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Structure, stability, mechanical and electronic properties of Fe-P binary compounds by first-principles calculations

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Abstract

The equilibrium crystal structure, stability, elastic properties, hardness and electronic structures of Fe-P binary compounds (Fe₃P, Fe₂P, o-FeP₂, o-FeP₂, FeP₂, m-FeP₄.1, o-FeP₄, m-FeP₄.2) are investigated systematically by the first principles calculations. The calculated Formation enthalpy is used to estimate the stability of the Fe-P binary compounds. The Fe₃P has the largest formation enthalpy as -44.950 kJ/mol and o-FeP₂ has the smallest as -78.590 kJ/mol. The elastic constants are calculated by the stress-strain method and the Voigt-Reuss-Hill approximation is used to estimate the elastic moduli. The mechanical anisotropy of Fe₃P compounds are studied by the anisotropic indexes and plotting 3D surface contour of Young’s modulus. The electronic structures and chemical bonding characteristics of Fe-P binary compounds are interpreted by the band structures and density of states. Finally, the sound velocity and Debye temperatures of Fe-P binary compounds are discussed.

Keywords: Intermetallics; Phosphide; First principles calculations; Elastic properties; Electronic properties

1. Introduction
Iron - steel industry has been developing fast since the last century, which is a symbol for the modern industry. A common non-metal element such as phosphorus would form the enrichment region in casting process or some heat treatment condition, (For example, grain-boundary segregation). Phosphorus would combine with iron to form the Fe-P binary compounds including Fe₃P, Fe₅P, FeP, FeP₂, and FeP₄ according to Fe-P equilibrium phase diagram.[1] Moreover, phosphorus is usually considered hazardous to the properties of the steel. But the phosphorus existing in the steel is inevitable. In order to control the effect of phosphorus in the iron and steels, first of all, we should know the structure, stability and properties of the iron phosphides.

As a traditional industry, most researches about the properties of steels depended on the experimental discovery. Therefore, it is difficult to explore the performance of these compounds at electron-atomic level. The development of first-principle calculations based on density functional theory [2,3] has made it possible to get the fundamental properties with electron-atomic level or materials under the difficult experimental conditions. Nevertheless, only few reports on iron phosphides. Li et al. [4] calculated the elastic constants and formation enthalpy of Fe₃P by first principle pseudo-potential plane wave method. They have found that both of hexagonal and orthorhombic Fe₃P intermetallic compounds were ductile. The hexagonal structure was more stable than orthorhombic structure for Fe₃P. Chen et al. [5] investigated the magnetic property of Fe₃P. They understood the magnetic properties of the compound even under considerable high pressures above 5.0 GPa. Tobola et al. [6] investigated the magnetism and band structure of Fe₃P by neutron diffraction experiment and KKR-CPA calculation method. However, most physical and chemical properties of Fe-P binary compounds are rarely reported systematically as so far. In this paper, the stability, mechanical properties and electronic structures of all Fe-P binary compounds are
investigated and discussed for the first time with first-principle calculation method.

2. Calculation methods and models

![Figure 1](image.png)

**Fig. 1.** Cut-off energy testing

The first-principle calculations of Fe-P compounds have been performed by density functional theory (DFT) which is implemented in Cambridge sequential energy package (CASTEP) code [7]. Generalized gradient approximation (GGA) approach in the form of Perdew Burke Ernzerhof (PBE) is used to calculate the exchange and correlation functional [8]. The interactions between ionic cores and valence electrons are indicated by ultra-soft pseudo potentials. For Fe and P, the valence electrons considered are 3p^64s^23d^6 and 3s^23p^3, respectively. A plane wave expansion method is applied for the optimization of the crystal structure. A special \( k \)-point sampling in the first irreducible Brillouin zone is confirmed by Monkhorst-Pack scheme, and the \( k \) point mesh is selected as \( 3 \times 3 \times 9, 9 \times 9 \times 12, 6 \times 6 \times 12, 6 \times 12 \times 6, 9 \times 6 \times 15, 6 \times 3 \times 6 \) and \( 9 \times 3 \times 6 \) for Fe,P, Fe,P, o-FeP-1, o-FeP-2 (CoAs-structure and MnP-structure, simplified as o-FeP-1 and o-FeP-2), FeP, m-FeP-1, o-FeP and m-FeP-2, respectively. A kinetic energy cut-off value of 400.0 eV is used for the plane wave expansion in reciprocal space. The selected \( k \) point is three times as much as the default values, and the cut-off energy has been tested. The result as shown in Fig. 1, the total energy will stay constant when the cut-off energy larger than 380eV for these compounds. So the selected values are suitable for the chosen system. The Broyden-Fletcher-Goldfarb-Shannon (BFGS)
method is applied to relax the whole structure based on total energy minimization. The total energy changes during the optimization processes are finally converged to $1 \times 10^{-6}$ eV and the forces per atom are reduced to 0.05 eV / Å.

