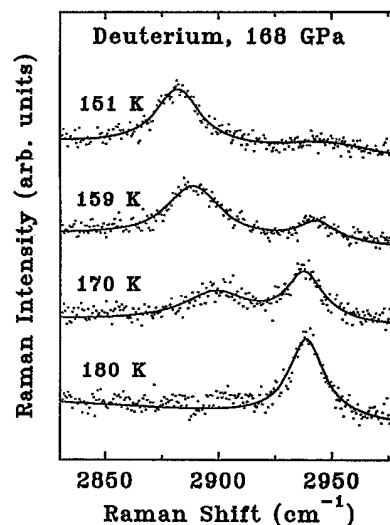

FIG. 1. Megabar phase diagram of deuterium. The small circles with error bars are from reversed isobaric temperature cyclings of this study. The larger open circles identify invariant points in the system. The diamonds are the results reported by Cui et al. [7].
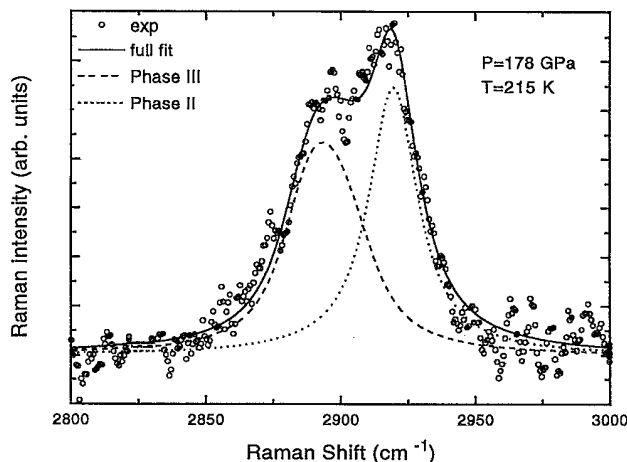

FIG. 3. Detail of a spectrum measured at 178 GPa and 216 K. The dashed lines are fits to the spectra assuming Lorentzian line shapes for both peaks [28]. The best-fit parameters are ν_0 (phase I) = 2905.0($\pm$2.5) cm^{-1}, $\Delta\nu$ = 9.0($\pm$4.5) cm^{-1}, linewidth γ = 11.0($\pm$0.1) cm^{-1} for both vibrons, T_c = 215.4($\pm$1.0), A = 260($\pm$16), and a = 2.51($\pm$0.2) with b = 0.75. The larger apparent linewidth for a phase III vibron (noted in previous work [8,10] but not explained) arises from the larger pressure dependence of the peak position in that phase (Fig. 4). This effect is stronger in the region where the frequency shifts rapidly with pressure (i.e., near the transition).

and 216 K, including the contributions to the observed line shape. A finite discontinuity of 9.5 cm^{-1} is observed at this point. Thus the I-III transition is discontinuous above the triple point p_1. The discontinuity becomes unresolvable (<4 cm^{-1}) at 186 GPa and 254 K, above which a continuous vibron shift is observed. This result is consistent with a second invariant point p_2 at 179–185 GPa and 220–250 K. If the I-III boundary changes from first order to second (or higher) order, this is a tricritical point; if the boundary formally ends, it is a true critical point.

This (tri)critical behavior requires the transition to be nonreconstructive. The functional dependence of the phase III vibron on $\tau = T/T_c$ reveals further insight into the nature of the transition. The behavior of vibron frequencies along a series of isobars is shown in Fig. 4. The total decrease in vibron frequency in phase III is about 100 cm^{-1}, independent of the continuous versus discontinuous extent of the transition [29].

We find there is a remarkable correspondence between the measured $\nu(\tau)$ and the order parameter $Q(\tau)$ for a Maier-Saupe orientational transition [30]. This transition describes, e.g., classical ordering of quadrupoles in the $Pa3$ structure [31] and ordering of nematic liquid crystals [30]. The agreement between the Maier-Saupe theory and our results is extremely good (cf. Fig. 4) except for the low temperatures, where quantum effects become more important. The theory includes a homogeneous external field γ, which in the fits shown on Fig. 4 increases by a factor of 2.5 from 168 to 188 GPa. The physical meaning of this field in our case is that the hexagonal lattice im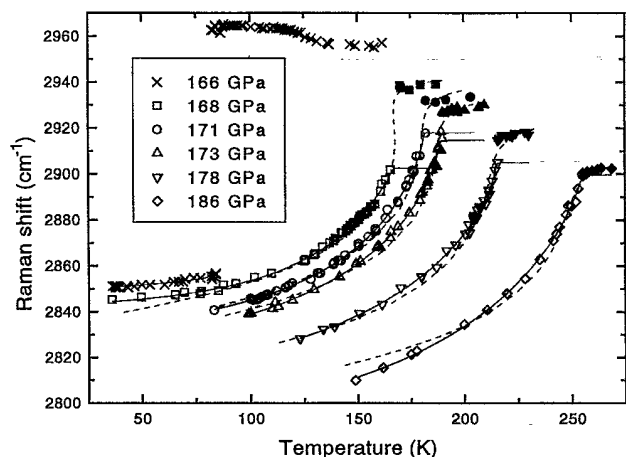poses a crystal field and thus an additional anisotropy compared to pure molecular field. That the effective field increases with pressure is consistent with the increase in density. In the Maier-Saupe model, when the field increases, the transition ends in a critical point, which in Fig. 4 would correspond to $P \approx 171$ GPa. Proper accounting for hexagonal anisotropy, instead of introducing an effective external field, may move the critical point to a higher pressure [32], approaching the (tri)critical point determined from the above phenomenological fit. Irrespective of the position of the (tri)critical point, the analyses indicate that in contrast to the I-II transition [1,4], the I-III transition is similar to classical orientational ordering.

