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# Data-driven discovery and DFT modeling of Fe<sub>4</sub>H on the atomistic level

Dejan Zagorac<sup>a,b,\*</sup>, Jelena Zagorac<sup>a,b</sup>, Milos B. Djukic<sup>c</sup>, Burak Bal<sup>d</sup>, J. Christian Schön<sup>e</sup>

<sup>a</sup>Materials Science Laboratory, Institute of Nuclear Sciences “Vinča”, University of Belgrade, Belgrade, Serbia

<sup>b</sup>Center for synthesis, processing, and characterization of materials for application in extreme conditions “CextremeLab”, Belgrade, Serbia

<sup>c</sup>University of Belgrade, Faculty of Mechanical Engineering, Kraljice Marije 16, Belgrade 11120, Serbia

<sup>d</sup>Department of Mechanical Engineering, Abdullah Gül University, 38080 Kayseri, Turkey

<sup>e</sup>Max Planck Institute for Solid State Research, Nanoscale Science Department, Stuttgart, Germany

## Abstract

Since their discovery, iron and hydrogen have been two of the most interesting elements in scientific research, with a variety of known and postulated compounds and applications. Of special interest in materials engineering is the stability of such materials, where hydrogen embrittlement has gained particular importance in recent years. Here, we present the results for the Fe-H system. In the past, most of the work on iron hydrides has been focused on hydrogen-rich compounds since they have a variety of interesting properties at extreme conditions (e.g. superconductivity). However, we present the first atomistic study of an iron-rich Fe<sub>4</sub>H compound which has been predicted using a combination of data mining and quantum mechanical calculations. Novel structures have been discovered in the Fe<sub>4</sub>H chemical system for possible experimental synthesis at the atomistic level.

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\* Corresponding author. Tel.: +381-11-340-8545.

E-mail address: [dzagorac@vinca.rs](mailto:dzagorac@vinca.rs)

## 1. Introduction

Because of the common occurrence of elemental iron (Fe) and hydrogen (H) in the universe, due to being the final and starting elements in the nuclear burning processes in stars, possible Fe-H compounds have attracted significant attention from scientists, both in fundamental science and engineering. Furthermore, molecular compounds have been detected in extreme conditions or small amounts at very low temperatures. The two elements form a metallic alloy above 3.5 GPa that has been advanced as a possible explanation for the low density of Earth's "iron" core (Badding *et al.*, 1991, Saxena *et al.*, 2004). However, those compounds are unstable when brought to ambient conditions, and eventually decompose into separate elements. Still, the Fe-H-based compounds have been extensively investigated at high pressure and/or temperature conditions mainly due to their importance in the investigation of Earth's core. For example, there are studies of hydrogen as one of the light elements in the Earth's core and the first observation of hydrogen in an iron lattice at high pressure, (Ikuta *et al.*, 2019) of the dynamical stability of Fe-H in the Earth's mantle and core regions (Isaev *et al.*, 2007), and the sound velocity measurements in dhcp-FeH up to 70 GPa (Shibazaki *et al.*, 2012), and similarly X-ray diffraction and Mossbauer spectroscopy investigations of fcc iron hydride FeH at high pressures (Narygina *et al.*, 2011), work on Fe-C and Fe-H systems at pressures of the Earth's inner core (Bazhanova *et al.*, 2012), studies of the melting phase relations of FeH<sub>x</sub> up to 20 GPa (Sakamaki *et al.*, 2009), or work on new iron hydrides under high pressure (Pepin *et al.*, 2014).