By using the stress-strain method according to the generalized Hooker’s law, the elastic constants of the Fe$_x$P$_y$ compounds are calculated. Several different strain modes are imposed on the crystal structure, and then the Cauchy stress tensor for each strain mode is estimated. Finally, the related elastic constants are identified as the coefficients in strain-stress relations as shown in Eq. (1) [9]

$$
\begin{pmatrix}
\sigma_1 \\
\sigma_2 \\
\sigma_3 \\
\tau_4 \\
\tau_5 \\
\tau_6
\end{pmatrix} = 
\begin{pmatrix}
c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16}
c_{22} & c_{23} & c_{24} & c_{25} & c_{26}
c_{33} & c_{34} & c_{35} & c_{36}
c_{44} & c_{45} & c_{46}
c_{55} & c_{56}
c_{66}
\end{pmatrix}
\begin{pmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\gamma_4 \\
\gamma_5 \\
\gamma_6
\end{pmatrix}
$$

(1)

where, $c_{ij}$ is the elastic constant, $\tau_i$ and $\sigma_j$ are the shear stress and normal stress, respectively. The total number of independent elastic constants is determined by the symmetry of the crystal. For high symmetry point group, the required different strain patterns for the $c_{ij}$ calculations can be greatly reduced. [9]

The cohesive energy and formation enthalpy are calculated to estimate the chemical stability of Fe$_x$P$_y$ compounds. These two energy parameters are defined in Eqs. (2) and (3) [10]

$$
E_{coh}(Fe_xP_y) = \frac{E_{tot}(Fe_xP_y) - xE_{iso}(Fe) - yE_{iso}(P)}{x + y}
$$

(2)

$$
\Delta_r H(Fe_xP_y) = \frac{E_{tot}(Fe_xP_y) - xE_{bin}(Fe) - yE_{bin}(P)}{x + y}
$$

(3)

where $E_{coh}(Fe_xP_y)$ and $\Delta_r H(Fe_xP_y)$ are the cohesive energy and formation enthalpy of Fe$_x$P$_y$ per
atom, respectively. $E_{\text{tot}}(\text{Fe}_x\text{P}_y)$ is the total energy of Fe$_x$P$_y$ phase, $E_{\text{iso}}$ is the total energy of a single Fe or P atom and $E_{\text{bin}}$ refers to the cohesive energy of the Fe or P crystal, respectively. [10]

3. Results and discussions

3.1 Stability

![Fig. 2. The Fe-P equilibrium phase diagram](image)

Fig. 2 shows the Fe-P equilibrium phase diagram [1] and the five Fe$_x$P$_y$ binary phases are Fe$_3$P, Fe$_2$P, FeP, FeP$_2$, and FeP$_4$. With the increase of phosphorus content, the melting points of the Fe-P compounds increased. FeP$_4$ has the highest melting point as 1700°C among the Fe-P compounds. The melting point of Fe$_3$P is the lowest may be ascribed to the weak covalent bonding between Fe atom and P atom. In fact, one example is Fe$_3$P as a common phase in grain-boundary segregation in some type steel material.
Fig. 3. The crystal structure of Fe-P compounds. The blue balls represent Fe atoms, the red balls refer to P atoms.

Fig. 3 shows the crystal structure of Fe-P compounds. The Fe₃Pₓ binary compounds contains four different types of crystal system, including tetragonal (Fe₃P), hexagonal (Fe₂P), orthorhombic (o-FeP₁, o-FeP₂, FeP₂, o-FeP₄), and monoclinic (m-FeP₄₁, m-FeP₄₂). The calculated lattice parameters of Fe, P and Fe-P compounds have been optimized, which are listed in Table 1. By compared these results, it can be seen that the calculated lattice parameters of o-FeP₂ compounds are in good agreement with other calculated results and experimental values. [11-20] The average deviation of our result to experimental data for lattice parameters is less than 5.6%, which can be attributed to the approximation method in the work and thermodynamic effects on the crystal structures.
Fig. 4. The formation enthalpy ($\Delta H$) and the spin-polarized formation enthalpy ($\Delta H^*$) of Fe-P binary compounds.

The cohesive energy and formation enthalpy are used to evaluate the stability of Fe-P binary compounds. As defined in Eqs. (2)-(3), the lower value for these two thermodynamic parameters, the more stable for the compound. The cohesive energy mainly reflects the stability of the combination with two atoms, while the formation enthalpy mainly reflects the stability of the formation of compounds. As shown in Table 1, the calculated cohesive energy and formation enthalpy of studied Fe-P binary compounds are negative, which shows that Fe-P compounds are thermodynamically stable. The formation enthalpy without spin-polarized of Fe-P compounds are -67.068, -81.957, -78.580, -78.590, -69.200, -49.533, -48.395 and -49.370 kJ/mol, and the calculated spin-polarized formation enthalpy of Fe-P compounds are -44.950, -61.510, -78.580, -78.590, -69.200, -49.533, -48.395 and -49.370 kJ/mol for Fe$_x$P$_y$, Fe$_2$P, o-FeP$_1$, o-FeP$_2$, FeP$_2$, m-FeP$_4$, o-FeP$_4$, and m-FeP$_4$ phases, respectively. Fig. 4 shows the formation enthalpy ($\Delta H$) and the calculated spin-polarized formation enthalpy ($\Delta H^*$) curves as a function of P atom content for Fe-P binary compounds. Obviously, with the increase of phosphorus content, the formation enthalpy of Fe$_x$P$_y$ compounds decrease at first and then increase. Which may due to the proportion of anti-bonding states decreasing at first and then increasing. For the $\Delta H$, among all Fe-P binary
compounds, o-FeP₄ has the largest formation enthalpy value as -55.275 kJ/mol, and o-FeP₂ has the smallest formation enthalpy value as -95.255 kJ/mol. The stability sequence of eight Fe-P phase forms the following order: o-FeP₂ > o-FeP₁ > Fe₃P > FeP₂ > Fe₃P > m-FeP₄₁ > m-FeP₄₂ > o-FeP₄. For the ΔH*, Fe₃P has the largest formation enthalpy value as -44.950 kJ/mol, and o-FeP₂ has the smallest formation enthalpy value as -78.590 kJ/mol. The stability sequence of these Fe-P phase forms the following order: o-FeP₂ > o-FeP₁ > Fe₂P > Fe₃P > m-FeP₄₁ > m-FeP₄₂ > o-FeP₄ > Fe₃P. Spin-polarization increased formation enthalpy of Fe₃Pₓ compounds, and the effect on the formation enthalpy weaken with the increased of phosphorus content. The stability sequence of the compounds changes with and without the spin-polarization. Form the result of the stability sequence it can be seen that the stability of Fe₃P and Fe₂P is reduced with the spin-polarization, which may due to the magnetic characters of Fe₃P and Fe₂P. According to the density of states, we can know that Fe₃P and Fe₂P have magnetic characters. In general, o-FeP₂ is the most stable compound among Fe-P compounds.

