On the stability of the metastable phase of atomic hydrogen

N N Degtyarenko, K S Grishakov
National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, Kashirskoe sh., 31, Russia, 115409

E-mail: nndegtyarenko@mephi.ru

Abstract. The possibility of metastable hydrogen formation was studied in details using the density functional theory. It was shown that the I4_1/amd structure of atomic metallic hydrogen could be dynamically stable in the pressure range of 175–500 GPa. The results of calculations of structural, energy characteristics and phonon spectra of the normal phase are presented.

1. Introduction
In Ref. [1], a high critical temperature of superconductivity $T_c$ ~200–400 K for atomic metallic hydrogen has been predicted. There are prospects for using atomic hydrogen as a substance with a high energy density of stored energy (HEDM) [2]. These prospects arouse exceptional interest in the issue of obtaining atomic hydrogen under normal conditions or technically achievable pressure values. According to classical papers [3-5], the atomic phase of hydrogen can be metastable when the pressure drops to atmospheric. In Ref. [6], the phonon spectrum without imaginary frequencies has been obtained at zero pressure. In Refs. [3-6] calculations were performed using the perturbation theory method, but more precise and powerful methods have been developed at now.

Currently, it is assumed that the molecular phase of hydrogen turns into a stable atomic metal phase at high pressures, estimated as about 450 GPa. When the pressure decreases, the various structures of molecular hydrogen must correspond to a stable phase, and atomic hydrogen must correspond to a metastable phase.

A significant number of papers have been devoted to the analysis of phase transitions of molecular phases with increasing pressure [7-11]. Based on theoretical calculations, it is predicted that phase transformations occur when molecular hydrogen is compressed. According to DFT LDA calculations [9], the phases: P6_3/m, C2/c, Cmca-12, and Cmca are stable in the pressure ranges, respectively, less than 70, 70–165, 165–260, and more than 260 GPa. The stability range of the atomic hydrogen phases I4_1/amd (480–1000 GPa) and R-3m (1000–1500 GPa) was calculated in Ref. [12]. According to Ref. [12], a transition of the molecular phase into atomic one occurs at a pressure of about 500 GPa, while the metallization of system occurs at about 400 GPa. Thus there is a pressure range of hydrogen metallic state.

An analysis of decay of the metal phase when pressure decreases below the transition pressure has been performed in Ref. [13]. It was shown that up to 10–20 GPa the metallic atomic phase is in a metastable long-lived state which decays instantly at lower pressures. This long-lived metastable state is caused by the impossibility to stabilize the hydrogen molecule in a high-density electronic liquid. At lower pressures a formation of the hydrogen molecules becomes energetically favorable.
The electron and phonon characteristics of the atomic hydrogen structure with $I\bar{4}1/amd$ symmetry at pressure of 500 GPa (at which this phase is equilibrium) were considered in Ref. [14]. The phonon spectra of atomic hydrogen structures with $I\bar{4}1/amd$ and FDDD symmetries has been calculated in Ref. [15]. It was shown that the metastable phase of atomic hydrogen with FDDD symmetry has dynamic stability in the range of 350–425 GPa. The phonon states density $g(\omega)$ does not contain imaginary frequencies in this range. The function $g(\omega)$ at pressure $P=300$ GPa contains imaginary frequencies, but in a region of imaginary frequencies it monotonically falls.

Summing up we conclude that the question about stability of the atomic phase under pressure decreases is still open.

2. Method
Calculations of the structural, electron and phonon characteristics of hydrogen crystal structures at different pressures were performed using the $ab$-initio method. The DFT approximation were used within the framework of the plane wave basis (Quantum Espresso ver 6.4 [16]) using the correlation functional GGA-PBE (Perdew-Burke-Ernzerhof) with norm-conserving pseudopotential. All calculations were performed in the spin-polarized approximation in order to adequately compare the calculated energy values for different phases. The cutoff energy was 1440 eV. Convergence threshold on total energy for ionic minimization was $10^{-9}$ eV. Convergence threshold for electronic selfconsistency was $10^{-13}$ eV. The accuracy of forces calculating was about $10^{-5}$ eV/Å. These parameters of calculation accuracy are especially important for correct calculation of phonon spectra in the metastable region of atomic hydrogen structures.

3. Results
In this article, the possibility of preserving the metastable state of metallic hydrogen at pressures below 300 GPa is studied in details. This was done by analyzing more than 40 different structures of molecular and atomic phases at a pressure of 200 GPa, including candidates for metastable atomic structures of hydrogen at normal pressure [6].

Optimization of geometry of the structures from Ref. [6] by the DFT method leads to a significant distortion and increase in the crystalline unit cell volume at zero pressure. Phonon spectra, calculated for these metastable atomic phases, have a significant range of imaginary frequencies, both at zero pressure and at pressures up to 300GPa.