The Fe-based alloys can form solid solutions with hydrogen, which under extreme pressure conditions can exhibit different stoichiometries and stabilities, e.g., remaining stable even at high temperatures and under normal pressure at temperatures below 90 K (Antonov *et al.*, 1998). From binary Fe-H compounds, it is possible to observe various possible chemical systems: molecular compounds (Andrews, 2004, Wang & Andrews, 2009), polymeric network compounds (Pépin *et al.*, 2017), iron-hydrogen complexes (Hieber & Leutert, 1931), biochemical compounds (Fontecilla-Camps *et al.*, 2009), metal alloys (Sakintuna *et al.*, 2007), etc. There is a large number of possible applications of iron hydrides in biocatalysis (Liu *et al.*, 2005), in the development of iron-based catalysts (Morris, 2015), Asymmetric Transfer Hydrogenation (De Luca *et al.*, 2019, Zuo *et al.*, 2016), or the formation of the gas phase and hydrogenation of carbon dioxide with diatomic FeH anions (Jiang *et al.*, 2017). Similarly, Fe-H show various possibilities for technological applications due to their specific electronic properties (Kvashnin *et al.*, 2018, Elsasser, Zhu, Louie, Fahnle, *et al.*, 1998), magnetic properties (Elsasser, Zhu, Louie, Meyer, *et al.*, 1998, Elsasser, Zhu, Louie, Fahnle, *et al.*, 1998), superconductivity (Kvashnin *et al.*, 2018, Bi *et al.*, 2019), and changes in crystal structures and properties at high pressure (Zarifi *et al.*, 2018) or changes in the composition in the Fe-H phase diagram (Machida *et al.*, 2019).

Iron hydrides, like hydridoiron (FeH) and dihydridoiron (FeH<sub>2</sub>), as well as other possible compounds of hydrogen and iron, have recently attracted much attention. In general, theoretical and computational investigations of both various hydrogen-iron compounds and very complex hydrogen-materials interactions are of great importance for a successful transition to a green and hydrogen-based economy. Recent *ab initio*-based computational studies on hydrogen embrittlement (HE) in metallic materials confirm the synergistic action of HE mechanisms depending on the hydrogen concentration and other factors (Djukic *et al.*, 2019, Djukic *et al.*, 2016, Lee, Djukic, *et al.*, 2023, Bal *et al.*, 2016, Lee, Bin Jamal, *et al.*, 2023). The present atomistic study proposes a novel predicted iron-rich Fe<sub>4</sub>H compound together with indications of a possible experimental synthesis at the atomistic level of monolayers of iron hydride. Even though Fe-H compounds have limited industrial applicability due to their instability, the theoretical *ab initio*-based computational studies of this type of materials are important for a better understanding of complex hydrogen-materials interactions (Popov *et al.*, 2018), including very complex hydrogen embrittlement phenomena in the industrial sector (Tuğluca *et al.*, 2018, Djukic *et al.*, 2015).

## 2. Theoretical Methods

Crystal structure prediction was carried out consisting of data mining methods, where the final structure optimization was conducted with two *ab initio* methods. Data mining (DM) based searches of the ICSD database (Zagorac *et al.*, 2019, Bergerhoff & Brown, 1987) were utilized, followed by structure optimization on the Density Functional Theory (DFT) level (Zagorac *et al.*, 2013, Škundrić *et al.*, 2021). The general approach to DM-based searches in the ICSD is to find all possible A<sub>4</sub>X structure prototypes, which might be observable under experimental

conditions (Zagorac *et al.*, 2013, Zagorac *et al.*, 2017). Moreover, we have used a more complex process, generally known as the “knowledge discovery in databases” process, KDD, which involves several important steps: selection, pre-processing, transformation, “Data Mining and Interpretation/Evaluation”, and post-processing. All potential structure candidates obtained from DM searches were submitted to the local optimization on the DFT level and further details of such DM-DFT searches can be found elsewhere (Zagorac, Zagorac, *et al.*, 2014, Škundrić *et al.*, 2021, Zagorac *et al.*, 2020).

