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First-principles calculation on the structure stability, elastic properties and electronic structure of P-doped Mg$_2$Si

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Abstract

In this study, the effect on the structure stability, elastic properties and electronic structure of P-doped Mg$_2$Si were studied by the first-principles pseudopotential plane wave method based on density functional theory. The lattice constants, formation enthalpy, cohesive energy, elastic constants, and elastic moduli of Mg$_2$Si, Mg$_7$Si$_4$P, Mg$_8$Si$_3$P and Mg$_8$Si$_4$P were calculated, and the electronic structure analysis was also performed. The occupation tendency, structural stability, bonding characteristics, orbital hybridization and the change of conductivity of doping P atoms in the matrix were further investigated. Among them, the research results of formation enthalpy, cohesive energy and elastic constant show that Mg$_2$Si, Mg$_8$Si$_3$P and Mg$_8$Si$_4$P can all exist stably in the system, and the crystal structure of Mg$_7$Si$_4$P can not exist stably. P atoms doping into the Mg$_2$Si lattice tend to occupy Si atoms position preferentially. The results of elastic modulus study show that Mg$_2$Si and Mg$_8$Si$_4$P are brittle phase and Mg$_8$Si$_3$P is ductile phase. The plasticity and toughness of Mg$_2$Si alloy system are improved by doping P atoms. The electronic structure analysis shows that the method of doping P atoms changes the orbital hybridization and bonding characteristics of the system. The Mg-P and Si-P covalent bond formed by Mg$_8$Si$_3$P and Mg$_8$Si$_4$P increase the structure stability. The energy band structure analysis also show reduction of the band gap from 0.224 to 0.184 eV for Mg$_2$Si with P dopants at the substitutional Si-sites and the band gap closure in the system with interstitial P-impurities. It enhances the metallic property of the material, and Mg$_8$Si$_3$P phase also transform from its semiconducting to metallic state. Consequently, this method both increases the carrier concentration and reduces the energy of free electron transition. The conductivity of the Mg$_2$Si alloy system will be improve.

1. Introduction

In recent years, with the continuous development of material lightweight technology in the field of rail transit, aerospace and other fields, the development and research of aluminum-based composite materials have attracted extensive attention in the field of materials and engineering circles. Mg$_2$Si has low density ($1.9 \times 10^3$ kg m$^{-3}$), high melting point (1085 °C), high specific strength, low coefficient of thermal expansion (TEC) ($7.5 \times 10^{-6}$ K$^{-1}$) and good thermal stability [1, 2]. It can be uniformly distributed in the aluminum matrix as reinforced particles, and firmly combine with the matrix. Their interface is clean with good compatibility. It greatly improves the tensile strength and wear resistance of the aluminum-based composite materials. However, Mg$_2$Si has intrinsic brittleness below 450 °C, and the ductility at room temperature is almost zero, which greatly limit its application and promotion in the engineering field [3]. Therefore, the modification of Mg$_2$Si intermetallic compounds has attracted widespread attention.

P element is one of the common modification elements in the preparation of Al/Mg$_2$Si composites [4]. Li and Liu [5] found that the Al-P and Al-Ti-B intermediate alloys have a better refining and modification effect on
the reinforced phase Mg$_2$Si. The morphology of the primary phase Mg$_2$Si changes from coarse dendrite to polyhedron, and their average particle size are about 100 μm to about 20 μm. Nasiri et al [6] found that 0.5% P could increase the tensile strength of Al-15% Mg$_2$Si alloy to 229 MPa and the elongation to 4%. Yeganeh et al [7] studied the effect of P on the microstructure and tensile properties of hot-extruded Al-25% Mg$_2$Si alloy, and found that the morphology of the primary Mg$_2$Si phase is changed with the addition of P. The morphology changes from coarse dendrite to polyhedron, and the size reduces from 220 μm to 22 μm. When the content of addition of P reaches to 1%, the specimen changes from as-cast brittle fracture to ductile fracture. Li et al [8] found that after adding 3% Al-3P master alloy to Al-12.67Mg-10.33Si alloy, the size of primary Mg$_2$Si is reduced from 100 μm to 20 μm, the shape changes from dendritic to polygonal shape, and the tensile strength increases from 252 MPa to 275 MPa. At present, there are a lot of experimental studies on the refinement and mechanical properties of Mg$_2$Si phase, but there are few reports on the effect of P on the microstructure and related properties of Mg$_2$Si phase in theory. In this study, the pseudopotential plane wave method was used to study the lattice constants, elastic constants and elastic modulus of three solid solutions forming in the P-doped Mg$_2$Si lattice. The electronic structure analysis was also performed. The occupation tendency, structural stability, bonding characteristics, orbital hybridization and the changes of conductivity of doping P atoms in the matrix were further investigated.

