Metallic atomic hydrogen at a pressure of 300-500 GPa

N N Degtyarenko and E A Mazur
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe sh. 31, 115409 Moscow, Russia
eugen_mazur@mail.ru

Abstract. Atomic metallic hydrogen with a symmetry FDDD of a lattice cell is shown to have a stable crystalline structure under hydrostatic compression in the pressure range of 350-500 GPa. The resulting phase is shown to have a stable structure regarding the collapse of the phonon spectrum. Ab-initio simulation method has been used to calculate the structural, electronic, phonon and other characteristics of the normal FDDD metallic phase of hydrogen at a pressure of 350-500 GPa.

1. Introduction
In the theoretical works [1-4] the normal properties of various crystalline phases of metallic hydrogen have been studied. There are definite prospects to use the atomic hydrogen as a substance with a high density of stored energy. These prospects seem to be extremely interesting in the issue of producing atomic hydrogen at high pressures and under normal conditions. In [5] the normal properties of the I41/amd phase of the atomic metallic hydrogen at a pressure of 500 GPa have been studied. In [6] the superconducting properties of I41/amd stable phase predicted in [5] have been investigated. The superconducting transition temperature $T_C = 217$ K at a pressure of 500 GPa has been obtained in [6] for the I41/amd metallic hydrogen. In [7] the metallic hydrogen at a pressure of 500 GPa has been discovered experimentally.

The phase transformations at the compression of the molecular hydrogen on the basis of theoretical calculations have been predicted. According to calculations by the DFT LDA method [8] the phases P63/m, C2c, Cmca-12 and Cmca should be stable in the pressure ranges $P < 70$, $P = 70-165$, $P = 165-260$, and $P > 260$ GPa, respectively. Later the pressure range limits were defined more precisely as $P < 110$ GPa for P63/m, $P = 110-245$ GPa for C2c, $P = 245-370$ GPa for and Cmca-12 and $P > 370$ GPa for Cmca.

These results are in excellent agreement with the calculations in [9]. Phase transition under pressure of was of 110 GPa was detected using both Raman scattering spectra and IR spectra [10]. No direct information about the structure of the phases was obtained in these experiments. The ranges of stability of atomic hydrogen phases has been calculated in [11] as 480-1000 GPa for I41/amd structure and 1000-1500 GPa for R-3m one. According to [11], the phase transition of the molecular phase to an atomic phase occurs at the pressure of 500 GPa. As follows from the results [12], metallization of the system occurs at a pressure of about 400 GPa, i.e. there exists a range of pressures exceeding 400 GPa for the metallic molecular phase.

The question arises: what is a lower limit for the pressure at which the dynamic stability of the crystal lattice is still maintained under decompression when the atomic structure is used as an origin.
Such a process corresponds to the movement along the path 2 in the terminology of [7] for the phase diagram in the opposite direction. In our previous work we have shown [5] that pressure less than 450 GPa is critical for stability of the crystal structure of the metallic hydrogen I41/amd phase. In the present paper, we found a new phase with FDDD symmetry which is similar to the I41/amd phase but has a lower critical pressure of about 350 GPa. In addition, the discovered FDDD phase has a significantly larger constant of the electron-phonon interaction. In accordance with calculations by Brovman and Kagan [1-4] the metallic hydrogen atomic phase may be metastable upon decompression down to the atmospheric pressure. A possibility of creating atomic metastable hydrogen phase, which is dynamically stable at the lower pressures, is a matter for the further research.

2. Method
Ab-initio calculations of the structural, electronic and phononic characteristics of the metal hydrogen crystal structures at a pressure of 500 GPa has been carried out. The DFT approximation with the plane wave basis and the correlation functional GGA–PBE (Perdew-Burke-Ernzerhof) with a pseudo-potential preserving the norm has been used. All the calculations were performed in the spin-polarized approximation to make possible an adequate comparison of the calculated energy values for different crystalline phases. The method of super cells with the periodic boundary conditions has been used to simulate the crystal. DFPT method with an extended number of unit cells has been used in the calculations of the phonon spectra.

3. Results
3.1. Structure geometry
Figure 1 shows a rectangular basic cell structure with the FDDD symmetry as well as the face-centered orthorhombic primitive cell with two atoms, the reciprocal cell and the isosurfaces of the two e-bands crossing the Fermi level. Red lines represent the path connecting points of high symmetry (G-X-Y-Z-G).