Full structural optimization on the DFT level was accomplished using the CRYSTAL 17 code (Dovesi *et al.*, 2017, Dovesi *et al.*, 2018), based on a Linear Combination of Atomic Orbitals (LCAO). A modified all-electron basis set (AEBS) labeled Fe\_86-411d41G\_towler\_1992b was chosen for iron (Valerio *et al.*, 1995, de P. R. Moreira *et al.*, 2000, Čebela *et al.*, 2023). In the case of hydrogen, the H\_3-1p1G\_gatti1994 basis set for the H atoms was used (Gatti *et al.*, 1994, Corno *et al.*, 2006, Jovanović *et al.*, 2020). A detailed overview of the used basis set can be found elsewhere (Doll, 2021). The analytical gradients concerning the atom positions (Doll *et al.*, 2001) and the cell parameters (Doll, 2010), as well as the local optimization routine (Civalleri *et al.*, 2001), were employed for the structure optimizations. Local optimizations were employed using different *ab initio* methods, which should confirm the quantitative /qualitative validity of the obtained results (Zagorac, Schön, *et al.*, 2014, Pejić *et al.*, 2022, Buyer *et al.*, 2022). In this DFT-level study, two different functionals and approximations were employed: the local density approximation (LDA) with the Perdew-Zunger (PZ) correlation functional (Perdew & Zunger, 1981), and the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional (Perdew *et al.*, 1996). For the integration over the Brillouin zone, a k-point mesh of 8 x 8 x 8 was generated using the Monkhorst-Pack scheme (Monkhorst & Pack, 1976). The energy convergence tolerance was set as  $10^{-7}$  eV/atom.

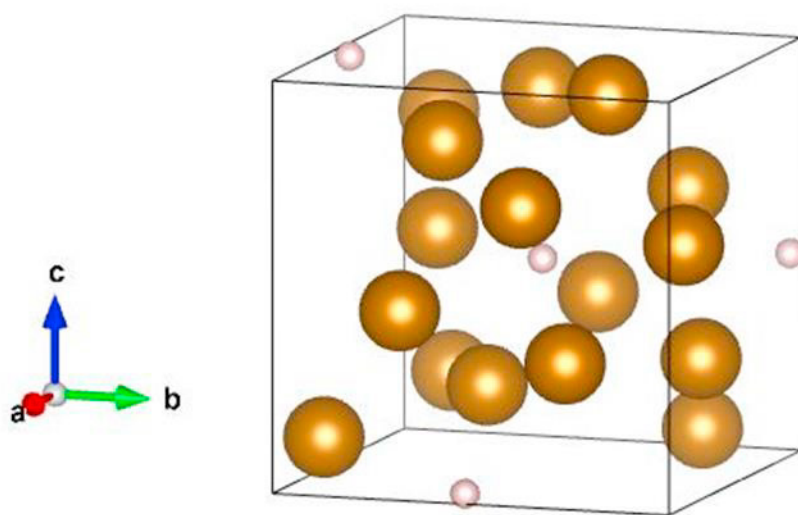


Fig. 1. Predicted  $\text{Fe}_4\text{H}$  compound which has been obtained using a combination of data mining (DM) and quantum mechanical (QM) calculations, exhibiting the  $\text{AlAu}_4$  type in the cubic  $P213$  (no. 198) space group.

### 3. Results and discussion

Usually, iron hydrides are investigated with a focus on the thermodynamic and kinetic stability of their compounds and their properties (structural, electronic, and mechanical) under extreme pressures and/or temperatures (Fu *et al.*, 2023, Pepin *et al.*, 2014). Most of these studies are focused on the investigation of hydrogen-rich Fe-compounds relevant to their specific properties or research of the Earth's core (Kvashnin *et al.*, 2018, Zhang *et al.*,

2018, Li *et al.*, 2017). However, there are only a few studies that are investigating the full Fe-H phase diagram and global energetically stable structures (Bazhanova *et al.*, 2012). Within this study based on the evolutionary structure prediction algorithm, low-enthalpy structures of all possible hydrides are found for compounds with the  $\text{Fe}_4\text{H}$ ,  $\text{Fe}_3\text{H}$ ,  $\text{Fe}_2\text{H}$ ,  $\text{FeH}$ ,  $\text{FeH}_2$ ,  $\text{FeH}_3$ , and  $\text{FeH}_4$  compositions (Bazhanova *et al.*, 2012), which suggest the possibility of eventually synthesizing an iron-rich  $\text{Fe}_4\text{H}$  compound in bulk.

