Phase diagram, stability and electronic properties of an Fe–P system under high pressure: a first principles study†

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Fe–P binary compounds have attracted much attention, particularly under high pressure, since they are the constituents of the Earth’s core. However, most studies focus on the single stoichiometry of Fe–P binary compounds at high pressure, and their whole phase diagram and relative stabilities have been unexplored thus far. Herein, first principles swarm structure predictions are performed to find stable structures of Fe–P compounds with various FePₓ (x = 1−4 and y = 1 or x = 1 and y = 2) compositions. Then, their phase diagram and relative stabilities are reliably determined based on predicted structures. Specifically, the FeP, Fe2P and Fe4P compounds are found to be stable in the pressure range of 0–400 GPa. The FeP compound decomposes into Fe2P and Fe4P above 214 GPa. FeP2 becomes unstable above 82 GPa. Notably, two new phases (i.e. C2/c-structured Fe4P and Cmcm-structured Fe5P) are found to be more stable than the previously reported phases. In addition, the XRD pattern of the predicted Cmcm-structured Fe5P matches the experimental patterns, and we are awaiting future experimental confirmation. Electronic band calculations show that the Fe–P binary compounds are metallic, with a pronounced Fe 3d component crossing the Fermi level. Cmcm-structured Fe5P is ferromagnetic. Our study not only provides useful information for the further study of Fe–P binary compounds but also for the determination of the Earth’s core components.

1. Introduction

Geochemical and geophysical studies show that light elements (i.e. hydrogen, oxygen, carbon, sulfur, phosphorus and silicon) play important roles in the Earth’s core.1,2 Early models of the Earth’s core consisted of a considerable amount of schreibersite, cohenite, and troilite.3 The Fe content of the Earth’s core is rather rich (90.67%).4 Several phases of iron compounds, such as iron–sulfur, iron–silicon, and iron–oxygen, with light elements under high pressure have been determined by a large number of experimental and theoretical studies.4–7 Notably, the phosphorus content of the Earth’s core was estimated to be around 0.20 wt%, and up to 4 wt% of phosphorus was found to be soluble in crystalline iron at 23 GPa in the Fe–S–P system.8,9 Since the structures of Fe–P compounds are similar to that of Fe–S, iron phosphides should have a stable composition in the cores. As a consequence, investigation of the structures and properties of iron-phosphorus (Fe–P) compounds is worthy of attention.

To date, extensive studies have been carried out on Fe–P binary compounds, and although most of these studies were based on single stoichiometry, the relative stabilities of the Fe–P binary compounds remain undetermined, particularly at high pressure. For example, several stoichiometric compounds (i.e. FeP, Fe3P, Fe2P, FeP4, FeP and FeP5) were separately investigated. FeP is known as mellinite, which is a mineral from Northwest Africa 1054 acapulcoite. The cubic polymorph with the P2₁₃ space group symmetry (AlAu₄-type structure) was determined using single-crystal X-ray diffraction data (XRD).10 Under high pressure, the FeP phase is relatively stable compared to Fe₃P + Fe.11 The tetragonal structure Fe₄P was discovered from schreibersite at ambient pressure.12 Its possible high-pressure polymorph is either a P4/mnc or Pnma structure, as predicted by theoretical calculations, and the pressure-induced phase transition from I4 to P4/mnc has been observed at 64 GPa.13 For the Fe₄P compound, it is a terrestrial garnet peridotite with implications for the Earth’s core. A hexagonal structure of Fe₃P with P62m symmetry exists at ambient conditions, and the Co₃Si-type structure (space group Pnma) is found to be more stable above 8.0 GPa (ref. 14) or 16.8 GPa,15 as observed through high-pressure and high-temperature X-ray diffraction experiments. Based on first principles calculations,
another $P3m$-structured Fe$_2$P was reported at 153 GPa.\textsuperscript{16} Several
studies on FeP have been carried out because FeP is also an
important member in the planetary cores. FeP crystallizes in the
regular MnP-type structure (space group $Pnma$) at ambient condi-
tions and undergoes a structural phase transition to a simple cubic
FeSi-type phase (space group $P2_13$) at 87.5 GPa.\textsuperscript{17–18} FeP$_2$ crystallizes
in the regular marcasite structure (space group $Pnma$) at ambient
conditions with no unpaired spins in the low-spin configuration.\textsuperscript{19}

Under high-pressure and high-temperature conditions, a new
phase of FeP$_2$ with $I4/mcm$ symmetry was observed at 70 GPa.\textsuperscript{20} Recent
studies show that Fe–P binary compounds (i.e. Fe$_3$P, Fe$_2$P, FeP,
FeP$_2$, and FeP$_3$) are stable at ambient pressure,\textsuperscript{21} in which all
the structures came from reported compounds. By all appearance,
it is necessary to establish the whole phase diagram of Fe–P binary
compounds under high pressure.

