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Crystal structure prediction for iron as inner core material in heavy terrestrial planets

Stefaan Cottenier [a,b,*], Matt I.J. Probert [c], Tim Van Hoolst [d], Veronique Van Speybroeck [a], Michel Waroquier [a]

[a] *Center for Molecular Modeling & QCMM Alliance Ghent-Brussels, Ghent University, Technologiepark 903, BE-9052 Zwijnaarde, Belgium*
[b] *Department of Materials Science and Engineering, Ghent University, Technologiepark 903, BE-9052 Zwijnaarde, Belgium*
[c] *Department of Physics, University of York, Heslington, York, UK*
[d] *Reference Systems and Planetology, Royal Observatory of Belgium, Ringlaan 3, BE-1180 Brussels, Belgium*

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ABSTRACT

The relative stability of different crystal structures for pure Fe under applied pressure is calculated from quantum mechanics, using the highly accurate APW + lo method. In the pressure range of 0–100 TPa, we corroborate the prediction that iron adopts subsequently the bcc, hcp, fcc, hcp and bcc structures. In contrast to previous studies, we identify a family of stacking fault structures that are competing with the ground state structure at all pressures. Implications for the properties of the inner core of the Earth and heavy terrestrial exoplanets are discussed.

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1. Introduction

It has become a routine practice nowadays in computational condensed matter physics to predict properties of a given solid based on nothing more than the fundamental laws of quantum physics (Hafner, 2008; Hafner et al., 2006; Segall et al., 2002; Wentzcovitch and Stixrude, 2010). The only input that is required, is an (approximate) description of the crystal unit cell: space group, lattice parameters, unit cell angles and Wyckoff positions. The predictive capabilities of these so-called '*ab initio*' or '*first-principles*' calculations are currently being pushed one step further, by dropping the requirement of supplying the crystal unit cell as input. It has become feasible to take as input only the chemical composition of a material (i.e. the type and number of elements in the unit cell), and leave the task of determining the lowest energy crystal structure to quantum physics (Woodley and Catlow, 2008). This approach is particularly useful in situations where it is difficult to obtain experimental information on the crystal structure, e.g. when the material is subject to extreme pressures and or temperatures.

The emerging possibility of *ab initio* crystal structure prediction requires efficient methods to search through the infinite space of possible crystal structures, and doing so within a finite time span. A considerable set of algorithms is now available for this purpose (Woodley and Catlow, 2008), of which we list here three that are used in particular for solids: the *random search method* (Freeman and Catlow, 1992; Pickard and Needs, 2006, 2009a,b, 2010a,b), a *genetic algorithm* (Abraham and Probert, 2006; Abraham and Probert, 2008; Glass et al., 2006; Oganov et al., 2006; Oganov and Glass, 2006; Oganov et al., 2007; Oganov et al., 2009) and *database mining* (Curtarolo et al., 2003; Curtarolo et al., 2005; Fischer et al., 2006). The random search method is conceptually most simple: a series of random unit cells with the specified chemical composition is generated, and each cell is geometry-optimized using tools that are available in nearly any *ab initio* code. This procedure maps every random guess to a local minimum in the search space, and the hope is that after a moderate amount of trials the global minimum will be among them. A genetic algorithm starts from a set of random guesses too, but this set is much smaller. After geometry-optimization to the nearest local minimum, the lowest-energy structures of the set are combined into a new structure, that is hoped to 'inherit' good properties from both 'parents'. This survival of the fittest goes on for a few generations, until the absence of further improvement indicates that the global minimum has (probably) been found. *Ab initio* data mining has a very different strategy. A database is created for a given type of formula unit (e.g. A_2B_3, where A and B run across the periodic table). For every chemical formula within this set, the total energy is computed for a (large) set of crystal structures that are compatible with this formula unit. A statistical analysis

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* Corresponding author.
E-mail address: Stefaan.Cottenier@ugent.be (S. Cottenier).

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subsequently points out correlations between crystal structures and energies in the set. By these correlations, predictions are possible for *all* structure types in the set based on *ab initio* calculations for only a few of them. This tremendously reduces the time needed to predict the structure for a new compound. A disadvantage of this method is that it cannot predict any new structure type that was not included in the initial set, and that it requires quite some work to build the initial data base. A random search and a genetic algorithm do not suffer from these problems, but their disadvantage is that every new prediction takes as much time as the previous one — there is no learning process as for data mining.

These new structure prediction tools have been applied in the recent past to problems that are of interest to Earth and planetary science (Oganov et al., 2006; Pickard and Needs, 2009b). The motivation is the lack of experimental structure information for solids subject to the high pressures and/or high temperatures in planetary interiors, which often cannot be reproduced in lab conditions. An example of such a problem is the deceivingly simple question of the crystal structure of the inner core material of terrestrial planets (Dubrovinsky et al., 2007; Ekholm et al., 2011; Mikhaylushkin et al., 2007; Oganov et al., 2005; Steinle-Neumann et al., 2001; Stixrude and Cohen, 1995; Tateno et al., 2010; Vočadlo et al., 2003; Vočadlo, 2007). In a first approximation, the chemical composition of such inner cores can be taken to be pure iron. In the Earth, this material is subject to a pressure of about 350 GPa and a temperature of 6000 K. A genetic algorithm search by Oganov et al. has shown (Oganov et al., 2005) that at 0 K and 350 GPa, pure iron adopts the hexagonal close packed (hcp) structure (there is a well-known phase transition from the bcc-Fe phase at ambient conditions to hcp-Fe at 14 GPa (Dewaele et al., 2006; Mao et al., 1990; Takahashi and Basset, 1964). In other planets, the pressure can be considerably higher. For example, the central pressure in Jupiter, which may contain an ice–rock–iron core, is about 4 TPa (Guillot and Gautier, 2007). More massive exoplanets exist with consequently larger central pressures (Schneider et al., 2011). Even exoplanets with an Earth-like composition and presumably an iron core beneath a silicate shell have been detected, with core pressures in the TPa range. A lower limit to the pressure in their core can be calculated as $P_c = 3GM^2/(8\pi R^4)$ by assuming the density to be homogeneous. This underestimates the central pressure by a factor two for the Earth and even more for more massive planets. The planet CoRoT-7b, probably the first known super-Earth (Queloz et al., 2009), has an estimated mass of $5.2 \pm 0.8\ M_{\mathrm{Earth}}$ and a radius of $1.58 \pm 0.10\ R_{\mathrm{Earth}}$ (Bruntt et al., 2010), indicating a central pressure of a few times 0.74 TPa. Theoretical models of the interior structure of terrestrial type exoplanets show that pressures in the iron core can be up to almost 10 TPa for masses of about 10 M_{Earth} and up to 50 TPa for masses of 100 M_{Earth} (Grasset et al., 2009; Seager et al., 2007; Valencia et al., 2007).