3.2 Elastic constants and polycrystalline moduli

The calculated elastic constants of the α-Fe, phosphorus and Fe-P compounds are listed in Table 2. The elastic stability conditions in various crystal systems can be expressed as [21,22]:

(1) orthorhombic (for o-FeP₁-1, o-FeP₁-2, FeP₂, o-FeP₄):

\[ c_{ii} > 0, c_{11}c_{22} > c_{12}^2, c_{11}c_{22}c_{33} + 2c_{12}c_{13}c_{23} - c_{11}c_{23}^2 - c_{22}c_{13}^2 - c_{33}c_{12}^2 > 0, \]
\[ c_{44} > 0, c_{55} > 0, c_{66} > 0. \]  \hspace{1cm} (4)

(2) tetragonal (for Fe₃P) and hexagonal (for Fe₂P):

\[ c_{11} > \sqrt{c_{12}^2}, 2c_{13}^2 < c_{33}(c_{11} + c_{12}), c_{44} > 0, 2c_{16}^2 < c_{66}(c_{11} - c_{12}). \]  \hspace{1cm} (5)

(3) monoclinic (for m-FeP₄₋₁, m-FeP₄₋₂):
\[ c_{11} + c_{22} + c_{33} + 2(c_{12} + c_{13} + c_{23}) > 0, c_{33}c_{55} - c_{35}^2 > 0, c_{44}c_{66} - c_{46}^2 > 0, c_{22} + c_{33} - 2c_{23} > 0, \]
\[ c_{22}(c_{33}c_{55} - c_{35}^2) + 2c_{23}c_{25}c_{35} - c_{25}^2c_{35} - c_{25}^2c_{33} > 0, \]
\[ 2[c_{15}c_{25}(c_{13}c_{12} - c_{12}c_{13}) + c_{15}c_{35}(c_{22}c_{13} - c_{12}c_{23}) + c_{25}c_{35}(c_{11}c_{23} - c_{12}c_{13})] - [c_{13}^2(c_{22}c_{33} - c_{23}^2) \]
\[ + c_{25}^2(c_{11}c_{33} - c_{13}^2) + c_{35}^2(c_{11}c_{22} - c_{12}^2)] + c_{55}g > 0(g = c_{11}c_{22}c_{33} - c_{11}c_{23}^2 - c_{22}c_{13}^2 - c_{33}c_{12}^2) \]
\[ + 2c_{12}c_{13}c_{23}) > 0, c_{ii} > 0(i = 1 - 6). \]

As shown in Table 2, the calculated elastic constants of each Fe-P compound satisfy the above criterion, which indicating that all of Fe-P compounds are mechanically stable. The calculated \( c_{11} \) and \( c_{22} \) of FeP\(_2\) are larger than other elastic constants which indicates that they have high incompressible under uniaxial stress along crystallographic a (\( \varepsilon_{11} \)) and b (\( \varepsilon_{22} \)) axis. o-FeP\(_2\) has the largest \( c_{33} \) value, which show that o-FeP\(_2\) is very incompressible under uniaxial stress along crystallographic c (\( \varepsilon_{33} \)) axis. The largest elastic constant is the \( c_{22} \) of FeP\(_2\) with 685.5 GPa. For two FeP polymorphs, the \( c_{22} \) of o-FeP\(_1\) is close to the \( c_{33} \) of o-FeP\(_2\) and the \( c_{33} \) of o-FeP\(_1\) is close to the \( c_{22} \) of o-FeP\(_2\), which indicates that in the terms of incompressible performance the b (\( \varepsilon_{22} \)) axis of o-FeP\(_1\) is close to the c (\( \varepsilon_{33} \)) axis of o-FeP\(_2\), and the c (\( \varepsilon_{33} \)) axis of o-FeP\(_1\) is close to the b (\( \varepsilon_{22} \)) axis of o-FeP\(_1\). \( c_{44}, c_{55} \) and \( c_{66} \) represents the shear modulus on (100), (010) and (001) crystal plane. From Table 2, one can see that Fe\(_2\)P has the largest \( c_{44} \) value and o-FeP\(_4\) has the smallest \( c_{44} \) value for all Fe-P binary compounds. For three FeP\(_4\) polymorphs, m-FeP\(_4\)\(_2\) has the largest \( c_{44} \) value as 147.5 GPa.

