



# Pressure-induced structural phase transition in iron phosphide



Haiyan Yan\*

College of Chemistry and Chemical Engineering, Shaanxi Key Laboratory for Phytochemistry, Baoji University of Arts and Sciences, Baoji 721013, China

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## ABSTRACT

The high-pressure structural stability of FeP is systematically explored up to 150 GPa by using first-principles calculations combined with crystal structure prediction techniques. We firstly predicted that FeP undergoes a structural phase transition from the low-pressure MnP-type phase to a simple cubic FeSi-type phase at high pressure of 87.5 GPa with a volume drop of 4.3%. The occurrence of this high-pressure FeSi-type phase follows the increased distortions of FeP<sub>6</sub> polyhedron in MnP-type phase and the coordination of Fe atoms increased from 6 to 7. Phonon calculations indicated that this FeSi-type structure is dynamically stable under high pressure as well as ambient pressure. The variations of elastic parameters (including elastic constants, elastic moduli, and sound velocities) of these two structures for FeP under pressure are also investigated for the first time. Further electronic structure calculations showed that FeSi-type structure exhibits a much weaker metallic character compared to the low-pressure MnP-type phase, originating from the increased Fe-*d*-P-*p* orbital hybridization under high pressure.

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## 1. Introduction

In the field of Earth sciences, the composition of the Earth's core is still a hot topic which is significant to understand the structure and dynamics of the Earth's interiors. In the past many years, it has been suggested that the Earth's core is dominantly iron and nickel, alloyed with a certain amount of light elements including sulfur (S), silicon (Si), oxygen (O), hydrogen (H), and carbon (C) according to cosmochemical and geophysical arguments [1–3]. A great deal of experimental and theoretical works thus have been carried out to determine phase diagrams of iron compounds with light elements under extreme conditions (high pressure and high temperature) relevant to the core's formation [4–9]. Besides, phosphide (P) has been recognized as another important components presented in the Earth's core by the reaction between molten iron and phosphorus. Moreover, the previous studies have demonstrated that the phosphorus possesses a much higher solubility in the melting iron than that of sulfur and the phase diagram of Fe–P compound is similar to that of Fe–S, a typical composition in Earth's interiors [10–12]. Therefore, the structural stability and properties of Fe–P compounds under high pressure are also important to the planetary cores.

In the Fe–P binary phase diagram, the structural stabilities of iron phosphides under high pressure have been performed on

Fe<sub>3</sub>P, Fe<sub>2</sub>P, and FeP. Fe<sub>3</sub>P was first thought to present a phase transition from ambient-pressure structure to AuCu<sub>3</sub>-type structure at 30 GPa and below 1000 K [13], but later argued to adopt an orthorhombic structure in a quenched sample from 21 GPa and 2100 K [14]. Subsequently, by using synchrotron X-ray diffraction and laser-heating diamond anvil cell techniques at 64 GPa and 1650 K, Gu et al. proposed [15] that Fe<sub>3</sub>P undergo a structural transformation from ambient *I-4* structure to a tetragonal *P4/mnc* structure which was further confirmed by the first principles calculations. However, the high-pressure structure of Fe<sub>2</sub>P is the subject of continuing debate because of its diverse magnetic properties at high pressure, and different candidates such as *Pnma*, *P4/nmm*, and *P-3m* phases have been proposed for Fe<sub>2</sub>P [14,16,17]. Compared to Fe<sub>3</sub>P and Fe<sub>2</sub>P, the experimental and theoretical investigations on the high-pressure behaviors of FeP are rarely studied, and there is lack of confirmed reports on the existence of pressure-induced structural phase transitions. A more recent experimental work [18] has proposed that no crystal structure and electronic structure changes of FeP occur up to 15.6 GPa and 1800 ± 200 K by combined *in situ* powder X-ray diffraction and Mössbauer spectroscopy. Therefore, the peculiarity and the absence of characterized high-pressure phase of FeP prompted our endeavor to investigate its structural stability behavior at higher pressure. Furthermore, the exploration of phase transition behavior of FeP would provide more insights into the pressure effect on other iron and light elements compounds. In order to address these points, we here presented extensive structure searches to explore the structural

\* Tel./fax: +86 917 3364589.

