Onset of Metallization and Related Transitions in Solid Hydrogen

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The onset of metallization in highly compressed solid hydrogen and a corresponding discontinuity in molecular vibrations have been linked in the literature to band-gap closure in an ordered hcp structure. We performed extensive first-principles calculations on the energetics and the electronic properties of solid hydrogen, and explored in detail variations in molecular orientations, bond lengths, and the c/a ratio, within an hcp lattice. We find that the commonly assumed structure is energetically unfavorable, and that lower-energy structures have wider band gaps to much higher density. Implications for the onset of metallization are discussed.

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The physics of dense solid hydrogen has been the subject of theoretical inquiry for over half a century [1]. Static calculations predict that under pressure the insulating molecular phase will undergo a band-overlap transition to a molecular metallic form, before ultimately transforming to an atomic, metallic phase above about 300 GPa (3 Mbar) [2]. A large number of recent experimental results have shed new light on this problem [3]. Experimental studies to ~300 GPa indicate that the molecular solid is stable to at least 250 GPa but undergoes a phase transition at 150 GPa (77 K) [4]. This transition is characterized by a discontinuity in the intramolecular vibrational mode (vibron) indicative of an abrupt change in bonding, possibly related to the onset of metallization [5]. Optical absorption and reflectance spectra, which show features suggestive of metallic behavior [5,6], have also been measured in this pressure range [7]. High-pressure diffraction studies have established that solid hydrogen has a hexagonal-closed-packed (hcp) structure to at least 38 GPa (relative density $\rho/\rho_0 = 5.6$) [8], and spectroscopic measurements indicate that the underlying hexagonal lattice persists above 150 GPa ($\rho/\rho_0 > 9$) [9].

Interpretation of these observations requires a detailed understanding of the evolution of the electronic structure under pressure, including information on the effects of crystal structure and molecular ordering on the electronic states [10]. Recent calculations by Raynor [11] and by Barbee *et al.* [12] indicated that at high densities the hcp structure with the molecules aligned parallel to the c axis (structure a) is more stable than previously proposed cubic phases [2]. Ashcroft [10,13] has shown, however, that the structure a leads to band-gap closure at lower densities relative to other structures and that, in general, the onset of band overlap is sensitive to the orientation of the molecules. Garcia *et al.* [14] have attributed the 150-GPa vibron discontinuity to band-gap closure associated with an orientational ordering transition to structure a. Chacham and Louie [15], using Hedin's *GW* approximation [16] which gives accurate band gaps for semiconductors, found that band overlap in structure a occurs at 151 GPa. These two studies [14,15] also showed that band-gap closure is shifted to much higher pressures by a spherical average over molecular orientations.

In this work we report extensive first-principles calculations on the energetics and electronic properties of solid hydrogen at high densities. We investigated in detail a wide range of molecular orientations at different densities, as well as variations in the molecular bond length and the c/a ratio of the underlying hcp lattice. Our study has lead us to conclusions that differ from previous work. These are summarized as follows: (1) The ordered structure a assumed in a number of previous studies is energetically unfavorable, compared to other molecular orientations, over a wide range of pressures. (2) We find a direct and consistent correlation between the energy of a particular orientation and the band gap in the insulating phase: *The lower the energy, the wider the band gap.* (3) The pressure at which the *energetically favored* configurations exhibit band-gap closure in the static lattice is much higher than that of structures considered previously (i.e., structure a). (4) Calculations employing spherical averages over all molecular orientations overestimate the gap-closure pressure and misrepresent essential features of the band structure. (5) The effect of band-gap closure on the molecular bond is large and appears closely associated with the transition to a monatomic, metallic phase.

Our work is based on density-functional theory in the local-density approximation (LDA) [17]. The configuration space associated with the molecular hcp structure is spanned by eight independent variables: the two bond lengths and the four orientational angles that determine the exact arrangement of the two molecules in each hcp unit cell, the c/a ratio, and the overall density. For a given pressure the density is determined by the equation of state [18]. Thus, in order to determine the optimal structure, within the assumption of an hcp static lattice, a complete search over the remaining seven variables is needed. This is clearly beyond the scope of first-principles calculations, and only limited searches are feasible. We have performed an extensive search for low-energy structures, allowing for both symmetric and asymmetric orientations of the two molecules. At densities that give insulating phases, with the bond length fixed at 0.74 Å (the experimental value in free hydrogen molecules) and the c/a ratio fixed at 1.633 (ideal hcp structure), we find that configurations with the molecular axes lying close to the a-b plane of the hexagonal lattice have the lowest energy. This trend becomes more pronounced with increasing density, but is eventually reversed at extremely high densities. For clarity, we shall concentrate here on three different structures which are shown in Fig. 1: The first (a) has both molecules oriented along the c axis; the second (b) has both molecules lying on the a-b plane with the molecular axes bisecting the angles between lattice vectors; and the third (c) has the two molecular axes tilted off the a-b plane by $\pi/5$, while their projections on the a-b plane coincide with those of structure b. In structures b and c the projections of molecular axes on alternate planes form an angle of $\pi/3$. These structures were chosen because in the insulating phase they correspond to the highest energy and smallest band gap (a), an intermediate energy and band gap (b), and the lowest energy and largest band gap (c) among the configurations we considered. Interestingly, the lowest-energy configuration for a pair of *isolated* hydrogen molecules resembles most closely the arrangement of molecules in the unit cell of structure c [19]. Ashcroft has argued that structures similar to b will have large band gaps [13], which is consistent with our LDA results.