2. Theoretical model and calculation method

2.1. Theoretical model

Mg$_2$Si is stable compound in Mg-Si binary alloys [9]. At room temperature and pressure, Mg$_2$Si is an anti-fluorite (CaF$_2$) structure, with a face-centered cubic lattice (fcc) and a space group of Fm3m (No. 225), which has a high degree of symmetry. The lattice constant of Mg$_2$Si is $a = b = c = 0.6351$ nm, $\alpha = \beta = \gamma = 90^\circ$, and the specific coordinates of the unit cell atom are as follows [10–12]: Mg (8c) $(0.25, 0.25, 0.25)$, Si (4a) $(0, 0, 0)$. The crystal structure is shown in figure 1(a). The doping methods of P atoms in the Mg$_2$Si unit cell system can be divided into lattice replacement and gap filling, which form substitutional solid solutions and interstitial solid solutions, respectively. The occupancy is shown in figures 1(b), (c). In the substitutional solid solution Mg$_2$Si$_x$P and Mg$_8$Si$_4$P, the positions of Mg and Si atoms are equivalent, and the doping situations can be determined. Therefore, we chose a P atom to replace the Mg atom and the Si atom, respectively. The concentration of solid solution was 8.33%. However, the positions occupation of interstitial solid solution Mg$_8$Si$_4$P is diverse. Considering the radius of P atom is small, the interstitial position distance of body center is large, and the lattice structure is loose, it is most likely to form the interstitial solid solution after doping P atoms. Therefore, the interstitial position in this study was the body center position surrounded by 8 Mg atoms. The concentration of solid solution was 7.69%.

2.2. Calculation method

In this study, the calculation was completed by using the CASTEP (Cambridge Serial Total Energy Package) software package in Material Studio, basing on the first principle pseudopotential plane wave algorithm of Kohn-Sham self-consistent density functional theory [13, 14]. The algorithm was modified by the ultra-soft pseudopotential as well as the generalized gradient approximation PBE scheme. According to this algorithm, the interaction between valence electrons and ions can be described approximately [15]. In this study, the cut-off energy of plane wave was 380 eV, and the Brillouin zone integration used the highly symmetrical k-point method in the form of Monkhorst-Pack, dividing the lattice according to $8 \times 8 \times 8$ [3]. The reciprocal space used a k-point space of 0.05 nm$^{-1}$. Firstly, the BFGS algorithm was used to geometrically optimize the doped system cell model [16]. Basing on the most stable structure of the crystal, the self-consistent iterative SCF calculation was carried out, and the Pulay density mixing method was used to deal with electronic relaxation. The specific optimization parameters were selected as follows: the convergence value of the total energy of the system was $1.0 \times 10^{-5}$ V/atom; the force on each atom was less than 0.01 eV/Å, and the internal stress deviation was less than 0.02 GPa; The maximum displacement between atoms was less than 0.0005 Å. The valence electron configuration used in the optimization calculation was as follows: Mg is 2p$^6$3s$^2$; Si is 3s$^2$3p$^2$; P is 3s$^2$3p$^3$. The above datas were selected as the optimal value based on convergence verification.

3. Results and discussion

3.1. Crystal structures and lattice constants

In order to study the effect of P-doped on the crystal structure and stability of Mg$_2$Si, the geometric optimization of Mg$_2$Si phase, Mg$_8$Si$_4$P phase, Mg$_8$Si$_3$P phase and Mg$_8$Si$_4$P phase were carried out respectively, and the results of the optimized lattice parameters are shown in table 1. It can be seen from the table 1 that the calculated lattice
parameters of the optimized Mg$_2$Si are consistent with the reference values, with an error of about 0.063%. Therefore, the correctness of the calculation method, the reasonable reliability of parameter setting and the effectiveness of the calculation results are verified. When P atoms were doped into the Mg$_2$Si unit cell, lattice distortion will occur. Because the radius of P atom is smaller than that of Mg atom and Si atom, the lattice parameters and the unit cell volume of the Mg$_7$Si$_4$P and the Mg$_8$Si$_3$P are reduced correspondingly when the substitutional solid solution is formed. When the interstitial solid solution is formed, the lattice parameter of the Mg$_8$Si$_4$P phase increases correspondingly, and it causes the cell volume to expand.