E-mail address: [hyyan1102@163.com](mailto:hyyan1102@163.com)

evolution of FeP and the chemical nature of their bonding with neighboring atoms up to 150 GPa using an unbiased structure searching method in combination with *ab initio* calculations. A FeSi-type high-pressure phase of FeP was uncovered above 87.5 GPa, thereby demonstrating the pressure-induced increase in the coordination of Fe atoms from 6 to 7. Further calculations are performed to investigate the lattice parameters, equation of state, electronic properties as well as transition pressures between these two phases, provided valuable insights into the high pressure behaviors of FeP.

## 2. Computational methods

The variable-cell high-pressure structure predictions with simulation cells containing up to four formula units (f.u.) were performed in the range of 0–150 GPa by using Crystal structure AnaLYsis by Particle Swarm Optimization (CALYPSO) code [19,20], designed to search for the structure possessing the lowest free energy at given pressure conditions. The effectiveness of this method has been demonstrated by recent successes in predicting high-pressure structures of various systems, ranging from elements to binary and ternary compounds [21–27]. The underlying *ab initio* structural relaxations and electronic calculations were performed using density functional theory within the Perdew–Burke–Ernzerh (PBE) of parameterization of the generalized gradient approximation (GGA) [28,29], as implemented in the VASP code [30]. The electronic wave functions are expanded in a plane-wave basis set with a cutoff energy of 450 eV, and all-electron projector-augmented wave (PAW) method [31] was utilized to describe the electron-ion interactions. Integration over the Brillouin zone was calculated using a Monkhorst–Pack grid [32], with the  $k$  meshes of  $8 \times 14 \times 7$  for MnP-type phase and  $10 \times 10 \times 10$  for FeSi-type phase. The Methfessel–Paxton electronic smearing method [33], with the smearing width of 0.2 eV, was used to improve convergence of the energies/forces in structural optimization. During the geometrical optimization, all forces on atoms were converged to less than 0.001 eV/Å and the total stress tensor was reduced to the order of 0.01 GPa. The phonon calculations were carried out by using a finite displacement approach through the PHONOPY program [34].

## 3. Results and discussion

According to the structural search results, at pressure points of 0, 25, and 50 GPa, FeP keeps the experimental MnP-type phase with space group  $Pnma$  ( $Z=4$ , Fig. 1a), validating our method adopted here. In this structure, iron atoms locate at the center of distorted octahedra consisted of six phosphorus atoms and this structure can be described as closely packed  $\text{FeP}_6$  edge- and face-sharing octahedra, the same to the post-troilite FeS. At ambient pressure, the calculated lattice parameters of MnP-type phase are  $a = 5.128$  Å,  $b = 3.036$  Å, and  $c = 5.763$  Å in a unit cell which are in good agreement with available experimental data ( $a = 5.1826(6)$  Å,  $b = 3.0976(3)$  Å, and  $c = 5.7838(7)$  Å;  $a = 5.193(1)$  Å,  $b = 3.099(1)$  Å, and  $c = 5.792(1)$  Å) [18,35]. In the  $\text{FeP}_6$  polyhedron presented in Fig. 1c, the Fe–P bond distances are calculated to be 2.246 ( $\times 2$ ) Å, 2.237 ( $\times 2$ ) Å, 2.225 Å, and 2.310 Å. In order to investigate the high-pressure behaviors of MnP-type phase according to Ref. [18], the pressure dependences of the unit-cell volume and lattice constants are plotted in Fig. 2b and c, along with the recent experimental data [18]. Strikingly, the calculated results are in agreement with these experimental results, indicating the reliability of our calculations. In addition, the obtained bulk modulus  $B_0$  and its pressure derivative  $B'_0$  of MnP-type phase are 210 GPa and 4.4, which also agree