![Figure 1](image)

**Figure 1.** (a) Rectangular unit cell of the structure with the FDDD symmetry; (b) four primitive orthorhombic cells; (c) reciprocal cell; (d) isosurfaces for the two bands crossing the Fermi level.

3.2. Structure parameters
The structure with the FDDD symmetry slightly differs from the I41/amd one described by us earlier in [5]. The rectangular cell (Figure 1a) contains 8 atoms and has a rectangular face with the sides difference of about 10% remaining at all pressures. The cell of the I41/amd structure contains only 4 atoms and has a square face. Nevertheless for both structures the primitive cell contains two hydrogen atoms. The common feature of these structures is the configuration of atoms in the first coordination sphere. Both the approximation method and the convergence conditions have been strictly maintained in calculation of these structures performed for the primitive cells. We obtained that the enthalpies of both structures differ only slightly when the zero-point oscillations addition to the phonon contribution
is excluded. For example, at $P = 500$ GPa the enthalpy values are equal to $H = -9.77$ eV/atom for the both crystalline phases and a difference occurs only in 3-4 digits after the decimal point. Such an equality holds for all pressures. A relatively larger difference, which is of the order of $10^{-2}$, is observed for the distances between atoms in the second coordination sphere and for relative value of the electron density between the second neighbours. Although the energy characteristics of these two structures are almost degenerate, due to these differences a dynamical stability of the FDDD structure is kept in a larger pressure range in comparison with the I41/amd phase.

### 3.3 Electron spectra

Calculation of the electron spectra were carried out for the FDDD structure with two atoms in the primitive cell. There are two filling bands in the obtained spectra (Figure 2). In the pressure range from 300 to 500 GPa the spectrum of filled states is practically unchanged. In vicinity of $X$ and $Z$ points the states are not filled.

![Figure 2](image1.png)

**Figure 2** Band structure of electrons for the FDDD phase at pressures of 500 GPa (a) and 300 GPa (b). The zero energy corresponds to the Fermi level.

![Figure 3](image2.png)

**Figure 3.** Dispersive dependences of the phonons for the FDDD phase at pressures of 500 GPa (a) and 300 GPa (b). Calculations have been carried out for the super-cell FDDD structure with the number of atoms of the order of 128.
3.4. Phonon spectra

As seen from Figure 3, there are no imaginary frequencies in the phonon spectrum at \( P = 500 \) GPa. The imaginary phonon frequencies are also absent along the (X-G-Y-Z-G) path for the pressure of 300 GPa. Influence of pressure on of the phonon dispersion curves is more noticeable than for the electron spectra. One of the phonon branches almost approaches the zero frequency on the X-Z segment. In addition, the estimated spectrum shifts up relative to the zero value with the frequency increase. At \( P = 300 \) and 500 GPa the maximum values of the phonon frequency correspond respectively to 300 and 370 meV.

Analysis of the states density curves revealed also that the imaginary phonon frequencies in the FDDD structure do not appear at pressures of 500 and 350 GPa (the curves tend to zero for zero energy). There appears a “tail” in the phonon density of states of the FDDD structure in the range of “negative” frequency at pressure of 300 GPa (the “negative” frequency denotes an imaginary values of the phonon frequency). Though the qualitative behavior of the phonon spectra at the different pressures is quite similar, the spectra become harder with pressure. The maximum value of the phonon energy of 350 meV is achieved at pressure of 500 GPa.

4. Conclusions

1. The structures of the metallic atomic hydrogen phase with both FDDD and I41/amd symmetries coexist in the pressure range of 450-500 GPa due to the small difference of their enthalpies even if the zero-point oscillations are taken into account.
2. The phase with the FDDD symmetry is dynamically stable in a wider range of pressures \( P=350-500 \) Gpa in comparison with the I41/amd phase.
3. In the range form 350 to 500 GPa the electron spectrum of the phase with the FDDD symmetry changes slightly with the pressure.
4. Value of the maximum phonon energy increases from 300 to 350 meV with pressure increase from 350 to 500 GPa.
5. At pressures below 450 GPa the atomic metallic phase with the FDDD symmetry coexists with a molecular metallic phase of hydrogen. Such a coexistence, in our opinion, represents the physical nature of the PRE phase in the metal hydrogen phase diagrams.
6. Calculation of the critical temperature using the method [13] gives the value of 250 K for the structure of the atomic hydrogen with the FDDD symmetry.

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