Recently, the first principles structural prediction method
has become an irreplaceable tool to discover new materials
and determine their stable structures.\textsuperscript{22–24} For example, a recent
breakthrough in the superconductivity field is the observation
of remarkably high superconductivity (with $T_c$ up to 203 K),\textsuperscript{25} in
which H$_3$S is the main stoichiometry of the superconducting
phase.\textsuperscript{26} This observation was achieved by direct investigation
on the theoretical prediction of high-$T_c$ superconductivity
in compressed solid H$_3$S.\textsuperscript{27} A new clathrate sodalite-like BN structure
was predicted with a high energy density and large hardness.\textsuperscript{28} The
reaction of iron with xenon has been predicted in the Earth’s inner
core environment through theoretical calculations, which provides
a solution to the missing Xe paradox.\textsuperscript{29} Numerous unusual sto-
ichiometric compounds with exotic physical or chemical properties
have been discovered under high pressure.\textsuperscript{30–37}

Herein, the most stable structures of the Fe–P binary
compounds (Fe$_3$P, Fe$_2$P, FeP, FeP$_2$, and FeP$_3$) are readily
determined using the first principles calculations in combination
with the swarm structural search technology.\textsuperscript{21,28} The relative
stabilities of these considered compounds are reliably estab-
lished. Two new phases ($C2/c$-structured Fe$_2$P, and $Cmcm$
-structured Fe$_2$P) are found to be more stable than the previously
reported phases. $Cmcm$-structured Fe$_2$P meets the Stoner crite-
rion and is ferromagnetic. Our study provides some useful
information for the investigation of the constituents of the
Earth’s core.

2. Computational details

To search the stable structures for the given chemical compo-
sitions, structural predictions of the Fe–P system were per-
amed at 0, 50, 100, 200, 300, and 400 GPa using the Crystal
structure AnaLysis by the Particle Swarm Optimization
(CALYPSO) code.\textsuperscript{23–29} The CALYPSO method can successfully
find stable structures just depending on chemical compositions
and has demonstrated success in predicting the high-pressure
structures of various systems.\textsuperscript{40–44} The ab initio structural
relaxations and electronic calculations are based on the density
functional theory (DFT) within the Perdew–Burke–Ernzerhof
(PBE) of the generalized gradient approximation (GGA),\textsuperscript{45} as
implemented in the Vienna ab initio simulation package (VASP)
code.\textsuperscript{46} The electron–ion interaction was described using the all-
electronic projector-augmented wave (PAW) method\textsuperscript{47} with
3$s^2$3$p^6$3$d^7$4$s^1$ and 3$s^2$3$p^3$ valence electrons for the Fe and P
atoms, respectively. Hubbard $U$ is necessary to correct the
effective on-site electron–electron interaction of the transition
metal, with valence electrons on the d and f orbits.\textsuperscript{48–49} Hubbard
$U$ parameters with $U = 2$ eV and $J = 0.95$ eV were applied to the
Fe atoms in the Fe$_2$P compounds.\textsuperscript{16} It successfully reproduces
the experimental magnetic moments of Fe atoms.\textsuperscript{50} As a conse-
quence, we chose Hubbard $U$ with 2 eV at a fixed value of 0.95 eV
(i.e. $U_{eff} = U − J$) to calculate the properties and fine structure
optimization. $U = 2.2$ eV was verified to be suitable to elemental
iron by the linear response approach.\textsuperscript{51} The cutoff energy of
700 eV and Monkhorst–Pack\textsuperscript{23} $k$-meshes with a grid spacing of
$2\pi \times 0.03$ Å$^{-1}$ were used to ensure that the total energy calcu-
lations converged well. The phonon calculations were carried
out using the finite displacement approach to determine the
dynamical stability of the predicted structures, as implemented
in the Phonon code.\textsuperscript{52} To study the interatomic interaction,
the integrated crystal orbital Hamilton populations (ICOHs) were
calculated as implemented in the LOBSTER package.\textsuperscript{53}