The configuration a has higher energy than either b or c for the range of densities where all three structures have a nonvanishing band gap (see Fig. 2). When the band gap of configuration a closes, the energy differences decrease, and eventually configuration a becomes the lowest-energy structure. Since the relative energy differences are sensitive to the presence or absence of a band gap, we attempted to estimate the effect on the energetics of the approximations used in the calculation. It is well known that LDA underestimates the band gap, whereas the *GW* approximation gives accurate results for semiconductor band gaps at normal pressure. The density dependence of the band gap is very close to linear [14,15] in the range $5 \leq \rho/\rho_0 \leq 10$. By expressing the band gap as $\varepsilon_{\text{gap}} = \varepsilon_1(\rho/\rho_0) + \varepsilon_0$ and comparing our LDA results to the results of the *GW* calculation [15] for structure a we find corrections to the LDA coefficients of $\Delta\varepsilon_1 = -0.2$ eV and $\Delta\varepsilon_0 = 4.0$ eV. These corrections can be used as a "scissor operator" applied to the antibonding states of our LDA calculation. The correction affects both the single-particle spectrum and the total charge density, providing a simple and straightforward correction to the total energy. This total energy, however, is not based on a self-consistent theory and further investigation of its validity is necessary. A scissor operator can be obtained from existing calculations for structure a only (no *GW* calculations exist for structures b and c). With this correction energetic comparisons can be made for densities up to $\rho/\rho_0 = 9.9$, since the LDA band gaps for structures b and c do not vanish up to this point. The corrected-LDA results indicate that structure a has higher energy than b or c to pressures beyond that of the vibron discontinuity (see Fig. 2).

We next consider the effect of relaxation of the c/a ratio and the molecular bond length, which in the calcula-

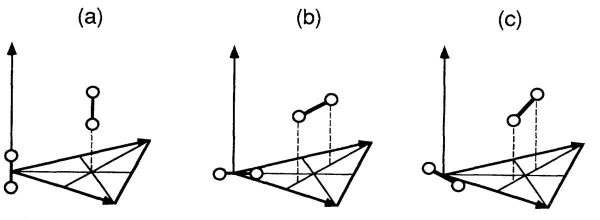

FIG. 1. The three molecular orientations a, b, and c discussed in the text. The arrows represent the lattice vectors of the hcp lattice.

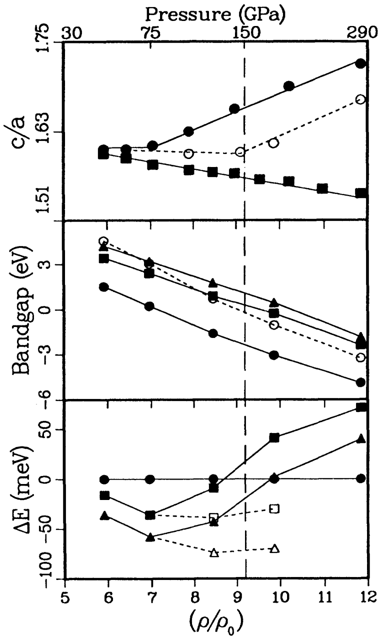

FIG. 2. Relative energy (in meV per hcp unit cell; bottom panel), indirect band gap (in eV; middle panel), and c/a ratio (top panel) as functions of relative density ρ/ρ_0. The circles correspond to structure a, the squares to structure b, and the triangles to structure c. Solid symbols are from the present LDA calculations; open symbols include "scissor" correction (see text). The pressure range (top abscissa) is obtained from the experimental equation of state (Ref. [18]). Lines are guides to the eye. The dashed line indicates the experimental vibron discontinuity pressure.

tions described above were held constant. There is experimental evidence that above ~20 GPa the c/a ratio decreases with increasing pressure. Our calculations indicate that the optimal c/a ratio for structure a remains close to the ideal value ($\sqrt{8/3}=1.633$) but starts increasing upon gap closure and eventually becomes *larger* than 1.633 at high densities. For structure b the optimal c/a ratio decreases monotonically and is always lower than the ideal value (see Fig. 2, top panel). Combining the information from the corrected-LDA relative energies and the behavior of the c/a ratio, we conclude that configuration a is the least favorable representation of the insulating phase. The calculated optimal bond length in all configurations is larger than the experimental value for free hydrogen molecules ($r_0=0.74$ Å) by approximately (3–4)%. The optimal bond length decreases with increasing density while the system is in the insulating phase, but starts to increase abruptly and continues to increase monotonically in the metallic phase (see Fig. 3). These results indicate that the molecular bonds undergo a significant weakening, akin to bond breaking, following closure of the band gap. Moreover, small changes in the bond length (of order few percent) give large variations in the band gap and consequently in the gap-closure pressure. Zero-point motion in free hydrogen molecules is of order 10% of r_0, and is even larger in the solid where the intramolecular interaction follows more closely a Morse-type rather than a parabolic potential [10].