well with the experimental results of 205(7) and 4.0 [18]. For higher pressures of 90, 100 and 150 GPa, a simple cubic FeSi-type phase (space group  $P2_13$ ,  $Z=4$ , Fig. 1b) was uncovered for FeP. This FeSi-type structure contains four FeP f.u. in a unit cell ( $a = b = c = 4.045$  Å at 100 GPa), in which two inequivalent atom Fe and P occupies the Wyckoff  $4a$  (0.409, 0.409, 0.409) and  $4a$  (0.092, 0.092, 0.092) sites, respectively. Compared to the ambient MnP-type structure, the coordination number of Fe ions in high-pressure FeSi-type structure increased up to 7, formed a  $\text{FeP}_7$  polyhedron building block shown in Fig. 1d. Additionally, the Fe–P bond lengths in the FeSi-type structure are also listed in the Fig. 1d.

Our computational approach is based on constant pressure static quantum mechanical calculations at  $T = 0$  K, so the Gibbs free energy ( $G = U + PV - TS$ ) is reduced to enthalpy ( $H = U + PV$ ). To determine the phase transition pressure point, we have plotted out the enthalpy differences curves of the predicted FeSi-type phase relative to the ambient-pressure MnP-type phase in Fig. 2a. In more detail, we have optimized these two structures at much more pressure points up to 180 GPa with certain pressure intervals. Due to the MnP–FeP phase is isostructural with FeS VI phase which has been recently predicted to transform to an orthorhombic  $Pmmn$  phase at 135 GPa [4]. So this  $Pmmn$  phase was also considered in Fig. 2a for comparison. From Fig. 2a, it is confirmed that the predicted FeSi-type phase becomes more stable than the MnP-type phase above 87.5 GPa. However, the  $Pmmn$ -FeP possesses larger enthalpy values compared to those of FeSi-type phase in the whole studied pressure range, and thus can be ruled out as existing high-pressure candidate. The corresponding volume drop at the phase transition boundary was also calculated and shown in the inset of Fig. 2b, and the obtained results suggest that MnP-type  $\rightarrow$  FeSi-type phase transition is first-order with volume drop of 4.3% which can be easily detected in further experiments. Meanwhile, both the variations of lattice parameters and Fe–P bond lengths of MnP-type and FeSi-type phases under high pressures are also presented in Fig. 2c and d. From Fig. 2d, the Fe–P bond length in MnP-type phase shows a nearly linear decrease with pressure and one can see that the trend of  $d_2 > d_4$  at ambient pressure changes to  $d_2 < d_4$  above 60 GPa, suggesting an increased distortion of  $\text{FeP}_6$  polyhedron under increasing pressures. The dynamical stability of a crystalline structure requires the eigen frequencies of its lattice vibrations be real for all wavevectors in the whole Brillouin zone. We need to check the dynamical stability of the proposed FeSi-type phase. Fig. 3 shows the phonon dispersion curves of the FeSi-type phase at 150 and 0 GPa, respectively. The absence of imaginary frequency suggests that the predicted FeSi-type phase is dynamically stable at both high and ambient pressures, which further supports the validity of this new structure.

To explore the elastic behaviors of FeP at high pressure, we have computed the single elastic constants of MnP-type and FeSi-type phases from stress–strain relations by applying both positive and negative strains on the order of maximum 1.0%. The elastic stabilities, incompressibility, and rigidity of these two structures are thus determined based on the calculated elastic constants and derived Hill elastic moduli [36]. No experimental data for single-crystal elastic constants of MnP–FeP are presently available for any ambient and elevated pressures. Our calculated elastic constants and derived Hill elastic moduli at high pressures (up to 150 GPa) are shown in Table 1 and Fig. 4a. In Table 1, one can see that the calculated elastic parameters for MnP-type phase are in a good accordant with the previous theoretical results [37,38] at ambient conditions, and the agreement of MnP-type phase supports the reliability of the elastic calculations for this new FeSi-type phase although there are no available results for comparison. From Fig. 4a and b, the elastic constants

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