The bulk modulus (B), shear modulus (G), Young’s modulus (E) and Poisson’s ratio (\( \sigma \)) of polycrystalline crystal are estimated with independent single crystal elastic constants according to the Voigt-Reuss-Hill (VGH) approximation [24]. The Voigt method is based on assumption of uniform strain throughout a polycrystal, which is given by:

\[ 9B_y = (c_{11} + c_{22} + c_{33}) + 2(c_{12} + c_{13} + c_{23}) \]  
(7)

\[ 15G_y = (c_{11} + c_{22} + c_{33}) - (c_{12} + c_{13} + c_{23}) + 3(c_{44} + c_{55} + c_{66}) \]  
(8)
the Reuss method assumes a uniform stress and gives $B$ and $G$ as functions of the elastic compliance constants $s_{ij}$, which is the inverse matrix of $c_{ij}$.

$$1/B_R = (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})$$ (9)

$$1/G_R = 4[(S_{11} + S_{22} + S_{33}) - (S_{12} + S_{13} + S_{23})]/15 + (s_{44} + s_{55} + s_{66})/5$$ (10)

the Voigt-Ruess-Hill (VRH) approximation is considered as a good estimated method for elastic modulus of polycrystalline.

$$G_H = (G_R + G_V)/2$$ (11)

$$B_H = (B_R + B_V)/2$$ (12)

the Young’s modulus ($E$) and Poisson’s ratio ($\sigma$) can be calculated by follows: [25,26]

$$E = 9BG / (3B + G)$$ (13)

$$\sigma = (3B - 2G) / (6B + 2G)$$ (14)

The calculated bulk modulus ($B$), shear modulus ($G$), Young’s modulus ($E$) and Poisson’s ratio ($\sigma$) of these Fe-P binary compounds are shown in Table 4. Bulk modulus reveals the compressibility of the solid under hydrostatic pressure and the values are 315.8, 304.1, 235.5, 250.7, 284.2, 152.5, 153.6 and 147.7 GPa for $\text{Fe}_3P$, $\text{Fe}_2P$, $\text{o}-\text{FeP}_1$, $\text{o}-\text{FeP}_2$, $\text{FeP}_2$, $\text{m}-\text{FeP}_4.1$, $\text{o}-\text{FeP}_4$ and $\text{m}-\text{FeP}_4.2$, respectively. The bulk modulus values of $\text{Fe}_3P$ and $\text{Fe}_2P$ is higher than other carbides, such as $\text{Fe}_3C$ (255 GPa) [28], TiC (242 GPa) [29] and Cr$_3$C (287.5 GPa) [30], but lower than h-WC (393.0 GPa) [31] and diamond (436.8 GPa) [32]. $\text{Fe}_3P$ has the largest value of bulk modulus among Fe-P binary compounds, which may owe to its strongest ionic bond between Fe atom and P atom. Because the ionic bond have no direction. The calculated values of shear modulus are 84.0, 132.2, 148.7, 148.0, 176.8, 127.0, 129.4 and 125.4 GPa for $\text{Fe}_3P$, $\text{Fe}_2P$, $\text{o}-\text{FeP}_1$, $\text{o}-\text{FeP}_2$, $\text{FeP}_2$, $\text{m}-\text{FeP}_4.1$, $\text{o}-\text{FeP}_4$ and $\text{m}-\text{FeP}_4.2$, respectively. The largest value of shear modulus belongs to $\text{FeP}_2$, and the
largest value of Young’s modulus is attributed to FeP₂. In addition, Fe₃P with the lowest P atom content has the largest bulk modulus as 315.8 GPa and the smallest shear modulus as 84.0 GPa. The result can be explained by the strong ionic bonding and weak covalent bonding of Fe₃P, because the ionic bond have no direction, covalent bond has directionality.

Fig. 5. Polycrystalline elastic moduli of Fe-P binary compounds.

Fig. 5 presents the bulk modulus, shear modulus and Young’s modulus curves as a function of P atom content for Fe-P system. With the increase of phosphorus content, the three moduli of the Fe-P compounds first decrease again increase to decrease again. The ratio of B/G (here B_H and G_H are used) can be used to indicate the ductile or brittle of the compounds, a high value is associated with ductility and a low value is associated with brittleness, the critical value is about 1.75. Fig. 6 shows the B/G and Poisson’s ratio curves as a function of P atom content for Fe-P system. When comparing the B/G value, it’s clearly imply that Fe₃P and Fe₂P are considered to be ductile compound since the value of B/G is larger than 1.75, m-FeP₄.2 has the smallest value as 1.18, indicating it’s the most brittle. The result is in good agreement with the analysis of density of states. Meanwhile, the Poisson’s ratio larger or smaller than 0.25 can also be used to indicate the ductile or brittle of the compounds. From Fig. 6, we can know that Fe₃P and Fe₂P can be classified as ductility,
which may owe to the strong metallic bonding in it. While three FeP$_4$ compounds, two FeP compounds and FeP$_2$ should be classified as brittleness, since the value of B/G is smaller than 1.75 and the value of Poisson’s ratio is smaller than 0.25. This may owe to the strong covalent bonding in it.

![Graph](image)

**Fig. 6.** The B/G and $\sigma$ values of the Fe-P binary compounds.

The hardness ($H_v$) is very important in the applications of Fe-P binary compounds. In the present paper, the hardness of two FeP compounds is estimated by a relatively semi-empirical equation \[33,44\]. The equation is defined as following:

$$H_v = AN_ae^{-\alpha_i}E_h,$$

$$N_a = \left(\sum_i n_iZ_i/2v\right)^{2/3}, f_i = 1 - \exp\left[-(x_A - x_B)^2/4\right], E_h = 39.74/d^{2.5} \tag{15}$$

where $H_v$ denotes the hardness, $A$ is a proportional coefficient, $\alpha$ is a constant. $A=14, \alpha =-1.191$. $n_i$ is the number of $i$ atom in the cell, $Z_i$ is the valence electron number of $i$ atom, $v$ is the cell volume. $x_A$ is the electronegativities of $A$ atom, $d$ is the bond length in angstroms. The calculated hardness of FeP compounds are shown in Table 3.