Although the dramatic increase of the infrared vibron oscillator strength in phase III indicates a lower symmetry than phase I [1,7,13,20], this does not imply that the high-temperature phase at $P > 167$ GPa has the same symmetry as phase I. In other words, the existence of another phase transition, subtle but involving a symmetry change, at lower pressure cannot be ruled out. Notably, at 168 GPa and 166 K, the Clapeyron slope of the I-III boundary changes. In addition, measurements of the vibron in phase I as a function of pressure reveal a $\sim$10 cm^{-1} frequency decrease at this pressure. These changes suggest the existence of an additional higher-temperature phase (I$'$) and an additional invariant point p_3 (e.g., I-I$'$-III triple point). Note that if the point p_2 is critical (and not tricritical), phase I$'$ *must* have the same symmetry as phase III and thus be different from phase I.

The results of this study are summarized in the generalized phase diagram shown in Fig. 5, where we show the location of phase boundaries, invariant points, and regions of continuous and discontinuous changes in vibron frequency. The transition to phase III is associated with both continuous and discontinuous vibron shifts below p_2 but only continuous shifts above p_2, and this change is distinct from the location of the additional invariant points (p_1 and p_3). Previously reported changes in roton spectra, which led to the suggestion of an additional phase
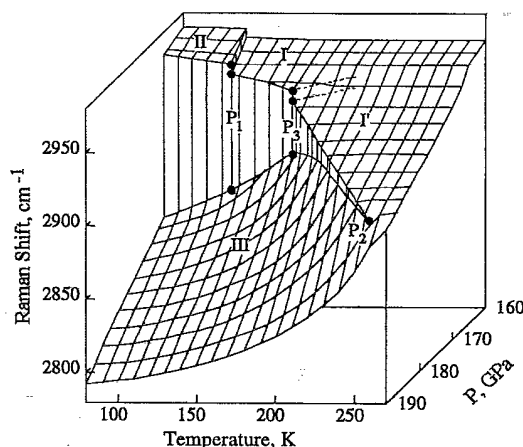

FIG. 4. Temperature dependence of the vibron frequencies for the I(II)-III transition at different pressures. Solid lines show T dependence of the order parameter for classical orientational ordering (Ref. [30]), defined as $Q + 1/2 = 3 \int_0^1 x^2 \exp[x^2 U(Q + \gamma)/T] dx / \int_0^1 \exp[x^2 U (Q + \gamma)/T] dx$. The dimensionless effective field γ changes from 0.008 (168 GPa) to 0.020 (188 GPa). Dashed lines show the phenomenological fit.

FIG. 5. Generalized P-T-ν phase diagram for deuterium. p_1, p_2, and p_3 refer to the proposed invariant points.

boundary running parallel to the I-III phase line [4], are likely to be associated with the fast but continuous frequency decrease below the transition temperature. There is now evidence for orientational order in both phases II and III. The new data indicate, however, that the two orderings are qualitatively different (e.g., different order of magnitude and opposite sign in the vibron shift, dramatically different IR activity, and the classical description demonstrated here for phase III); hence the structure and intermolecular interactions in phase III are fundamentally different. The work illustrates the importance of direct and accurate measurements and the continued richness of phenomena in this fundamental system.

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[27] Cui et al. [7] reported a significantly lower pressure value [$p_1 = 153(\pm 5)$ GPa, $128(\pm 2)$ K], although identical pressure calibration [12] was used. The lower value originated from the large pressure gradient in their samples and their use of the IR technique, which underestimates the phase III transition pressure when a large pressure gradient exists because of the high absorption of the phase III IR vibron [6,7].

[28] For the higher pressure spectra it is necessary to fit the spectra including the effects of pressure gradients. We assume that pressure gradients in the first approximation lead to a variation of the transition temperature T_c and pressure P_c across the sample which are related by $\Delta P_c = (dT_c/dP)\Delta T_c$, where $\Delta P_c = 2$–4 GPa [8,10]. The temperature dependence of the Raman frequency ν is assumed to be a function of $\tau = T/T_c$ only, and the observed spectra are a superposition of spectra at different P (and T_c) caused by a linear gradient across the sample. As such, we can write an analytical expression for the resultant spectrum in terms of $\nu(\tau)$ and its inverse function. This spectral function is convoluted with Lorentzian line shapes to take into account the intrinsic linewidth [A. F. Goncharov et al. (to be published)].

[29] This is what one expects for orientational ordering [1,4] where the order parameter Q changes from $Q \approx 0$ at $T \gtrsim U$ (U measures the orientational intermolecular interaction) to $Q \sim 1$ at $T \ll U$. Note that symmetry does not require that the free energy for such a transition be even with respect to Q, so the Landau expansion for the I-III transition should generally have cubic terms [see J. R. Cullen et al., Solid State Commun. **10**, 195 (1972)], and thus cannot give rise to a second-order transition, as proposed in [7].

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[32] An alternative interpretation is that the critical point is actually at 171 GPa. A sharp change in orientational ordering with temperature in the supercritical region [30] may render the appearance of a small discontinuity which causes the phenomenological fit to overestimate the limit of the first-order segment of the I-III transition.