3. Results and discussion

3.1. Phase stabilities of Fe–P compounds

Herein, we mainly considered Fe-rich phosphorus compounds
(i.e. Fe$_3$P, Fe$_2$P, FeP, FeP$_2$ and FeP$_3$) since the Fe content of the
Earth’s core is estimated to be around 90.67% and P content is
about 0.17%.\textsuperscript{5} In this study, the pressure ranges up to 400 GPa are
considered. The predicted structures of Fe–P binary compounds
were used to evaluate the formation enthalpy ($\Delta H$) relative to the
elemental solids Fe and P according to eqn (1), in order to explore
the thermodynamic stabilities of Fe–P compounds.

$$\Delta H(Fe_xP_y) = [H(Fe_xP_y) − mH(Fe) − nH(P)]/(m + n),$$

(1)

where $H = U + PV$ is the enthalpy of each composition and $\Delta H$ is
the enthalpy of formation per atom. Herein, $U$, $P$, and $V$ are
the internal energy, pressure, and volume, respectively. The relative
stabilities of the considered compositions at the selected pres-
ures of 0, 50, 100, 200, 300, and 400 GPa, with $\Delta H$ evaluated per
atom, are shown in Fig. 1a. The stable phase lies on the convex
hulls (the global stability lines). As can be seen, all the conside-
rered compositions are stable at 0 GPa, which is well in agree-
ment with the recent theoretical study.\textsuperscript{20} It should be noted that
the Fe$_2$P compound is not included in the study by Jing Wu
et al.\textsuperscript{21} $P2_13$-structured Fe$_2$P has been found from melilinite
and is confirmed to be stable at ambient pressure.\textsuperscript{49} The known
Fe$_3$P, Fe)$_2$P, FeP, FeP$_2$, and FeP$_3$ structures\textsuperscript{16,17,19,55,56} at ambient
pressure were well reproduced in our calculations, which vali-
dates our structure searching method applied to the Fe–P system.
In addition, our calculated lattice parameters for Fe$_3$P
(space group $I4$, 8 formula units per cell) are $a = b = 9.13$ Å and $c =
4.40$ Å, which are in excellent agreement with the experi-
mental values at $a = b = 9.10$ Å and $c = 4.46$ Å.\textsuperscript{77} These lattice
parameter calculations support the validity of the pseudo
potentials adopted in this study.
shown in Fig. 1b. For all the predicted structures, the calculated enthalpy of formation. Detailed information about the element solids in Fig. 2. The predicted structures, and their structural characters are shown predicted structures, and their structural characters are shown discussed later. To determine the interatomic interaction in the C2/c-structured Fe4P, the integrated crystal orbital Hamilton pairs at 200 GPa were calculated and are shown in Table S1. The values of ICOHP between the Fe–P and Fe–Fe pairs are −1.80 and −4.97 eV, respectively. The ICOHP value of the Fe–Fe pair is very close to −4.90 eV in Fe2SH3. Apparently, the Fe–Fe interaction plays an important role in determining the structural stability of the compound. Further analysis indicates that the major contribution of the Fe–Fe interaction originates from 4s–3d, which corresponds to the decomposed ICOHP of −1.908 eV per pair.

The Fe3P compound with the I4 structure symmetry is stable at ambient conditions, and the first phase transition is observed at 64 GPa. This phase is assigned as the P4/mmc or Pnma structure. Notably, we discovered an orthorhombic structure of Fe3P (space group Cmcm, 4 formula units per cell) above 58 GPa. This structure is much more stable than the Fe–Fe distance of 2.48 Å in bulk Fe with Im3m symmetry under ambient conditions and 2.44 Å in Fe3SH4 at 100 GPa. However, this structure is nonmagnetic, as will be discussed later. To determine the interatomic interaction in the C2/c-structure Fe3P, the integrated crystal orbital Hamilton populations (ICOHPs) for the Fe–P and Fe–Fe.

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Fig. 2 Crystal structures of the Fe6P and Fe3P compounds at 200 GPa. (a) Fe3P in the C2/c structure. (b) Coordination environment of the P atom in Fe6P. (c) Coordination environment of the Fe atoms in Fe6P. (d) Fe3P in the Cmcm structure. (e) Coordination environment of the P atom in Fe6P. (f) Coordination environment of the Fe atom in Fe3P. Here, the large shallow blue or dark blue and small orange spheres represent Fe and P atoms, respectively.