### 3.3 Anisotropy of elastic properties

The mechanical anisotropy is important in the applications of Fe-P materials. The fracturing
crack of materials forms not only in the substrate, but also in the inclusion. The formation and propagation of micro cracks is often related to the elastic anisotropy. Knowing the anisotropy of Fe$_x$P$_y$ compounds would be helpful to design and enhance some special device. To describe the degrees of anisotropy of Fe-P binary compounds, a numbers of indexes, including the shear anisotropic factors ($A_1$, $A_2$ and $A_3$), the percentages of anisotropy in the compression and shear ($A_B$ and $A_G$) and a universal elastic anisotropy index ($A^U$) are calculated by the following equations [34,35,36].

\[
A_1 = \frac{4C_{14}}{C_{11} + C_{13} - 2C_{12}} \quad \text{for (100) plane} \\
A_2 = \frac{4C_{33}}{C_{22} + C_{33} - 2C_{23}} \quad \text{for (010) plane} \\
A_3 = \frac{4C_{16}}{C_{11} + C_{22} - 2C_{12}} \quad \text{for (001) plane} \\
A_B = \frac{B_V - B_R}{B_V + B_R} \times 100 \\
A_G = \frac{G_V - G_R}{G_V + G_R} \times 100 \\
A^U = 5 \frac{G_V}{G_R} + \frac{B_V}{B_R} - 6 \geq 0
\]

where $B_V$, $B_R$, $G_V$ and $G_R$ are the bulk and shear modulus calculated with Voigt and Reuss methods, respectively. The calculated results are shown in Table 4. For $A_1$, $A_2$ and $A_3$, a value of unity imply isotropic and a non-unity value imply anisotropic for a crystal. For isotropic structures, the values of $A_B$, $A_G$ and $A^U$ are zero. Meanwhile the large discrepancies from zero indicate the highly mechanical anisotropic properties.

From Table 4, it can be seen that Fe is isotropic, Fe$_2$P and m-FeP$_4$2 have strong isotropy, and Fe$_3$P has the strongest anisotropy especially in (001) plane. Fe$_3$P has the largest value of $A_G$ as 22.43% among all Fe-P binary compounds, implying that the anisotropy in shear modulus for Fe$_3$P
is the strongest. However, the $A_1$, $A_2$, $A_3$, $A_4$ and $A_5$ can’t fully describe the elastic anisotropy. The $A_1$, $A_2$ and $A_3$ describe the anisotropy of the shear modulus in different crystal plane, the index $A^U$ is considered as an appropriate parameter to describe the degrees of elastic anisotropy of the compound. From the Table 4, Fe$_3$P has the strongest anisotropy of the Fe-P binary compounds, since the value of $A^U$ is 2.89, and m-FeP$_4$2 has the strongest isotropy among the Fe$_x$P$_y$ compounds, since the value of $A^U$ is 0.35.
Fig. 7. Contour plots of Young’s modulus of Fe-P compounds in 3-D space.
Fig. 8. Planar projections of Young’s modulus of Fe-P compounds at (100), (001) and (110) crystallographic planes.
The most straightforward way to illustrate the elastic anisotropy is to plot the Young’s modulus and shear modulus in three dimensions (3D) as a function of the crystallographic direction.

The directional dependence of Young’s modulus and shear modulus is given by [10,34,37,38,42,43]:

Fig. 9. Contour plots of shear modulus (GPa) of Fe-P compounds in 3-D space.
Hexagonal crystal (for Fe\textsubscript{2}P)

\[
\frac{1}{E} = (1 - l_{ij}^2)^2 s_{11} + l_{11}^2 s_{33} + l_{12}^2 (1 - l_{ij}^2)(2s_{11} + s_{44})
\]

\[
\frac{1}{G} = S_{44} + \left( S_{11} - S_{12} \right) - \frac{1}{2} S_{44} (1 - l_{ij}^2) + 2 \left( S_{11} + S_{33} - 2S_{13} - S_{44} \right) l_{12}^2 (1 - l_{ij}^2)
\]  

(22)

Orthorhombic crystal (for o-Fe\textsubscript{5}P\textsubscript{1}, o-Fe\textsubscript{5}P\textsubscript{2}, FeP\textsubscript{2}, o-FeP\textsubscript{4})

\[
\frac{1}{E} = s_{11} l_{11}^4 + s_{22} l_{22}^4 + s_{33} l_{33}^4 + (2s_{12} + s_{66}) l_{12}^2 l_{22}^2 + (2s_{13} + s_{55}) l_{13}^2 l_{33}^2 + (2s_{23} + s_{44}) l_{23}^2 l_{33}^2
\]

\[
\frac{1}{G} = 2S_{11} l_{11}^2 (1 - l_{11}^2) + 2S_{22} l_{22}^2 (1 - l_{22}^2) + 2S_{33} l_{33}^2 (1 - l_{33}^2) - 4S_{12} l_{12}^2 l_{22}^2 - 4S_{13} l_{13}^2 l_{33}^2 - 4S_{23} l_{23}^2 l_{33}^2
\]

\[
+ \frac{1}{2} S_{44} (1 - l_{11}^2 - 4l_{22}^2 l_{33}^2) + \frac{1}{2} S_{55} (1 - l_{22}^2 - 4l_{11}^2 l_{33}^2) + \frac{1}{2} S_{66} (1 - l_{33}^2 - 4l_{11}^2 l_{22}^2)
\]  

(23)

