Theory of High-Pressure Phases of Hydrogen

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The electronic structure and enthalpy are calculated as a function of pressure for several phases of molecular and metallic hydrogen. For the molecular solid we offer an alternative interpretation of the recently observed transition at 1.5 Mbar. For the intermediate pressure range from 3.8 ± 0.5 to 8.6 ± 1 Mbar, the most stable structures have low coordination numbers and are anisotropic. Among them a metallic filamentary primitive-hexagonal phase is particularly stable. For higher pressures, the bcc structure is the most stable.

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Predictions of the transformation of solid molecular hydrogen into a metal under very high pressures date from the 1930's.[1] Recent theoretical studies[2–4] estimate the transition pressure to be in the few hundreds of GPa (few Mbar) range, and include the possibility of high-temperature superconductivity in the metallic phase. Detailed experimental data[5–7] are available for the 0 to ~50-GPa pressure range. Despite the fact that the highest pressure achieved in solid hydrogen,[8] above 200 GPa, is within the range of some of the predictions for metallization, it is generally agreed that metallic hydrogen has not yet been observed. Recently, some evidence for a structural phase transition in solid hydrogen was deduced[8] from a sudden drop in the vibron frequency observed at 150 GPa.

The "conventional wisdom" about the metallic phase of hydrogen is that it would have a structure with a dense packing of atoms (i.e., bcc, fcc, or hcp) like most other simple metallic elements. In their seminal paper[1] Wigner and Huntington speculated that molecular hydrogen could transform under pressure into a low-coordination layerlike structure since the elements on the metal-nonmetal borderline of the periodic table seem to prefer such structures. Our total-energy calculations of several phases of hydrogen give support to this point of view. Among the structures studied, a filamentary primitive-hexagonal (PH) phase is the most stable in the pressure range of 380 ± 50 to 860 ± 100 GPa. Below 380 GPa an oriented moleculer–hexagonal-close-packed (m-hcp) phase is found to be the most stable, while above 860 GPa the body-centered-cubic (bcc) phase is preferred.

Ab initio pseudopotential calculations of the total energy of solids using a plane-wave basis[9] and the local-density approximation[10] have been successful in predicting the structural[11] properties of materials under pressure. Here the true potential $1/r$ for hydrogen is used instead of a psuedopotential, along with the Ceperley-Alder[12] exchange and correlation energy functional. All results reported here were obtained with a basis set of plane waves with kinetic energy up to 36 Ry. Increasing the energy cutoff to 64 Ry causes only slight changes in the calculated bulk moduli and equilibrium volumes. The total energy for each of the selected crystal structures was calculated for several volumes, and the resulting data points were fitted with the Murnaghan[13] and Birch[14] equations of state as well as with cubic splines. The variation in the properties obtained from the different fits is used as an estimate of the *numerical* uncertainty of the results.

The zero-point-motion (ZPM) energy contribution to the total energy of solid hydrogen cannot be neglected. We therefore augmented our calculations for the clamped nuclei by adding an estimation of the harmonic ZPM energy at each volume; that is, we used the quasiharmonic approximation. The energies of several phonons in each structure were calculated[15] from first principles using the frozen-phonon method, and then phonon spectra from other elements in the same structure were scaled accordingly to estimate the ZPM energy. For low pressures, the ZPM energy of the molecular phase is dominated by the vibrational energy of the H_2 molecule ($\hbar\omega/2 = 0.25$ eV), whereas at very high pressures the ZPM energy of the dense metallic phases with Ω_p, the *proton* plasma frequency.

In Fig. 1, the calculated equation of state of hydrogen $p(V)$ is compared with experiment and with two other calculations. Our results for $p(V)$ are similar to those calculated with the linear-augmented-plane-wave (LAPW) method,[4] as should be expected, since both use the local-density and the clamped-nuclei approximations. Our results are, however, different from those obtained