Here, we present the first predicted structures of an iron-rich  $\text{Fe}_4\text{H}$  compound which has been performed using a combination of data mining (DM) and quantum mechanical (QM) calculations. The first one denoted the  $\text{AlAu}_4$ -type modification shows a high-symmetry cubic structure appearing in the  $P213$  (no. 198) space group, (c.f. Fig. 1). It exhibits an  $\text{AlAu}_4$  prototype of a structure with the same cubic symmetry in the  $\text{Fe}_4\text{H}$  system as in the original compound (Büchler & Range, 1990). The second predicted structure is found in the  $\text{CrP}_4$  type (Jeitschko & Donohue, 1972), showing a low symmetry with a monoclinic  $C2/c$  (no. 15) space group, Fig. 2. These newly predicted structures are the first such results in the iron-rich  $\text{Fe}_4\text{H}$  compound to our knowledge, and recent experimental results on the successful deposition of polynuclear single-molecule magnets (SMMs) consisting of Fe and H atoms on functional surfaces by employing the electrospray ion beam deposition method suggest the possibility of a synthesis of bulk  $\text{Fe}_4\text{H}$  (Paschke *et al.*, 2020). Specifically, highly ordered  $\text{Fe}_4\text{H}$  submonolayers on functional surfaces of Au and graphene were obtained and studied by scanning tunneling spectroscopy (STS) (Paschke *et al.*, 2020).

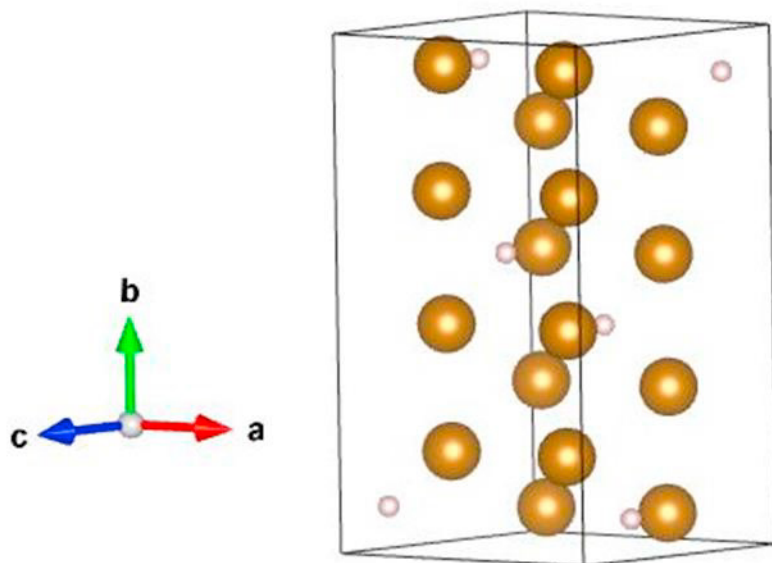


Fig. 2. Predicted  $\text{Fe}_4\text{H}$  compound which has been obtained using a combination of data mining (DM) and quantum mechanical (QM) calculations, exhibiting the  $\text{CrP}_4$  type in the monoclinic  $C2/c$  (no. 15) space group.

#### 4. Conclusions

In the past, most of the work on iron hydrides has been focused on hydrogen-rich compounds since they have a variety of interesting properties under extreme conditions. However, we present the first atomistic study of an iron-rich  $\text{Fe}_4\text{H}$  compound for which several such modifications have been predicted using a combination of data mining and quantum mechanical calculations resulting in novel modifications. In particular, the high-symmetry cubic  $\text{AlAu}_4$  type and the low-symmetry monoclinic  $\text{CrP}_4$  type have been identified as low-energy minima. The Density Functional Theory (DFT) with two different approximations and functionals, (LDA-PZ) and (GGA-PBE), was utilized for the calculations. The feasibility of the synthesis of one of these predicted modifications in this study is supported by recent

results in the experimental synthesis of Fe<sub>4</sub>H structures e.g. by using deposition of polynuclear single-molecule magnets (SMMs) on functional surfaces by employing the electrospray ion beam deposition method.

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