3.2. Geometry structure of the stable phases

Two new phases (i.e. C2/c-structured Fe6P and Cmcm-structured Fe3P) were discovered by comparing previous structures and our predicted structures, and their structural characters are shown in Fig. 2. The predicted C2/c-structured Fe6P (4 formula units) is more stable than the phase with P213 symmetry above 37 GPa (Fig. S3a†). Its lattice parameters are \( a = 7.342 \) Å, \( b = 3.772 \) Å, and \( c = 5.627 \) Å at 200 GPa. The structure contains two inequivalent Fe atoms occupying 8f (0.297, 0.337, 0.850) and 8f (0.900, 0.671, 0.551) sites and one equivalent P atom sitting at the 4e (0.000, 0.170, 0.750) position (Fig. 2a). To distinguish the two Fe atoms at different sites, we labelled the inequivalent Fe atoms with two different colors (Fig. 2c). In this structure, each P atom is in 12-fold coordination with the Fe atoms (Fig. 2b), forming a tetrakaidecahedron. The adjacent polyhedrons are interconnected through common edges or co-vertices. The distance of the two nearest Fe–Fe is 2.11 Å, which is smaller than the Fe–Fe distance of 2.48 Å in bulk Fe with Im3m symmetry under ambient conditions and 2.44 Å in Fe3SH4 at 100 GPa. However, this structure is nonmagnetic, as will be discussed later. To determine the interatomic interaction in the C2/c-structure Fe6P, the integrated crystal orbital Hamilton populations (ICOHPs) for the Fe–P and Fe–Fe.

Under high pressure, the relative stabilities of our considered compositions are significantly different from that at ambient pressure. Specifically, the Fe3P compound becomes unstable above 82 GPa, whereas the iron-rich compounds are relatively stable under high pressure. These phases of Fe6P, Fe5P, and Fe4P are stable in the entire considered pressure range (0–400 GPa). Notably, the Fe3P phase is unstable compared above 214 GPa (Fig. S2†) and decomposes into Fe2P plus Fe4P. The pressure–composition phase diagram of the Fe–P system is shown in Fig. 1b. For all the predicted structures, the calculated phonon dispersion curves confirm their dynamical stability with no imaginary frequencies observed in the entire Brillouin zone (Fig. S4†).
nearest neighbours of Fe atoms, forming a P–Fe hendecahedron (Fig. 2e). The adjacent polyhedrons have common edges. The two inequivalent Fe atoms are labelled with two different colors (Fig. 2f). The nearest Fe–Fe distance in the Cmcm phase is 2.10 Å, which is comparable to 2.14 Å in Fe4P. Unlike Fe4P with C2/c symmetry, the Cmcm-structured Fe3P structure is magnetic. An experimental study investigated the phase transitions of Fe3P, in which the P4/mnc or Pnma structure is stable above 64 GPa. However, our predicted Cmcm phase is more stable than the P4/mnc or Pnma phase at 64 GPa. The specific ΔH values of the three Fe3P phases can be found in Table S2.† To confirm the existence of the Cmcm phase, the simulated XRD pattern of the Cmcm phase is shown in Fig. 3 along with the experimental patterns. Several possible structures of Fe3P are also included in Fig. 3. Clearly, the main peak of Cmcm-structured Fe3P is close to the experimental peaks or that of the other phases. Thus, Cmcm-structured Fe3P might disappear under these experimental conditions.

3.3. Electronic properties of stable phases

The electronic band structures and projected density of states (PDOS) of the Fe4P and Fe3P compounds are shown in Fig. 4. Similar to the electronic properties of the other Fe–P species, there are several bands crossing the Fermi level, which indicate that they are metallic. As can be seen in Fig. 4, there is a common character of a pronounced Fe 3d component near the Fermi level. Interestingly, the Cmcm-structured Fe3P is a ferromagnetic phase with the magnetic moment of 3.31μB per cell at 200 GPa by our calculations. Its electronic band structures and spin-polarized DOS based on spin up and spin down can be found in Fig. 4c and d. The calculated DOS per Fe atom at the Fermi level is about 1.0 eV \(^{-1}\) (Fig. 4d), which satisfies the Stoner criterion.\(^\text{61}\)

4. Conclusion

To find the stable phases of Fe–P binary compounds, we explored the crystal structures and stabilities of the Fe–P system with Fe\(_x\)P\(_y\) (\(x = 1–4\) and \(y = 1,\) or \(x = 1\) and \(y = 2\)) compositions under high pressure using first principles calculations combined with swarm structural searches. It is found that the FeP, Fe2P and Fe4P compounds are stable in the whole pressure range of 0–400 GPa, and Fe3P becomes unstable above 214 GPa. Several phases of iron-rich compounds can be synthesized at elevated conditions, which may be the possible phases in the Earth’s cores. The FeP and Fe2P compounds are metallic, with a pronounced Fe 3d component across the Fermi level. Our study provides the theoretical basis for the further investigation of Fe–P binary compounds. It is also important to explore the constituents of the Earth’s core.

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Notes and references