3.2. Formation enthalpy and cohesive energy

Formation enthalpy (H$_{\text{form}}$), which is one of the standards to measure the stability of phase structure, is the energy released or absorbed after the reaction of substances. It can represent the degree of difficulty in the formation of intermetallic compounds. When the formation enthalpy is negative, the larger the absolute value is, the easier the intermetallic compound is to form and the stronger the alloying ability is. The formula for calculating formation enthalpy is shown as follows [14, 17]:

![Crystal structure of Mg$_2$Si (a), Mg$_7$Si$_4$P (b), Mg$_8$Si$_3$P (c) and Mg$_8$Si$_4$P (d).](Figure 1)
In the above formula, $E_{\text{tot}}$ represents the total energy of the unit cell; $N_{\text{Mg}}, N_{\text{Si}}$ and $N_{\text{P}}$ represents the number of Mg, Si and P atoms in the unit cell model; $E_{\text{solid}}^{\text{Mg}}, E_{\text{solid}}^{\text{Si}}$ and $E_{\text{solid}}^{\text{P}}$ are the average single-atom energy of Mg, Si and P atoms in the solid states, respectively. The calculation results of $E_{\text{solid}}$ of Mg, Si and P atoms in this work are listed in table 2. Table 3 lists the calculation results of the formation enthalpy of each phase after P doping. It can be seen from the table 3 that the calculated formation enthalpy is close to the reference value given in the literature, which proves that the calculation parameter settings are reasonable.

Additionally, the structural stability of the crystal is closely related to its cohesive energy ($E_{\text{coh}}$). The cohesive energy is the energy released by the combination of free atoms into a crystal. It can also be defined as the work done by the outside world when a crystal is broken down into a single atom. The larger the absolute value of cohesive energy is, the stronger the bonding force between the atoms in the crystal is, and the more stable the structure is.

\[
E_{\text{coh}} = \frac{(E_{\text{tot}} - N_{\text{Mg}} E_{\text{solid}}^{\text{Mg}} - N_{\text{Si}} E_{\text{solid}}^{\text{Si}} - N_{\text{P}} E_{\text{solid}}^{\text{P}})}{(N_{\text{Mg}} + N_{\text{Si}} + N_{\text{P}})}
\]

In the above formula, $E_{\text{tot}}$ represents the total energy of the unit cell; $N_{\text{Mg}}, N_{\text{Si}}$ and $N_{\text{P}}$ represents the number of Mg, Si and P atoms in the unit cell model; $E_{\text{solid}}^{\text{Mg}}, E_{\text{solid}}^{\text{Si}}$ and $E_{\text{solid}}^{\text{P}}$ are the average single-atom energy of Mg, Si and P atoms in the solid states, respectively. The calculation results of $E_{\text{solid}}$ of Mg, Si and P atoms in this work are listed in table 2. Table 3 lists the calculation results of the formation enthalpy of each phase after P doping. It can be seen from the table 3 that the calculated formation enthalpy is close to the reference value given in the literature, which proves that the calculation parameter settings are reasonable.

In order to analyze the formation capacity of each phase more intuitively, the calculated results are drawn in figure 2. The formation enthalpy of each phase is negative, which indicates that all phases before and after doping can form stably in the system. The absolute value of formation enthalpy increases in the following order: $\text{Mg}_7\text{Si}_4\text{P} < \text{Mg}_8\text{Si}_3\text{P} < \text{Mg}_2\text{Si}$. Wherein the absolute value of formation enthalpy of $\text{Mg}_8\text{Si}_3\text{P}$ phase is the largest, which indicates that it is the easiest to form in the system. In some extent, P atoms tend to preferentially replace Si atoms in the $\text{Mg}_2\text{Si}$ lattice and have the best alloying capacity after doping.
A crystal is formed. The formula for calculating cohesive energy is shown as follows [14, 17]:

\[
E_{\text{coh}} = \frac{E_{\text{tot}} - N_{\text{Mg}}E_{\text{atom}}^{\text{Mg}} - N_{\text{Si}}E_{\text{atom}}^{\text{Si}} - N_{\text{P}}E_{\text{atom}}^{\text{P}}}{N_{\text{Mg}} + N_{\text{Si}} + N_{\text{P}}}
\]  

