Mechanism of the transition of solid hydrogen to the conducting state at high pressures

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Abstract. The density functional theory is applied for the calculation of the dependence of pressure and profiles of proton–proton pair correlation function of hydrogen on density in the range 1.14–2.0 g/cm$^3$ at temperature 100 K. The calculated range of pressures is 300–2600 GPa, which corresponds to the solid phase of hydrogen. The transition at pressure 607 GPa is found, which is characterized by a noticeable jump of electrical conductivity and a sharp decrease in the number of molecules of H$_2$. The structural transition is characterized by the first peak of the pair correlation function at a distance of 0.92 Å, which corresponds to the interatomic distance in the ion H$_3^+$ and does not depend on density. Therefore, the nature of the transition combines ionization with structural changes.

1. Introduction

The assumption of the existence of metallic hydrogen was first put forward in the work of Wigner and Huntington in 1935 [1]. The first-order phase transition was predicted. The mechanism of the transition based on the dissociation to an atomic lattice through compression of solid molecular hydrogen was suggested. The predicted pressure was 0.25 Mbar. This problem is included in the list of the 30 most important and interesting problems of physics and astrophysics at the beginning of the 21st century compiled by V Ginzburg [2]. It is also mentioned that the metal conductivity in hydrogen may occur in the fluid state. In the experiments [3–6] the phase transition in warm dense hydrogen was detected based on the measurements of various parameters such as conductivity and reflectivity. The density jump is observed in [3–5]. Metallic hydrogen is suggested to be a high temperature superconductor, predicted in [7], with critical temperatures higher than room temperature [8]. Other predictions suggest solid metallic hydrogen is metastable at room temperature [9–11]. The formation of the conducting solid hydrogen observed experimentally at pressure 500 GPa and temperature 5.5 K in [12]. However, the nature of the transition remains unclear. In this paper, we have suggested the mechanism of the transition in solid dense hydrogen.
2. Calculation method
The quantum molecular dynamics within the framework of the density functional theory (DFT) is applied. VASP plane wave code [13–16] is used. The generalized gradient approximation for the exchange and correlation functional in the parametrisation of Perdew, Burke and Ernzerhof [17] is applied. The electron-ion interaction is described by the projector augmented wave method potential. The wave functions are the solution of the Kohn–Sham equations and corresponding energy levels determine the ground state of the system for the given configurations of particles.

The applicability of VASP for the calculations at high pressures and temperatures is discussed in [18, 19]. In particular, the influence of the core electrons on the thermodynamic functions is analyzed within the framework of the pseudopotential approach in comparison with full-electron calculations. However, since we consider hydrogen, in our opinion there is no influence of the core electron effects and the approach is applicable for the wider range of parameters in contrast to aluminum and tungsten considered in [18, 19].

Proton–proton pair correlation function $g(r)$ (PCF) and pressure are calculated for the hydrogen densities, where the transition to the conducting state is expected. The results are averaged over a set of ionic equilibrium configurations obtained within the framework of the quantum molecular dynamics. The particle trajectories are calculated by integration of the Newton classical equations of motion with forces found by means of Hellmann–Feynman theorem. Depending on the particle density in the computational cell, the trajectories have 4000–20 000 steps with the time step 0.5 fs. The values of pressure at each time step are used for averaging.

The range of densities studied is $\rho = 1.14–2 \text{ g/cm}^3$. The temperature 100 K is considered. Calculations are performed in the canonical ensemble with the Nosé–Hoover thermostat [20, 21], which controls the ionic temperature. The electron temperature coincides with the ion temperature and is established by the Fermi–Dirac distribution.

The cutoff of the plane basis set is 1200 eV, which provides the convergence of the results. The initial configuration consists of 24 particles in the unit cell of $C2/c$ space group, which is the most stable at pressure 3 Mbar and higher, as it is shown in [22]. The calculations are performed for 192 particles in the computational cell of $C2/c$ space group with the periodic boundary conditions. The $3 \times 3 \times 3$ Monkhorst–Pack [23] $k$-mesh is used. The convergence of the results on number of particles and $k$-points is checked.