Monoclinic crystal (for m-FeP\textsubscript{4}.1, m-FeP\textsubscript{4}.2)

\[
\frac{1}{E} = l_{11}^4 s_{11} + l_{22}^4 s_{22} + l_{33}^4 s_{33} + 2l_{11}^2 l_{12}^2 s_{12} + 2l_{11}^2 l_{13}^2 s_{13} + 2l_{12}^2 l_{23}^2 s_{23} + 2l_{13}^2 l_{23}^2 s_{25} + l_{11}^2 l_{23}^2 s_{44}
\]

\[
+2l_{13}^2 l_{23}^2 s_{46} + l_{11}^2 l_{23}^2 s_{55} + l_{12}^2 l_{23}^2 s_{66}
\]  

(24)

Tetragonal (for Fe\textsubscript{3}P)

\[
\frac{1}{E} = s_{11} (1 - l_{ij}^2)^2 + s_{33} l_{11}^4 + (2s_{13} + s_{44}) l_{12}^2 (1 - l_{ij}^2)
\]

\[
\frac{1}{G} = 2S_{11} l_{11}^2 (1 - l_{11}^2) + 2S_{22} l_{22}^2 (1 - l_{22}^2) + 2S_{33} l_{33}^2 (1 - l_{33}^2) - 4S_{12} l_{12}^2 l_{22}^2 - 4S_{13} l_{13}^2 l_{33}^2 - 4S_{23} l_{23}^2 l_{33}^2
\]

\[
+ \frac{1}{2} S_{44} (1 - l_{11}^2 - 4l_{22}^2 l_{33}^2) + \frac{1}{2} S_{55} (1 - l_{22}^2 - 4l_{11}^2 l_{33}^2) + \frac{1}{2} S_{66} (1 - l_{33}^2 - 4l_{11}^2 l_{22}^2)
\]  

(25)

where \(s_{ij}\) are the elastic compliance constants, and \(l_{1}, l_{2}\) and \(l_{3}\) are the directional cosines. The surface contours of the Young’s modulus and shear modulus of Fe-P binary compounds are illustrated in Fig. 7 and Fig. 9. For an isotropic system, the graph would be a sphere. Obviously, Fe\textsubscript{2}P, Fe\textsubscript{3}P, FeP\textsubscript{2}, m-FeP\textsubscript{4}.1 and o-FeP\textsubscript{4} show a strong anisotropic character in Young’s modulus, and Fe\textsubscript{3}P, two FeP compounds, FeP\textsubscript{2} and o-FeP\textsubscript{4} show a strong anisotropic character in shear modulus.

The surface contour of two FeP compounds and m-FeP\textsubscript{4}.2 in Fig.7 is close to an cylinder, which means that the Young’s modulus of these compounds have weaker anisotropy than other
compounds. Projections of the Young’s modulus on the (100), (001) and (110) planes shows more details about the anisotropic properties of Young’s modulus as shown in Fig. 8. Obviously, Young’s modulus has a strong directional dependence on these planes. From Fig. 8, we can see that FeP₂ shows the maximum Young’s modulus along the [010] and [110] direction, and Fe₃P shows the minimum Young’s modulus along the [010] direction one the (100) and (001) plane. For Fe₂P, the planar contours on the (001) planes is close to an ellipse, which means that the Young’s modulus of Fe₂P on the (001) planes has weaker anisotropy than other compounds.

3.4 Electronic structures

The electronic structures and chemical bonding characteristics of FeₓPᵧ compounds are indicated by the electron density distribution map, total density of states (TDOS) and partial density of states (PDOS).
Fig. 10. Total electron density distribution through (-0.563 0.318 0.763), (0.561 -0.764 -0.318), (-0.021 -0.020 0.999), (-0.039 -0.355 -0.934), (1 0 0), (0 0 1) and (-0.012 -0.012 0.999) slice intersecting both Fe and P atoms for (a) α-FeP-1, (b) α-FeP-2, (c) FeP₂, (d) α-FeP₄, (e) m-FeP₄₁, (f) FeP and (g) Fe₃P compounds, respectively.

The calculated total electron density distribution maps of Fe-P compounds are shown in Fig. 10. Electronic mainly concentrated on the iron atoms. For α-FeP-1, α-FeP-2, Fe₂P and Fe₃P, the electron density values are large than zero even in the interstitial regions, which indicate the metallic nature of these compounds. The elongated contours along Fe-P bond axis show the covalent interaction. m-FeP₄₁ has the strongest covalent bonding between P and P.
Fig. 11. The total density of states (TDOS) and partial density of states (PDOS) for Fe$_x$P$_y$ compounds, dashed lines represent the Fermi level.