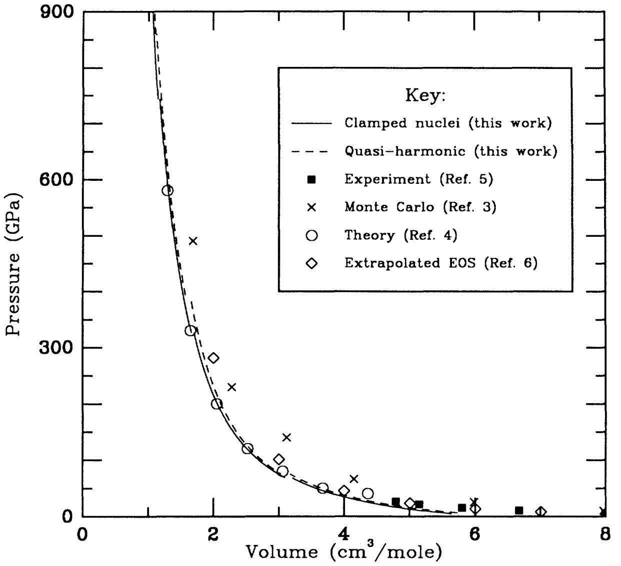

FIG. 1. Comparison of the present results for the calculated equation of state with other calculations and experiment. The solid line is obtained using the clamped-nuclei approximation and the dahsed line is obtained in the quasiharmonic approximation. The circles are the results of the LAPW calculations and the crosses are the Monte Carlo calculations. The squares are experimental values and the diamonds represent an equation of state extrapolated from experiment.

by Ceperley and Alder[3] who used a Monte Carlo approach. Although in principle the Monte Carlo approach treats the electronic and ionic motions exactly, in practice the numerical calculations are performed with periodic boundary conditions imposed on a small crystal where the number of primitive unit cells equals the number of integration k points in the Brillouin zone. As previously noted,[4] a large number of integration k points are necessary to obtain satisfactory convergence. The erratic behavior of the molecular bond length calculated by the Monte Carlo approach[3] could be a symptom of these convergence problems and the origin of the above discrepancy between the calculated $p(V)$ curves.

The equation of state of hydrogen has been accurately measured[5,6] for pressures up to 26.5 and 37 GPa. In the lower pressure range, the equation of state of solid molecular hydrogen is dominated by quantum anharmonic effects, of which the free rotation of the hydrogen molecules is an extreme example. Our calculated equation of state does not include these quantum anharmonic effects and therefore is not valid for the low-pressure Van der Waals–bonded quantum solid. It is only when the Pauli repulsive force between electrons becomes the dominant contribution to the pressure that the calculated equation of state should be compared to experiment.

The experimental equation of state does not extend to very high pressures,[5,6] but Fig. 1 shows that our results are in reasonable agreement with the equation of state extrapolated from experiment.[6] The agreement improves when we include the effects of ZPM within the quasiharmonic approximation (Fig. 1); however, our calculations still predict smaller volumes at fixed pressure. Corrections to the calculated equation of state from anharmonic effects and to the empirical extrapolation from structural phase transitions will improve the agreement between the two curves.

Calculations for the molecular phase were done using the Pa3 structure (α-N_2) and the m-hcp structures. As a test, the structure of the solid halogens Cl_2, Br_2, and I_2 (*Bmab* space group) was also considered, but it was found to be less stable than Pa3 at all densities. It is well known that the local-density approximation underestimates the band gap of insulators (predicting a zero gap for Ge, for example), but gives reliable values for the derivative of gaps with respect to pressures. The calculated band gap at zero pressure was ~ 9 eV. Using the experimental value of the band gap[16] (~ 17 eV) together with the calculated pressure derivative of the gap yields an estimated metallization pressure of $\gtrsim 200$ GPa. If the gap adjustment is not made for the local-density calculation, the metallization pressure is ~ 40 GPa.

The usual caveat of this approach for predicting stable structures is that only a few candidate structures were tested. The plot (Fig. 2) of the enthalpy versus pressure for several solid-hydrogen phases serves more as an indicator of what type of bonding is preferred in a certain pressure range. The numerical errors in the calculated enthalpies are non-negligible in the energy scale of the plot and could shift the relative position of the enthalpy

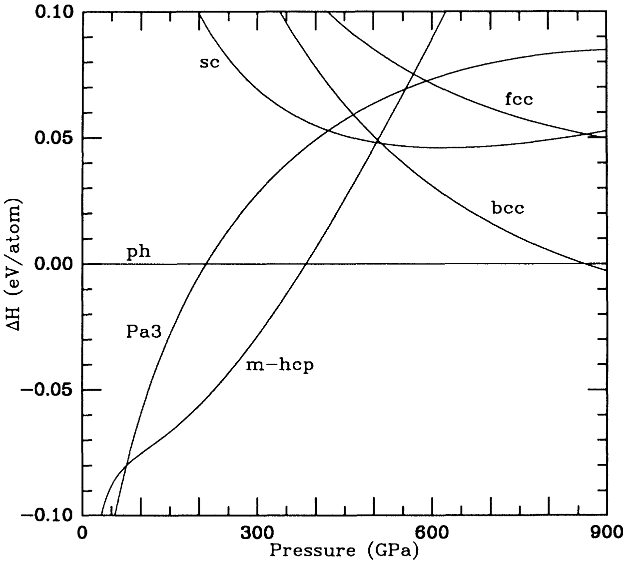

FIG. 2. Calculated enthalpies as a function of pressure are compared for several structures within the quasiharmonic approximation. The enthalpy of the primitive-hexagonal phase was chosen as a reference. The error in the calculated enthalpies could be of the order of 10 meV.