Studying inner core material in this unexplored TPa range was one of the motivations for a recent work by Pickard & Needs (Pickard and Needs, 2009b), where the random search method was used to predict the crystal structure of pure Fe up to 50 TPa (at 0 K). They examined unit cells with 4, 6, 8 and 10 atoms, and concluded that no other structures than the high-symmetry bcc, fcc and hcp structures were competing for the ground state. The hcp phase remains the most stable one up to 8 TPa, a pressure at which the fcc phase takes over. At 24 TPa, hcp has the lowest energy again, and at 35 TPa there is a dramatic take-over by the bcc-phase (dashed lines in Fig. 1).

The bcc–hcp–fcc–hcp–bcc pressure sequence for pure iron is an interesting result, which triggers new questions. Before anything else, one can wonder about the reliability of this result. Total energies in the random search by Pickard & Needs have been obtained by density functional theory, using a plane wave basis set and pseudopotentials. A pseudopotential replaces the atomic-like region near the nucleus, where the wave functions vary steeply, with a much 'softer' potential that removes the sharp peaks from the wave functions. A good pseudopotential should affect only the core region of the atom, and should not disturb the behavior in the valence region, which is where the chemistry happens. Pseudopotentials are unavoidable if one wants to use a plane wave basis set, as the number of basis functions needed to describe the steep but otherwise uninteresting parts of the wave functions close to the nuclei would be prohibitively large. Nevertheless, the introduction of a pseudopotential is always a potentially dangerous action, that might lead to artifacts and unphysical results. Plane wave calculations for a given pseudopotential must be checked with respect to results obtained by so-called 'all-electron' calculations, which use a more complex type of basis functions and which therefore allow to work with the unmodified, true potential. This has been done extensively in the past for Fe pseudopotentials that are used for plane wave calculations for common Fe-containing solids. The extremely short Fe–Fe-distances in Fe under GPa and TPa pressures, however, forced Pickard & Needs to generate a new, dedicated pseudopotential: the pseudized regions of two neighboring atoms should not overlap, and with common Fe pseudopotentials at these pressures this does happen. Therefore, before accepting the predicted high-pressure behavior of Fe as numerically correct, a thorough verification with an all-electron method is required. A second question, of quite a different nature, deals with the absolute reliability of the predicted high-pressure phases. Only unit cells with 4, 6, 8 and 10 atoms were examined by Pickard & Needs. While this is good as a first survey, it certainly doesn't cover all possibilities. In order to find out whether relevant phases might have been missed, more work is needed.

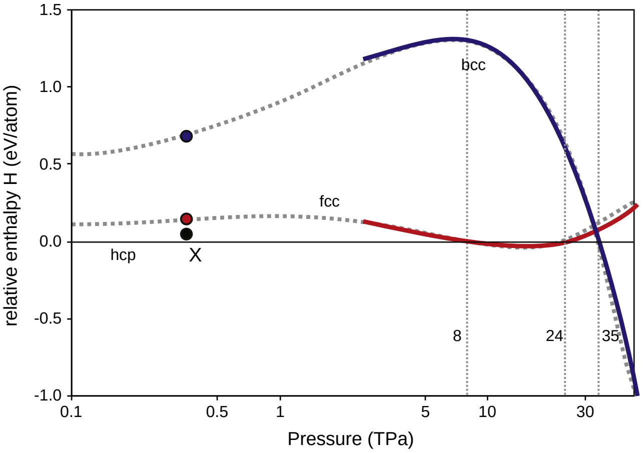

Fig. 1. Comparison of the 0 K relative enthalpy for fcc-Fe and bcc-Fe with respect to hcp-Fe, as a function of pressure (logarithmic scale). Smooth dotted lines are the pseudopotential results by Pickard and Needs, 2009b. Full lines as well as the 0.35 TPa values for bcc and fcc are all-electron results from this work. Vertical dotted lines indicate the transition pressures between the different phases. The 0.35 TPa value for structure X is a pseudopotential result obtained in this work.

The present paper has two goals. First, we will examine the pressure sequence of the high-symmetry phases of Fe with an all-electron method, in order to assess the reliability of the high-pressure pseudopotentials used by Pickard & Needs. Secondly, we will do a rather basic structure prediction attempt for Fe with only 3 atoms in the unit cell — simpler than all cases studied by Pickard & Needs. This will yield a structure that does compete with the high-symmetry phases, and that has given us the inspiration to examine the behavior of a family of stacking-fault based crystal structures under pressure. This will eventually lead us to the conclusion that the crystal structure of the inner cores of the Earth and heavy terrestrial planets might show a complex coexistence of many stacking faults.

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