The TDOS and PDOS of Fe$_x$P$_y$ compounds are shown in Fig. 11. The nature of magnetic characters can be understood from the spin-polarized total density of states. Comparing the up with
down densities, it can be seen that the up and down states are not symmetric for Fe$_3$P and Fe$_2$P, which indicates they have magnetic characters. Actually, the low and high valence band is almost symmetric, and it is near to the Fermi level that the up and down states are dissymmetric. While for other compounds, the up and down states are symmetric, so they have no magnetic characters. No energy gap near to the Fermi level can be seen for Fe$_3$P, Fe$_2$P, o-FeP$_1$, and o-FeP$_2$, which indicates the metallicity and electronic conductivity of these binary compounds. Based on the analysis of band structure, the energy gap near to the Fermi level for FeP$_2$, o-FeP$_4$, m-FeP$_{4-1}$ and m-FeP$_{4-2}$ are 0.573, 0.903, 0.924 and 1.16 eV, respectively. So these four compounds are considered to be semiconductor, and the electroconductibility of m-FeP$_{4-2}$ is the worst. Other compounds belong to conductor. We can see that the TDOS values in Fermi levels increased as the Fe atom content increased. The Fe$_3$P has the strongest metallicity, which is consistent with the opinion of B/G and Poisson’s ratio ($\sigma$). The Fe-d bands of m-FeP$_{4-1}$ have a peak, which shows that the electron of d bands is relatively local state. From the Fig. 11, it can be seen that the ground state properties of Fe-P binary compounds are determined by 3d bands of Fe. At the low energy part, the band from -9 eV to -5 eV is mainly contributed by 3p bands of P. The Fe-d bands are overlapped with the P-p bands in the energy range from -4 eV to 3 eV for three FeP$_4$ compounds, which indicates the covalent interactions because of the strong hybridization between Fe-d bands and P-p bands. It’s similar with the energy range from -2 eV to 3 eV of FeP$_2$. The Fe-d band hybridizes weakly with the P-p in the energy range from -5 eV to -2 eV for o-FeP$_1$ and o-FeP$_2$. We can see that the FeP$_4$ compounds have the strongest covalent interaction among all Fe$_x$P$_y$ compounds from Fig. 11, which lends to the highest melting point. This result is in consistent with the Fe-P equilibrium phase diagram. The valence electrons of Fe and P atom considered are $3p^63d^64s^2$ and $3s^23p^3$. For Fe$_3$P, the
position of Fe-d bands does not coincide with the P-p bands, which shows the interaction between the electrons of P and Fe atom. The Fe 3d orbitals loses an electron and forms the partially fulled state, the P 3p orbitals gets three electrons and forms the entirely fulled state. In addition, the partially fulled and entirely fulled states are stable state. The electron transfer path implies ionic interaction in Fe₃P compounds. In a word, with the increase of phosphorus content, the covalent interaction of the Fe-P binary compounds strengthens, and the ionic interaction and metallicity weakens.

According to above discussions, Fe₃P and Fe₂P have magnetic characters. m-Fe₃P-2 is considered to be semiconductor. The bonding behaviors of Fe-P binary compounds are the combinations of metallic, covalent and ionic bonds. For Fe₃P and Fe₂P, the chemical bonding is dominated by the Fe-P ionic bonds. The chemical bonding of o-FeP₁, 0-FeP₂, FeP₂, m-Fe₃P₁, o-FeP₄ and m-Fe₃P₂ is dominated by the Fe-P covalent bonds but also possesses the ionic and metallic character, which may lead to the high melting point.

3.5 Debye temperature

It is certain that the sound velocity and Debye temperature can be used to evaluate the chemical bonding characteristics and thermal properties of compounds. The sound velocity and Debye temperature at the low-temperature are calculated with the previously obtained bulk modulus (B) and shear modulus (G). The Debye temperature can be calculated by the following equation: [39,9]

\[
\Theta_D = \frac{h}{k_B} \left[ \frac{3n}{4\pi} \left( \frac{N_A \rho}{M} \right) \right]^{1/3} V_n
\]

(26)

where, \(\Theta_D\) represents Debye temperature; \(h\) and \(k_B\) is Plank and Boltzmann constant, respectively; \(n\) is the total number of atoms per formula; \(N_A\) is the Avogadro constant; \(M\) is the molecular weight
per formula; $\rho$ is the theoretical density, and the $v_m$ is the average sound velocity defined as:

$$v_m = \left[ \frac{1}{3} \left( \frac{2}{v_s^3} + \frac{1}{v_l^3} \right) \right]^{-1/3}$$

(27)

$$v_s = \sqrt{G/\rho}$$

(28)

$$v_l = \sqrt{\left( \frac{B}{3} + \frac{4}{3} G \right) \frac{1}{\rho}}$$

(29)

where, $v_t$ is the transverse sound velocity and $v_l$ is the longitudinal sound velocity; $B$ and $G$ are isothermal bulk modulus and shear modulus. [22,40,41].

The value of Debye temperature and sound velocities of Fe-P binary compounds are listed in Table 5. Debye temperature reflects the strength of chemical bonding in crystal structure. From the Table 5, we can see that the Debye temperature increases with P atom content increases in the Fe-P binary compounds expect for FeP$_2$. Moreover, Fe$_3$P has the lowest Debye temperature and highest B/G ratio, which indicates the strongest metallic character. It is consistent with the previous calculations on the density of states. Besides, the average sound velocities of these Fe$_x$P$_y$ compounds are relatively large about 5500 m/s except Fe$_3$P. A reasonable explanation is these compounds with high bulk and shear modulus and low density, the $v_t$ and $v_s$ are correlated to bulk modulus, shear modulus and density.

4. Conclusions

In general, we have investigated stability, mechanical properties and electronic structures of all Fe-P binary compounds with first-principles calculations. The cohesive energy and formation enthalpy indicate that they are thermodynamically stable. The elastic constants of the Fe$_x$P$_y$ compounds satisfy the mechanical stability criterions. Fe$_3$P has the largest bulk modulus as 315.8 GPa and the smallest shear modulus as 84.0 GPa. FeP$_2$ exhibits the largest shear and Young's
modulus as 176.8 and 439.3 GPa, respectively. The hardness of two FeP compounds is 33.39 GPa.

Fe₃P and Fe₂P are considered to be ductile compound, which may own to the strong metallic bonding in it. The 3D surface contour of Young’s modulus and shear modulus is plotted to verify the mechanical anisotropy of Fe-P binary compounds, Fe₃P has the strongest anisotropy among the FeₓPₙ compounds. The bonding behaviors of Fe-P binary compounds are the combinations of metallic, covalent and ionic bonds. Fe₃P and FeP₂ have the smallest and largest Debye temperature as 497.1 K and 822.4 K, respectively.

