Anomalous low-frequency excitations in diamond-cell studies of hydrogen at megabar pressures

R.J. Hemley and H.K. Mao

Geophysical Laboratory and Center for High-Pressure Research, Carnegie Institution of Washington, 5251 Broad Branch Road N.W., Washington, DC 20015, USA

Received 10 October 1991; accepted for publication 11 January 1992
Communicated by J.I. Budnick

We report observations of an intense Raman peak at 240 cm$^{-1}$ that appears abruptly above 150 GPa at low temperatures (e.g., 77 K) in diamond-cell samples of hydrogen and deuterium. The band disappears above a critical temperature. The spectral changes are interpreted as evidence for a new high-pressure transformation.

1. Introduction

The physics of highly compressed matter is of great current interest because of the new structural, dynamical, and electronic properties potentially attainable for materials at very high pressures. An excellent system for examining these phenomena is provided by solid hydrogen, which is predicted theoretically to exhibit a range of unusual properties at high pressures, including pressure-induced metallization. The characterization of solid hydrogen at very high densities has relied exclusively on spectroscopic techniques used with the diamond cell [1–9]. High-pressure Raman measurements of the vibron, for example, have documented the stability of the molecular solid to $\sim$250 GPa and the presence of a low-temperature phase transition at 150 GPa [1]. The phase transition was not anticipated by theory and has been the subject of several subsequent experimental studies [2–7]. Measurements of the Raman spectrum below 1000 cm$^{-1}$ to 162 GPa [5] and the observation of the termination of the phase boundary at a critical point [6] indicate that the phase transition does not involve crystallographic changes. The transition is not accompanied by a significant discontinuity in optical properties in the visible [2,7], but appreciable changes in near-infrared spectra begin at this pressure [8,9] and an increase in visible reflectance and absorption occurs at higher pressures ($>250$ GPa) [2]. That the transition is predominantly an electronic change, possibly due to indirect gap closure, with or without an associated minor structural or orientational transition, is consistent with the growing body of data.

In addition to the high-pressure phenomena recently documented in hydrogen, diamond itself has been shown to exhibit previously unknown optical and Raman transitions at these pressures (above 150 GPa) [2,10,11]. In fact, considerable effort has been directed toward discriminating between contributions to the high-pressure spectra from the sample and those from the diamond anvils. The high-pressure spectra of diamond itself are of intrinsic interest, in view of the importance of understanding the properties of carbon at ultrahigh pressures, particularly pressure-induced phase transitions in diamond [12]. Further characterization of hydrogen and diamond above 150 GPa is needed to understand the nature of the high-pressure, low-temperature phase of hydrogen (including its relationship to metallization) and to obtain more information on the behavior of diamond itself. In addition, detailed interpretation of the optical properties of hydrogen in diamond cells requires further information on the hydrogen–diamond interface [9], including possible physical and chemical interactions between the carbon and hydrogen samples at megabar pressures [2].

Measurements of low-frequency Raman spectra at
higher pressures are critically important for understanding the behavior of hydrogen and diamond above 150 GPa because such spectra are sensitive to the structural state of the materials [5,11]. The low-frequency rotational-librational bands of hydrogen vary continuously across the 150 GPa transition [5]. However, orientational ordering transitions are predicted in this pressure range (see, e.g., ref. [1]), and this ordering is expected to have a significant effect on electronic properties [13–15]. Such ordered states would give rise to characteristic changes in the low-frequency spectrum as the rotational excitations are replaced by new librational transitions. In the course of extending low-frequency Raman measurements of hydrogen to higher pressures [16], we have unexpectedly encountered an extremely intense feature in spectra of these diamond-cell samples. The band has an initial frequency of 240 cm$^{-1}$, appears abruptly at pressures above 150 GPa at low temperatures, and has an unusual temperature dependence. The behavior is interpreted as evidence for a new high-pressure transformation.

2. Methods

The experiments were performed on samples of hydrogen loaded in modified (Mao–Bell) megabar diamond cells, as in previous experiments [17]. Single-bevel type Ia diamonds having low (but often variable) fluorescence levels were used as anvils. Samples were loaded at room temperature, and the pressure was generally increased above 50 GPa while the sample was held below 100 K using a liquid nitrogen cryostat. The pressure was typically determined from small chips of ruby embedded in the samples [18]. The final relative volume of the ruby in the hydrogen at high pressure was less than 5% in most experiments but was varied over the range 0–25%. Several experiments were performed without ruby [19]; in these, the pressures were determined from the shift of the hydrogen or deuterium vibron, which has been calibrated against the ruby $R_1$ shift to pressures above 200 GPa [20].