Results of enthalpy $H$ calculations for these structures are shown in Fig. 1. Qualitatively, two groups of structures, i. e. atomic and molecular, can be distinguished which specific enthalpies differs by 0.3 eV/atom at a pressure of $P=200$ GPa. Dispersion of $H$ values for the structures within the groups is even smaller.

![Figure 1](image_url)

**Figure 1.** Enthalpy per atom for various structures of molecular and atomic phases of hydrogen at a pressure of 200 GPa.

Among the atomic solid hydrogen structures represented in the upper band of Fig.1 most of phases contains imaginary frequencies in the phonon spectrum. Because of brevity of the article we cannot
analyze all structures, but note as a common feature a presence of maximum on the $g(\omega)$ curves in the region of imaginary frequencies. Increase and broadening of the maximum under pressure decrease, indicates that these structures are dynamically unstable.

However, the structure of atomic metallic hydrogen with $I4_1/amd$ symmetry proved to be dynamically stable down to pressures of $P\approx 175$ GPa. This threshold is significantly lower than estimations made in Ref. [15]. Fig. 2 presents pressure dependence of difference of enthalpies of the atomic structures with symmetries $I4_1/amd$, FDDD, and IA3D and the molecular solid phase with CMCA symmetry. It is shown that at pressures less than 425 GPa, the structures of atomic hydrogen are nonequilibrium or metastable.

![Figure 2](image)

**Figure 2.** Enthalpy difference of the atomic hydrogen structures with $I4_1/amd$, FDDD and IA3D symmetries and the molecular solid phase with CMCA symmetry as a function of pressure $P$.

Enhancement of the calculation accuracy up to parameters specified in section 2 proved to be particularly important for correct calculation of phonon spectra in the region of metastability of atomic hydrogen structures with $I4_1/amd$ symmetries. Fig. 3 shows changes in $g(\omega) = \text{PhDOS}(\omega)$ for pressures in the range of 175-300 GPa. As seen, imaginary frequencies are absent for all pressures.

4. **Conclusions**

When the pressure decreases, the dynamic stability of the metastable atomic hydrogen phase $I4_1/amd$ is determined by processes occurring near the minimum of potential energy surface (PES) of this structure:

(i) at pressures > 450 GPa, the minimum in PES of atomic metallic hydrogen $I4_1/amd$ is well defined;

(ii) at intermediate pressures 400–175 GPa the energy barriers of atomic hydrogen $I4_1/amd$ on PES gradually decrease, while the barriers of the molecular phase increase;

(iii) at lower pressures <175 GPa, the molecular phase predominates in PES.

As follows from these results, $I4_1/amd$ structure of atomic hydrogen is metastable down to pressure of about 175 GPa. High accuracy of calculations is needed to obtain correct results for pressures lower than 300 GPa.

Important issues for further study are determining the temperature stability, lifetime, and other properties of metastable metallic hydrogen, such as superconductivity. Is it possible to create a dynamically stable phase of atomic hydrogen at lower pressures, is still an open question.
Figure 3. Density of phonon states \( g(\omega) = \text{PhDOS}(\omega) \) for metastable structure of atomic hydrogen I\(_4\)/amd at pressures \( P = 175, 200, 250 \) GPa.

Acknowledgments
The work was performed within the framework of the Program for improving the competitiveness of National Research Nuclear University MEPhI.

References
[1] Ashcroft N W 1968 Phys Rev Lett 21 1748
[2] Silvera I F, Cole J W 2010 J. Phys.: Conf. Ser. 215 012194
[3] Kagan Yu M, Brovman E G 1972 Sov. Phys. Usp. 14 809
[4] Brovman E G, Kagan Yu, Kholas A 1972 JETP 34 1300
[5] Kagan Yu, Pushkarev V V, Kholas A 1977 JETP 46 511
[6] Brovman E G, Kagan Yu, Kholas A 1971 JETP 61 2429
[7] McMahon J M, Morales M A, L’Aquila, Ceperley D M 2012 Rev. Mod. Phys. 84 1607
[8] Saitov I M 2019 JETP Letters 110 184
[9] Azadi S, Foulkes W M C 2013 Phys. Rev. 88 014115
[10] Pickard C J, Needs R J 2007 Nat. Phys. 3 473
[11] MaoH K, Hemley R J 1994 Rev. Mod. Phys. 66 671
[12] McMahon J M, Ceperley D M 2011 Phys. Rev. Lett. 106 165302
[13] Burmistrov S N, Dubovskii L B 2017 Low Temperature Physics 43 1152
[14] Degtyarenko N N, Mazur E A 2016 JETP Let. 104 319
[15] Degtyarenko N N, Mazur E A, Grishakov K S 2017 JETP Let. 105 664
[16] Giannozzi P, et al. 2009 J. Phys.: Condens. Matter 21 395502