(2)

In the above formula, \(E_{\text{tot}}\) represents the total energy of the unit cell; \(N_{\text{Mg}}, N_{\text{Si}}, \) and \(N_{\text{P}}\) represents the number of Mg, Si and P atoms in the unit cell model; \(E_{\text{atom}}^{\text{Mg}}, E_{\text{atom}}^{\text{Si}}, \) and \(E_{\text{atom}}^{\text{P}}\) are the energy of the isolated atoms of Mg, Si and P in the free state, respectively. The calculation results of \(E_{\text{atom}}\) of Mg, Si and P in this work are listed in table 2. Table 3 lists the calculation results of the cohesive energy of each phase after P doping. It can be seen from the table that the calculated cohesive energy is close to the reference value given in the literature. It proves that the calculation parameter settings are reasonable.

It can be seen from figure 2 that the cohesive energy of each phase is negative, which indicates that all phases before and after doping can exist stably in the system. The absolute value of cohesive energy increases in the following order: \(\text{Mg}_2\text{Si} < \text{Mg}_8\text{Si}_3\text{P} < \text{Mg}_8\text{Si}_4\text{P} < \text{Mg}_7\text{Si}_4\text{P}\), in which the absolute value of cohesive energy of \(\text{Mg}_7\text{Si}_4\text{P}\) phase is the largest. It indicates that the structural stability of \(\text{Mg}_7\text{Si}_4\text{P}\) phase is the best. The absolute value of cohesive energy of \(\text{Mg}_2\text{Si}\) phase is the lowest, and its structural stability is the weakest, indicating that the thermodynamic stability of the system can be improved when P is doped into the \(\text{Mg}_2\text{Si}\) lattice.

3.3. Elastic properties

Elastic constant \(C_{ij}\) is often used to characterize the important parameters of material resisting external stress and deformation, which plays an important role in the determination of mechanical properties. For cubic crystal system, a set of strain can be applied to the crystal with the elastic deformation range, and the corresponding stress can be obtained by calculation for cubic crystal system. The elastic constant is obtained by fitting the stress-strain relation of generalized hooke’s law [20]. According to the mechanical stability judgment conditions of cubic crystal system, the independent elastic constants \(C_{11}, C_{12}\) and \(C_{44}\) must satisfy formula 3 at the same time for the crystal to exist stably [21].

\[
C_{11} > 0, \ C_{44} > 0, \ C_{11} - C_{12} > 0, \ C_{11} + 2C_{12} > 0
\]  

(3)

Table 4 shows the calculation results of \(E_{\text{atom}}\) of Mg, Si and P in this work. Table 3 lists the calculation results of the cohesive energy of each phase after P doping. It can be seen from the table that the calculated cohesive energy is close to the reference value given in the literature. It proves that the calculation parameter settings are reasonable.

It can be seen from figure 2 that the cohesive energy of each phase is negative, which indicates that all phases before and after doping can exist stably in the system. The absolute value of cohesive energy increases in the following order: \(\text{Mg}_2\text{Si} < \text{Mg}_8\text{Si}_3\text{P} < \text{Mg}_8\text{Si}_4\text{P} < \text{Mg}_7\text{Si}_4\text{P}\), in which the absolute value of cohesive energy of \(\text{Mg}_7\text{Si}_4\text{P}\) phase is the largest. It indicates that the structural stability of \(\text{Mg}_7\text{Si}_4\text{P}\) phase is the best. The absolute value of cohesive energy of \(\text{Mg}_2\text{Si}\) phase is the lowest, and its structural stability is the weakest, indicating that the thermodynamic stability of the system can be improved when P is doped into the \(\text{Mg}_2\text{Si}\) lattice.

The calculated elastic constants of Mg$_2$Si and its solid solutions are shown in table 4. It can be seen from the table that the independent elastic constant calculated in this work is close to the reference value given in the literature. Among them, Mg$_2$Si, Mg$_7$Si$_4$P and Mg$_8$Si$_3$P meet the stability criteria, but the \(C_{44} < 0\) of Mg$_8$Si$_3$P indicates that Mg$_8$Si$_3$P is unstable under the action of applied stress. From a kinetic point of view, Mg$_8$Si$_3$P phase can not be formed in the process of P-doped Mg$_2$Si system. Therefore, the Mg$_8$Si$_3$P phase will not be discussed further.