The measurement techniques have been described previously [20,21]. An important feature of the measurements is the high spatial resolution achieved with our optical system. This is made possible by the angular incidence of the laser excitation and the close proximity of the lens used to collect the Raman signal while the sample is held at low temperature (windowless cryostat). As a result, we can probe the sample and tips of the diamond anvils (<10 µm surface layer) without spectral contributions from the interior of the anvils [21]. The high spatial resolution also makes it possible to completely eliminate possible optical spectral features from the ruby in those samples containing this material. Optical spectra were measured with variable wavelengths of argon-ion lasers to distinguish between Raman and fluorescence peaks.

In order to characterize such phenomena and to better understand the range of possibilities presented by new data, it is most important to assure the validity of the experimental observations. Measurement redundancy and control experiments on a variety of materials are critical in order to determine whether or not new optical features are due to hydrogen within the cell. This report represents a summary of results obtained from approximately thirty separate experiments on hydrogen and deuterium, including control experiments on other materials, each reaching pressures above 100 GPa. Experiments were also performed on hydrogen and deuterium samples differing in sample thickness from 0.5 to 3 µm. Combined with the spatial filtering techniques, the various sample thicknesses helped distinguish between spectral features of the sample and those of the anvil tips, since the larger fractions of the diamond are probed with thinner samples [21].

3. Results

Raman spectra of hydrogen as a function of pressure at 77 K are shown in fig. 1. These spectra were all measured above the 150 GPa transition [1]; that is, in each case the vibron characteristic of the high-pressure phase was measured along with the low-frequency region. The low-frequency region is characterized by broadened bands identified as large-amplitude librational bands that correlate with the $S_0(0)$ and $S_1(0)$ rotational envelopes observed at low pressure [5]. In addition, the sharper bands associated with the Raman-active optical phonons are
observed. The large number of runs that we have performed have allowed us to establish that these features are associated with bulk hydrogen. When the pressure is increased further, however, an intense peak at 240 cm$^{-1}$ grows in over a small pressure interval. The band undergoes a small frequency shift with pressure (e.g., reaching 280 cm$^{-1}$). The intensity of the peak is higher than that of the low-frequency envelopes observed at lower pressures and becomes even stronger than the high-frequency vibron. The peak also appears to be asymmetric, being slightly skewed to the high-frequency side.

Representative spectra from different experiments (distinct samples and diamond-anvil pairs) are compared in fig. 2. These experiments demonstrate that the 240 cm$^{-1}$ peak is reproducible in different samples, but its onset pressure can be variable (150 to 200 GPa). Spectra measured on decreasing pressure show that the new feature exhibits a large hysteresis, the band remaining at sample pressures as low as 50 GPa before disappearing (77 K). We performed a series of experiments using deuterium to obtain information on possible isotope effects on the measured spectra. Both the low- and high-frequency spectrum of deuterium were measured to pressures above its high-pressure transition [3,16,20]. In the first experiment, the intensity of the low-frequency peak increased dramatically at 195 GPa. Its frequency was within 10 cm$^{-1}$ of that of the peak observed with hydrogen, as shown in fig. 2. In a second experiment the transition appeared to occur at 160 GPa. In fig. 2, we also show the pressure-induced peak at 600 cm$^{-1}$, which has been shown to be due to diamond itself [11]. The appearance of the low-frequency Raman band is typically followed by the appearance of fluorescence bands at higher pressures.
that the band can remain strong even when the vibron is very weak. Also, the onset is not accompanied by a major discontinuity in the vibron frequency (any change $\Delta \nu$ is less than 2 cm$^{-1}$, unlike the 150 GPa transition where $\Delta \nu \approx 100$ cm$^{-1}$ [1]). We therefore conclude that the new Raman feature is not a librational (or other vibrational) mode associated with bulk hydrogen. A detailed study of the low-frequency librational and phonon modes of (bulk) hydrogen in the high-pressure phase will be presented elsewhere [16].

