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Compressibility of a periodic lattice of atomic hydrogen

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Abstract - *We report on the compressibility of a pseudo-cubic P1 lattice of atomic hydrogen from 0 up to 3000 GPa by modeling the lattice under hydraulic stress using the Density Functional Theory (DFT). The lattice compression does not fit well to the known Murnaghan's equation* $\Delta V/V = 1 - e^{-P/c}$ *and shows sharp increase near 2500 GPa. On the other hand, the bulk modulus shows anomalous behavior in the vicinity of 280 GPa. We also obtain the values of ground state energy and enthalpy for pressure up to 2500 GPa, above this pressure the convergence fails as the H-H distance approaches the bonding length in* H_2*.*

Key Words: Solid, atom, hydrogen, extreme, pressure, DFT.

1. INTRODUCTION

Hydrogen is known to occur in metallic solid state at extremely high pressure above 200 GPa [1]. Experimental studies show that there are several crystallographic forms of solid hydrogen [2]. At lower pressure the hydrogen occurs in a molecular form of solid, where molecules of hydrogen reside at crystallographic sites in certain space group. At higher pressure, there is a transition from molecular solid to atomic solid, which is composed of atomic hydrogen in periodic lattice of highly symmetric space group. The existence of molecular solid hydrogen is interesting but reasonable. Because there is only one electron presented in the atomic hydrogen, the binding of hydrogen atoms in bulk solid state is lacking enough Coulomb attraction in contrast to the growing Coulomb repulsion between the protons. The molecular hydrogen H_2 seems to be the only case where the repulsion force between two protons can be compensated by bonding of 2 electrons at the ambient condition. Indeed, the internuclear distance in H_2 (~0.74Å) is a shortest chemical bond known today and appears as a critical value for any solid form of hydrogen. This value should be a lowest possible H-H contact distance in the solid hydrogen. Reasonably, under ambient condition hydrogen never occurs in solid state as its individual molecular paired states are of much lower energy. It is interesting how the quantum wave functions for solid hydrogen behave under 0.74Å threshold. In this study, we show for the atomic hydrogen arranged in a pseudo-cubic lattice that up to 2500 GPa, the lattice constant (i.e. the H-H contact distance), the unit cell volume, ground state energy and enthalpy continuously change without any singularity. However, at 2510 GPa the H-H distance reduces to 0.902Å and at 2525 GPa it falls to below 0.743Å in a sharp drop. Although all mentioned physical quantities vary smoothly, the bulk modulus on the other hand shows a clear peak structure: it peaks up at 282 then drops back immediately at 283 GPa. At higher pressure until 2500 GPa the bulk modulus changes smoothly.

2. COMPUTATION METHOD

Since hydrogen has only one electron and its orbital structure is simple, there is no need for complicated modeling approaches, but one should keeps in mind that the 1s electrons may be sufficiently delocalized and its orbital energy very large. Here we utilize a simple LDA functional with plane wave basis (CA-PZ) embedded in Castep code [3]. Hydrogen needs to be set as spin polarized with a large ***k***-point grid of 25×25×25. The energy cut-off is 1200 eV. The pseudopotential is norm-conserving. The electron-correlation aspects are not relevant, as we have only 1s-1s combination so the approach like LDA+U etc are not desirable. At the first attempts, we do not implement the relativity correction, because the electrons are moving slowly in hydrogen atom. For stress, only the diagonal elements of the stress tensor are non-zeros and set equally increased in a 10 GPa step. Where the better accuracy is needed the 1 GPa step applies. The convergence for energy is 10^{-6}. A model structure is a pseudo-cubic P1 structure of starting *a* = *b* =*c* = 0.900Å.

3. RESULTS AND DISCUSSION

Fig. 1 shows the evolution of relative volume changes ΔV/V (volume strains) according to pressure and the fit to the Murnaghan's equation $\Delta V/V = 1 - e^{-P/c}$ [4]. Although this equation was empirically obtained from experimental data at the MPa range, it shows to fit quite well also at higher pressure in many solid compounds. However, for our case, the Murnaghan's fitting is not good, as it results in lower values of strains below 280 GPa and higher strains above this pressure. While the Murnaghan's fit is smooth, the inset of Fig. 1 shows that there is a sharp drop of lattice constant (therefore, of H-H distance) from 0.902 to 0.743Å at 2525 GPa. It drops further to 0.697Å at 2600 GPa, and then to the lowest 0.653 Å at 2700 GPa. Unfortunately, we could not obtain the values of the bulk modulus above 2515 GPa, so we do not know how this evolves with increasing stress. The smoothness of change from 0 until 2515 GPa is also illustrated in Fig. 2, where the ground state energy and the enthalpy are showed. Above 2515 GPa the ground state energy also drops visibly together with a collapse of the H-H distance from 0.902 to 0.743Å. It is interesting that the solid hydrogen at 2525 GPa exhibits the interatomic distance exactly equal to the H-H distance in the molecular hydrogen.