Based on the calculated independent elastic constants and the Voigt-Reuss-Hill approximation, the bulk modulus \(B\), shear modulus \(G\), young’s modulus \(E\), poisson’s ratio \(\nu\) and cauchy pressure \(C_{12} - C_{44}\) of each doped phase can be further calculated. The calculation formulas are as follows [19]:

\[
G = \frac{(3C_{44} + C_{11} - C_{12})}{5}
\]  

(4)

\[
B = \frac{(C_{11} + 2C_{12})}{3}
\]  

(5)

\[
E = 9BG/(3B + G)
\]  

(6)

\[
\nu = (E - 2G)/2G
\]  

(7)

The stiffness of polycrystalline materials is related to their young’s modulus \(E\), shear modulus \(G\) and poisson’s ratio \(\nu\). The larger the young’s modulus \(E\) and shear modulus \(G\) of the materials are, the smaller the poisson’s ratio \(\nu\) of the materials is, the higher the materials stiffness will be. Furthermore, the elastic deformation resistance of the materials will be stronger, and the plasticity will be worse. Table 5 shows the calculation results of the elastic modulus of each doped phase. Figure 3 shows the change curve of elastic
modulus after fitting. By analyzing the change curve in figure 3, it can be seen that the young’s modulus and shear modulus of the intrinsic Mg₂Si phase are the largest, which are 108.109 GPa and 45.759 GPa respectively. The poisson’s ratio of the intrinsic Mg₂Si phase is the smallest, which is 0.181. Compared with Mg₈Si₃P and Mg₈Si₄P, Mg₂Si phase have the highest stiffness and the worst plasticity. Besides, it also shows that doping P element in Mg₂Si lattice can reduce the stiffness of the system and improve plasticity. Among them, the young’s modulus and shear modulus of the Mg₈Si₃P phase are the smallest, which are 64.302 GPa and 24.893 GPa, respectively. The poisson’s ratio is the largest, which is 0.292. These data analysis indicate that the Mg₈Si₃P phase have the smallest stiffness and the best plasticity.

In addition, mechanical properties such as brittleness and ductility of polycrystalline materials can also be determined by the ratio of shear modulus G to bulk modulus B (G/B) [22]. When G/B is less than 0.57, the materials have certain ductility. Conversely, when G/B is more than 0.57, the materials are brittle. According to the change curve in figure 3, the G/B values of Mg₂Si and Mg₈Si₄P are both greater than 0.57, which indicates that both phases are brittle phases. The G/B value of Mg₈Si₃P is less than 0.57, which is ductile.

### Table 5. Elastic modulus of Mg₂Si, Mg₈Si₃P and Mg₈Si₄P.

| Compound       | G/GPa | B/GPa | E/GPa | v     | G/B   | C₁₂−C₄₄/GPa |
|----------------|-------|-------|-------|-------|-------|-------------|
| Mg₂Si          | 45.739| 56.533| 108.109| 0.181 | 0.809 | -19.740     |
| Mg₂Si[21]      | 46.200| 52.500| 107.100| 0.160 | 0.880 | -24.100     |
| Mg₂Si[19]      | 45.360| 52.580| 105.690| 0.170 | 0.860 | -23.020     |
| Mg₈Si₃P        | 24.893| 51.417| 64.302 | 0.292 | 0.484 | 8.580       |
| Mg₈Si₄P        | 31.884| 53.800| 79.873 | 0.253 | 0.393 | 0.330       |

Figure 3. Elastic modulus curve of Mg₂Si(a), Mg₈Si₃P(b) and Mg₈Si₄P(c).
Mg₂Si is the largest, which indicates that the plasticity of Mg₂Si crystal can be improved after P doping Mg₂Si. The plasticity of the crystal is the best when the P atoms displace the Si atoms position in the Mg₂Si lattice. The ductility of the materials can also be judged by Cauchy pressure $C_{12} - C_{44}$. When the values of $C_{12} - C_{44}$ is more than 0, the materials are ductile. When the values of $C_{12} - C_{44}$ is less than 0, the materials are brittle. According to the curve in figure 3, the $C_{12} - C_{44}$ value of Mg₂Si is negative, and it can be judge that Mg₂Si is the brittle phase. The values of $C_{12} - C_{44}$ in the other two phases are greater than 0. Consequently, Mg₈Si₃P and Mg₈Si₄P are extended phase. Comparing the $C_{12} - C_{44}$ values of Mg₈Si₃P and Mg₈Si₄P, the $C_{12} - C_{44}$ values of Mg₈Si₃P is higher. The results show that the method of doping P atoms into the Mg₂Si lattice can transform it from a brittle phase to an extended phase, which can better improve the plasticity of Mg₂Si compounds. The toughness and plasticity of the crystal are the best when P atoms replaced the Si atoms in the Mg₂Si lattice. These results are consistent with the above analysis results.