Our final point concerns the effect of rotational motion on the electronic structure. Spectroscopic results indicate that up to at least 162 GPa the hydrogen molecules undergo significant rotational or large-amplitude librational motion [9]. Previous theoretical studies attempted to include the effects of rotational motion by considering the limit of a uniform average of the core charge on the surface of a sphere and calculating the bands of this average crystal structure [14,15]. However, this order of taking the limit is incompatible with the Born-Oppenheimer approximation. In addition, a spherical average imposes a symmetry on the electronic states that misrepresents essential features of the band structure. In structure a the minimum gap is in the ΓK direction which lies on the $k_z=0$ plane of the Brillouin zone (BZ) [14,15]. For the energetically favored structures b and c the gap along ΓK opens considerably, but the breaking of axial symmetry gives antibonding states of lower energy at the surface of the BZ, with $k_z=\pi/c$. The new minimum indirect band gap is no longer along ΓK. Similar effects on the band structure were predicted by Ashcroft on the basis of a two-plane-wave model [13]. The spherical average preserves the axial symmetry of structure a and the minimum indirect gap remains along the ΓK direction (see, e.g., Ref. [15]), which is unrealistic and leads to an overestimate of the gap-closure pressure.

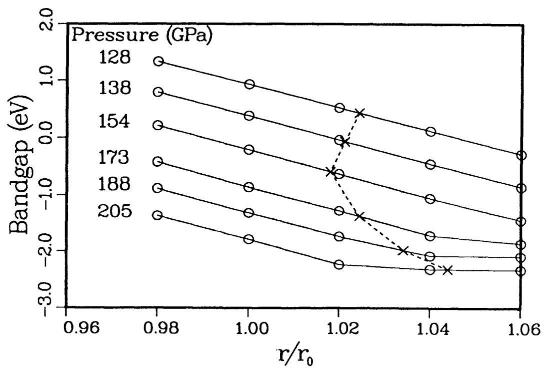

FIG. 3. Band gap as a function of relative bond length r/r_0 and pressure for structure a. The crosses indicate the optimal bond length. These results include the "scissor" correction (see text). Uncorrected results exhibit similar behavior, with the onset of gap closure at lower pressure (approximately 90 GPa).

Based on the above discussion, we infer that if there exists a dominant orientation, it should be similar to the structure c, with molecules tilted approximately $\pi/5$ out of the a-b plane; confirmation of the predicted new class of structures should be possible by measurement of superlattice reflections in the x-ray-diffraction pattern for hcp [8,13]. The spectroscopic evidence for the persistence of rotational motion to high pressure [9] can then be interpreted as arising from tunneling between low-energy configurations with molecular axes close to the a-b plane (with tilt angles between 0 and $\pi/5$), and formation of near-planar rotors in an anisotropic hcp structure [8,10]. It is possible that any discrete ordering transition may tend to *increase* the band gap, rather than decrease or close the gap as previously suggested [14]. Lastly, we conclude that zero-point motion, which affects both the bond lengths and orientational distributions of the molecules, is likely to have a profound effect on the band structure.

Our detailed study of the structure and energetics leads us to the following new insights concerning experimentally observed changes in hydrogen at 150 GPa. The vibron discontinuity may correspond to transitions among the low-energy hexagonal structures examined here (i.e., b and c, or molecular superstructures based on these configurations). Such transitions could give rise to a sudden change in the vibron frequency, as individual molecules sample a stronger effective intermolecular interaction after the transition, without any change in overall lattice topology. This would be consistent with the continuity of low-frequency lattice vibrational modes in the range of 150 GPa [9]. This interpretation does not presuppose metallic behavior, and it remains to be shown whether it is also consistent with other aspects of the vibron transition, namely, the observed isotope effect [3,20], temperature dependence [21,22], and critical point [22]. Alternatively, it is possible that the vibron discontinuity signals the onset of metallization, which may be driven by disorder (e.g., merging of band tails in the gap) or associated with a low-temperature excitonic phase [22]. This second possibility does not require a change in either crystal structure or ordering. Both possibilities are related to the range of molecular configurations that are allowed energetically and are induced by zero-point rotational and vibrational motion.

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[18] We use the experimental equation of state, which has been determined by x-ray diffraction to 38 GPa; see Ref. [8]. Extrapolation to higher pressures gives a lower bound on the density. Determination of the equation of state from the present static-lattice calculations neglects zero-point contributions and gives consistently higher densities than the experimental curve, in agreement with other LDA calculations [see R. J. Hemley *et al.*, Phys. Rev. B **42**, 6458 (1990)].

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