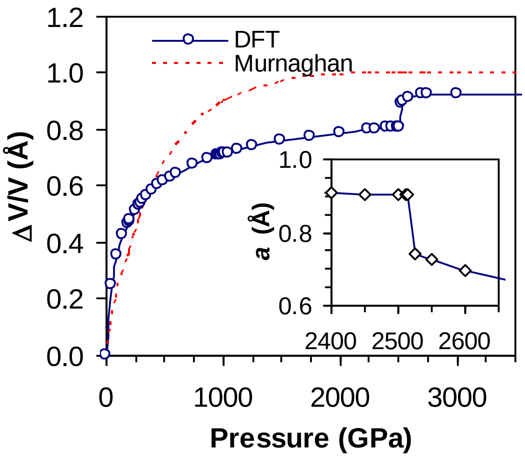

Fig -1: Relative volume change according to pressure and fitting to Murnaghan's equation [4]. The inset shows the change of lattice constant *a.*

Looking for the change of the ground state energy from 2515 to 2525 GPa we obtain 0.53 eV, which is nearly equal to the change of binding energy of a molecular hydrogen H_2 from a starting H-H distance 0.90Å to an optimized distance 0.749Å (0.61 eV). We could not obtain the enthalpy above 2515 GPa.

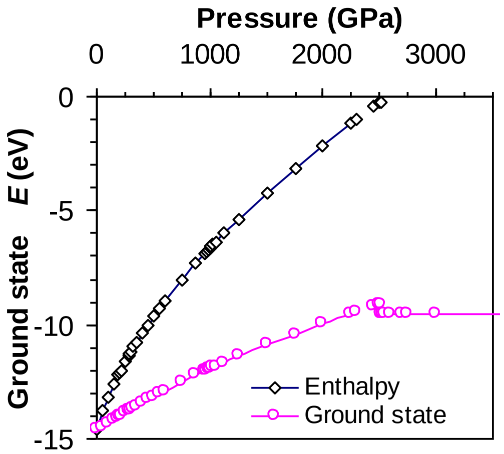

Fig-2: The changes of enthalpy and ground state energy according to pressure

Fig. 3 shows the change of the bulk modulus upon increasing stress. As seen, there is a smooth change of the modulus up to 282 GPa (almost unchanged slope) which is followed by a sudden drop at exactly 283 GPa. This behavior is very interesting as it happens when all other quantities such as lattice constant, ground state energy and enthalpy remain with no singularity. Obviously, it does not associate with a change of symmetry, but to the change in orbital ordering, that is to the transition of electronic state. Recall that, hydrogen is known to occur the atomic solid state at the pressure higher than 250 GPa, so the value of 282 GPa may relate to this transition (H-H distance at 282 GPa is 1.217Å).

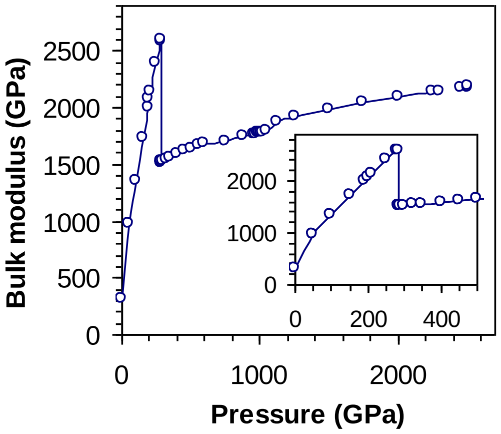

Fig -3: The change of bulk modulus according to pressure. The inset enlarges a peak at 282 and a drop at 283 GPa.

It is evident from Fig. 3 that above 282 GPa the change of the bulk modulus again becomes smooth, although some slight variations can be seen around 1000 GPa. Unfortunately, we do not have the results for the bulk modulus above 2015 GPa.

3. CONCLUSION

The results demonstrate that, (1) a critical change of the bulk modulus at 282 GPa can be assigned to the liquid to solid phase transition of the molecular hydrogen (H-H = 1.217Å), whereas (2) the area from 283 to 2015 GPa relates to the compressed solid molecular hydrogen (H-H = 1.217 - 0.902Å). (3) Another critical change (the first order phase transition) occurred at 2515-2525 GPa corresponds to the formulation of atomic solid hydrogen (H-H = 0.902 - 0.743Å).

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