It is therefore possible that the band is a vibrational mode in a new phase of diamond forming at the tip of the anvil. The variable onset pressure could indicate that the onset is strongly dependent on non-hydrostatic stress conditions of the sample or diamond. These tend to vary from one run to the next because of differences in anvil geometry and gasket variability [17]. The appearance of the band precedes the onset of strong luminescence from the anvils. The new feature, however, does not correlate with any known bands in carbon phases (including vibronic transitions associated with defects in type I diamonds [23]), nor does it match stress-induced changes that we have documented so far in diamond anvils under similar conditions [11]. Experiments on samples of Ne, NaCl, and Al$_2$O$_3$ conducted to date have failed to show the peak, although in each case the 600 cm$^{-1}$ Raman band appears and strong luminescence starts at higher pressures [2,10,11]. This observation could mean that the transition is triggered by the presence of hydrogen and that the peak is due to diamond in the presence of hydrogen (or deuterium) either bound chemically or in contact physically as a distinct phase. For example, the transition may be associated with plastic flow of the diamond and could involve incorporation of hydrogen into the anvil either in microcracks or by pressure-induced chemical reactions [2]. The onset pressure of $>150$ GPa may then be indicative of higher chemical reactivity of hydrogen in its high-pressure phase. The lack of a significant shift on isotopic substitution indicates that the mode does not involve hydrogen or deuterium motions, and no other bands associated with known C–H (C–D) stretching vibrations have been observed. The high spatial resolution of the measurement shows that if the new feature arises from the anvil, the transformed por-

4. Discussion

The remarkable features of the new band are its high intensity, abrupt but variable onset pressure, and temperature dependence. It is important to examine whether the band arises from a structural or an orientational transition in bulk solid molecular hydrogen. In each of the measurements carried out so far, the new peak appears once the hydrogen samples have transformed to the high-pressure phase (above 150 GPa at 77 K). Since pressure-induced molecular ordering transitions are predicted in this $P$–$T$ range [1,16,22], one possible assignment for the new feature is a librational transition arising from an orientational ordering transition in the high-pressure phase above 150 GPa, as indicated above. However, the lack of an isotope effect, the variable onset pressure, and large hysteresis are inconsistent with this interpretation. Furthermore, the intensity of the new band does not scale with that of the vibron: we find
tion is highly localized at the tip, estimated to be within <10 μm of the sample. In view of the small volume of the transformed region, the very high intensity indicates that the scattering cross section for the band is remarkably large, exceeding that of both the hydrogen vibron and the T_{2g} diamond phonon. The results show there is a high degree of resonance enhancement (also observed for the 600 cm⁻¹ band of diamond [11]) although further work is required to determine a quantitative excitation profile. Finally, the temperature dependence of the band is not observed for the stress-induced Raman features previously shown to be intrinsic to diamond [11].

On the basis of the unusual temperature dependence and effect of isotopic replacement, it is useful to consider the possibility that the new band arises from a non-vibrational excitation (e.g., electronic Raman [24]). A key observation here is the fact that the transition occurs in the general pressure range of both the vibron transition and increases in near-infrared reflectivity and absorption in hydrogen [8,9]. It is important to emphasize, however, that the transformation documented here and that of the vibron do not have identical onset pressures and that no hysteresis is observed in the latter. Both the vibron discontinuity and the new Raman feature are not observed above critical temperatures, but the values for T_c differ [6]. It is useful to note that the critical temperature (∼180 K) for the new band is approximately half the excitation frequency. Raman excitations associated with low-energy excitons or the formation of an excitonic phase (ground state) [6], a superconducting gap (which can give rise to an asymmetric peak at 2Δ; see, e.g., ref. [25]), electron–hole condensation (perhaps photo-generated), or related phenomena showing critical behavior are possibilities to be tested. If hydrogen enters the high-pressure carbon structure, it could act as a doping impurity to produce unusual optical and electronic properties, perhaps analogous to the observations of novel properties in doped fullerenes (see e.g., ref. [26]). These possibilities must remain at this point speculative: examination of each, together with a more quantitative analysis than is currently possible, will require further measurements and the continued development of high-pressure techniques.

Acknowledgement

We are grateful to J.F. Shu, M. Hanfland, W. Vos, and R.E. Cohen for help with the experiments and/or useful discussions. This work was supported by N.S.F. (grant DMR-8912226 and EAR-8904080) and N.A.S.A. (grant NAGW-1722).

References