Acknowledgments

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References


Table 1: The space group, calculated lattice parameters, V_{cell}, cohesive energy (kJ/mol), formation enthalpy Δ_H, and the calculated spin-polarized formation enthalpy Δ_H^* (kJ/mol) of Fe-P binary compounds.

<table>
<thead>
<tr>
<th>Substances</th>
<th>space group</th>
<th>Composition at %P</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>V_{cell}(Å³)</th>
<th>E_{coh}</th>
<th>Δ_H (kJ/mol)</th>
<th>Δ_H^* (kJ/mol)</th>
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<td>Fe</td>
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<td>0</td>
<td>3.402</td>
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<td>3.402</td>
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<td>-898.415</td>
<td>0</td>
<td>0</td>
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<td>8.598</td>
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<td>-848.235</td>
<td>-67.068</td>
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<tr>
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<td>5.053</td>
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<td>-791.300</td>
<td>-95.255</td>
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<tr>
<td>m-FeP₄.1</td>
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<td>10.939</td>
<td>557.632</td>
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<td>-49.553</td>
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<td>m-FeP₄.2</td>
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<td>4.540</td>
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a Cal. in Ref. [11]  
b Exp. in Ref. [12]  
c Exp. in Ref. [13]  
d Cal. in Ref. [4]    
e Exp. in Ref. [14]  
f Exp. in Ref. [15]  
g Exp. in Ref. [16]  
h Exp. in Ref. [17]  
i Exp. in Ref. [18]  
j Exp. in Ref. [19]  
k Cal. in Ref. [20]
Table 2 Single crystalline elastic constants ($c_{ij}$, in GPa) of Fe-P binary compounds.

<table>
<thead>
<tr>
<th>Substances</th>
<th>Fe</th>
<th>Fe$_3$P</th>
<th>Fe$_2$P</th>
<th>o-FeP$_1$</th>
<th>o-FeP$_2$</th>
<th>FeP$_3$</th>
<th>m-FeP$_{4,1}$</th>
<th>o-FeP$_4$</th>
<th>m-FeP$_{4,2}$</th>
<th>P</th>
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<tbody>
<tr>
<td>$c_{11}$</td>
<td>266.4$^a$</td>
<td>418.2</td>
<td>460.3</td>
<td>502.5</td>
<td>506.4</td>
<td>570.0</td>
<td>335.9</td>
<td>367.5</td>
<td>279.9</td>
<td>188.4</td>
</tr>
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<td>$c_{22}$</td>
<td>418.2</td>
<td>460.3</td>
<td>476.4</td>
<td>280.1</td>
<td>685.5</td>
<td>325.2</td>
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<td>529.9</td>
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<td>344.2</td>
<td>374.3</td>
<td>285.5</td>
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<td>171.3</td>
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<td>91.6</td>
<td>76.7</td>
<td>147.5</td>
<td>19.9</td>
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<td>183.9</td>
<td>177.1</td>
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<td>228.4</td>
<td>109.3</td>
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<tr>
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a Cal. in Ref. [7]  
b Cal. in Ref. [23]  
c Cal. in Ref. [4]

Table 3 Polycrystalline elastic properties of Fe-P binary compounds, including Bulk modulus (B), Shear modulus (G), Young’s modulus (E), Poisson’s ratio ($\sigma$) and Vickers hardness ($H_v$).

<table>
<thead>
<tr>
<th>Substances</th>
<th>Fe</th>
<th>Fe$_3$P</th>
<th>Fe$_2$P</th>
<th>o-FeP$_1$</th>
<th>o-FeP$_2$</th>
<th>FeP$_3$</th>
<th>m-FeP$_{4,1}$</th>
<th>o-FeP$_4$</th>
<th>m-FeP$_{4,2}$</th>
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<tbody>
<tr>
<td>B (GPa)</td>
<td>186.5$^a$</td>
<td>315.8</td>
<td>304.8</td>
<td>243.0</td>
<td>262.8</td>
<td>296.8</td>
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<td>154.5</td>
<td>147.7</td>
<td>38.4</td>
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<tr>
<td>B (GPa)</td>
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<td>303.5</td>
<td>228.1</td>
<td>238.7</td>
<td>271.7</td>
<td>152.3</td>
<td>152.7</td>
<td>147.6</td>
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<tr>
<td>B (GPa)</td>
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<td>304.1</td>
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<td>152.5</td>
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<td>125.4</td>
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<td>E (GPa)</td>
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<td>439.3</td>
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<tr>
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a Cal. in Ref. [7]  
b Cal. in Ref. [23]  
c Cal. in Ref. [4]
Table 4 Anisotropic factors of Fe-P binary compounds.

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<thead>
<tr>
<th>E</th>
<th>A_1</th>
<th>A_2</th>
<th>A_3</th>
<th>A_{gf}(%)</th>
<th>A_{g}(%)</th>
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<td>2.71</td>
<td>2.71</td>
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<td>0.94</td>
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<td>0.13</td>
<td>4.29</td>
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<td>0.55</td>
<td>27.79</td>
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<td>2.81</td>
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Table 5 The theoretical density (\(\rho\), g/cm\(^3\)), longitudinal sound velocity (\(v_l\), m/s), transverse sound velocity (\(v_t\), m/s), average sound velocity (\(v_m\), m/s) and Debye temperature (\(\Theta_D\), K).

<table>
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<tr>
<th>species</th>
<th>(\rho)</th>
<th>(v_l)</th>
<th>(v_t)</th>
<th>(v_m)</th>
<th>(\Theta_D)</th>
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<td>4830.8</td>
<td>5402.9</td>
<td>668.6</td>
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<td>7955.9</td>
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