3. Pair correlation function of the solid hydrogen
We started calculations from the density $\rho = 1.14 \text{ g/cm}^3$, which corresponds to the pressure 306 GPa. The initial structure is the monoclinic lattice of the $C2/c$ space group with 24 particles in the primitive cell. In [22] it is shown that this structure describes the experimental data and represents the structure of the phase III in solid hydrogen at pressures up to 450 GPa. The calculated proton-proton pair correlation function is shown in figure 1.

The first peak of $g(r)$ corresponds to the interatomic separation 0.74 Å in $\text{H}_2$ molecule and it remains at the same value for the following compression up to the density $\rho = 1.562 \text{ g/cm}^3$ and pressure 607 GPa. Compression to the density 1.563 g/cm$^3$ leads to the origin of the peak of the PCF at distance 0.92 Å as it is shown in figure 2.

The peak of the PCF in density range $\rho = 1.563–1.572 \text{ g/cm}^3$ corresponds to the distance 0.92 Å, which coincides with the interatomic separation in the $\text{H}_3^+$ ion [24]. The distance remains unchanged in the pressure range from 607 to 836 GPa. The transition is also characterized by the conductivity jump. Upon further compression the first maximum of the PCF corresponds to the average distance between the particles at a given density, indicating full dissociation of hydrogen ions. Therefore, on the basis of these results the following mechanism of the transition in solid hydrogen can be assumed, consisting of two stages. The first stage is a partial ionization.
Figure 1. The pair correlation function of solid hydrogen at density 1.14 g/cm$^3$ and temperature 100 K.

Figure 2. The pair correlation function of solid hydrogen at densities 1.563 (red squares connected by line) and 1.572 g/cm$^3$ (blue circles connected by line).

The reactions (1) and (2) are the most probable mechanism of the formation of the H$_3^+$ ions, as it is shown in [25]. We assume that both reactions occur simultaneously and the distance of molecular hydrogen to form H$_2^+$ molecular ions:

$$H_2 \rightarrow H_2^+ + e.$$  \hspace{1cm} (1)

The next step is the formation of H$_3^+$ ions. By analogy with the case of a rarefied gas plasma H$_3^+$ ions are formed by the reaction of hydrogen molecules with H$_2^+$ ions

$$H_3^+ + H_2 \rightarrow H_3^+ + H.$$  \hspace{1cm} (2)

The reactions (1) and (2) are the most probable mechanism of the formation of the H$_3^+$ ions, as it is shown in [25]. We assume that both reactions occur simultaneously and the distance of
the first peak of the PCF shifts form 0.74 to 0.92 Å under compression from the density 1.562 to 1.563 g/cm³. The dynamics of these processes requires more detailed analysis and is not considered in the current work.

4. Conclusions
In this work, ab initio molecular dynamics and quantum simulation techniques based on the density functional theory are used to calculate pressure and proton-proton pair correlation functions in the range of densities where the transition to the conducting state in solid hydrogen is observed experimentally.

A mechanism of the transition is suggested which is related to the partial ionization of H₂ molecules to form H⁺₂ molecular ions with subsequent reaction of H⁺₂ ions with H₂ molecules to form H⁺₃ ions. The crystalline structure formed is characterized by the interatomic separation of the H⁺₃ ion and does not depend on solid hydrogen density.

Thus, the nature of the transition consists of ionization, i.e. plasma transition and change in the structure of dense matter.

Acknowledgments
The authors would like to thank V Brazhkin and V Ryzhov for useful discussions. The present calculations were carried out on the computing clusters MVS-100K of the Joint Supercomputer Center RAS and K-100 of the Keldysh Institute of Applied Mathematics RAS. The work is supported by the Russian Science Foundation (grant No. 14-50-00124).

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