curves. We estimate that the convergence with respect to the number of integration k points and the errors introduced by the use of the Murnaghan equation-of-state fit could displace the enthalpy curves by as much as 10 meV. Errors in the estimation of the ZPM energy of different phases should be of the same order of magnitude. We use this value for estimating the error in the calculated transition pressures.

For pressures below 50 GPa the enthalpies of the Pa3 and m-hcp phase are indistinguishable within the accuracy of our calculations. For pressures above 80 ± 15 GPa the m-hcp phase is more stable than the Pa3 structure despite the fact that it packs the oriented hydrogen molecules in a much less efficient way. This shows that significant intermolecular chemical bonding occurs and that chemical effects determine the actual structure of the molecular phase.

Our calculations of total energy as a function of the orientation angle of the molecules also show that the H_2 molecules are already oriented in this pressure range. We stress that in the uniaxial m-hcp structure the molecules can orient parallel to the hexagonal axis without modifying the symmetry; therefore, there is no phase transition associated with the orientation. In contrast, for the molecular-fcc to Pa3 transition there is a change in symmetry. The calculated c/a ratio in the m-hcp phase is 1.56 in the clamped-nuclei approximation. For the zero-pressure Van der Waals solid the molecules are isotropic and we should expect a c/a ratio close to the ideal value $(\frac{8}{3})^{1/2}$. We therefore interpret the observed[5] deviation of the c/a ratio from the ideal value above ~ 10 GPa as the effect of the orientation of the H_2 molecular axis parallel to the hexagonal axis. According to these estimates the phase transition observed at 150 GPa may be associated with a structural (or metal-insulator) phase transition rather than with an orientational ordering of the molecular solid as previously suggested.[8]

For pressures above 380 ± 50 GPa we find that a highly anisotropic filamentary primitive-hexagonal phase with $c/a \simeq 0.6$ is the most stable. Our calculations also show that other low-coordination structures such as diamond and graphite have enthalpies lower than the molecular and densely packed phases but higher than the primitive-hexagonal phase. In the 380 to 860 GPa range we expect that the most stable structures should have low coordination numbers.

The existence of a primitive-hexagonal structure was anticipated in a perturbative calculation by Brovman, Kagan, and Kholas[17]; however, they overestimated its stability and Straus and Ashcroft[18] showed that the stability of the anisotropic structures would disappear when phonon effects were included. Our results show[19] that the difference in enthalpy between the filamentary and densely packed structures is sufficiently large that the former remain stable even when the phonon contributions are added.

It is a general feature of our calculations that for $P \lesssim 8$ Mbar, open structures of metallic hydrogen with low coordination (PH, simple cubic, diamond) are more stable than the higher-coordination, densely packed structures (bcc, fcc, and hcp). This is a clear indication of the preference of molecular hydrogen to transform into low-coordination structures under pressure. Plots of the charge density[19] reveal a large covalent contribution to the metallic bonding for those structures; i.e., the bonds are anisotropic and oriented. We note that this type of bonding is considered to be favorable for the occurrence of superconductivity in metals.[20]

Two transitions are expected for hydrogen under pressure, a structural phase transition to a more densely packed structure and a metal-insulator transition. Up to now only an unspecified phase transition has been observed[8] at 150 GPa. Our calculations suggest that the structural phase transition will be from a molecular phase to a layered or filamentary phase with low coordination at 380 ± 50 GPa and to a densely packed structure (bcc) at 860 ± 100 GPa. The identification of the structure of solid hydrogen observed above 150 GPa would be very helpful in completing the picture of the high-pressure properties of hydrogen. If that transition is to a nonmolecular but insulating and low-coordination phase, it would be consistent with the results of our calculations. A metal-insulator phase transition is expected near 200 GPa in the m-hcp phase, but this transition pressure is harder to predict because of the shortcomings of local-density theory and the fact that structures with similar enthalpies (e.g., diamond and graphite) may have completely different band structures.

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