### 3.4. Electronic structure analysis

In order to reveal the interaction between atoms in Mg₂Si-P system, the energy band structure, total (partial) state density and differential charge density in the most stable system of Mg₂Si phase doped P atoms have been calculated. The effects of P doping on the orbital hybridization, bonding characteristics, and electrical conductivity of Mg₂Si lattice systems are discussed in depth. Figures 4 to 7 are the total (partial) state density, band structure, and differential charge density diagram of Mg₂Si, Mg₈Si₃P and Mg₈Si₄P, respectively. (The dashed line in figure 4 to figure 6 represent the Fermi energy level, which are represented as the zero point of energy).

#### 3.4.1. State density and band structure

In this work, We have computed by means of GGA-PBE the band structures and the total (partial) state density of P-doped Mg₂Si. According to the space group of Mg₂Si (Fm3m, No. 225), the band structure were calculated along the following path at the first Brillouin zone: W(0.5, 0.25, 0.75), L(0.5, 0.5, 0.5), G(0, 0, 0), X(0.5, 0, 0.5), W(0.5, 0.25, 0.75), K(0.375, 0.375, 0.750). In addition, the dopants lower the Mg₂Si crystal symmetry from Fm3m (No. 225) to Pm3m (No.221) when they are introduced into interstitial positions and substitutional Si.
sites. So the band structure were calculated along the following path at the first Brillouin zone: X(0.5, 0.0, 0.0), R(0.5, 0.5, 0.5), M(0.5, 0.5, 0), G(0, 0, 0), R(0.5, 0.5, 0.5).

According to figure 4(a), the bonding electrons of Mg$_2$Si are mainly distributed in the range of $-9$ to $15$ eV. The density of electronic states between 6 and 9 eV below the Fermi level is dominated by the contribution from the Si-3s electrons, and between 0 and 5 eV below the Fermi level, it is dominated by the contribution from the Si-3p, Mg-2p and Mg-3s electrons. In contrast, the Si-3p electrons contribute more to the formation of valence bands, which indicate that electrons are mainly localized around Si atoms. In addition, considering the existence of covalent bonds between Si and Mg atoms, it indicates that the interaction among Si-3p, Mg-2p and Mg-3s electrons are the main factor for maintaining the stability of the Mg$_2$Si phase. The density of electronic states between 0 and 15 eV above the Fermi level is dominated by the contribution from the Mg-2p, Mg-3s and Si-3p electrons. According to the band structure of Mg$_2$Si in figure 5(a), it can be seen that the valence band and conduction band of Mg$_2$Si are mainly contributed by Si-3p, Mg-2p and Mg-3s electrons.

Figures 4(b), (c) and 5(b), (c) are the energy state densities of each sublayer of Mg$_8$Si$_3$P and Mg$_8$Si$_4$P, respectively. Compared with state density of Mg$_2$Si, the study found that the energy range of the bonding electrons of Mg$_8$Si$_3$P and Mg$_8$Si$_4$P have changed. Their energy range became $-11$ eV to 5 eV. Compared with the band structure of Mg$_2$Si, both the conduction band and the valence band of the two-phase energy band structure have negative shifts. The band structure of Mg$_8$Si$_3$P and Mg$_8$Si$_4$P show obvious impurity levels. The results show that the bonding characteristics and hybridization of electron orbital in Mg$_2$Si system are changed after doping P atoms.

In contrast, the energy state density of the Mg and Si sublayer electrons of the Mg$_8$Si$_3$P phase do not change much. But the partial state density of the P sublayer electrons have a high energy value in the valence band interval. The density of electronic states between 11 and 12 eV below the Fermi level is dominated by the contribution from the Si-3s electrons, and between 7 and 10 eV below the Fermi level, it is dominated by the contribution from the Si-3s electrons. However, between 1 and 6 eV below the Fermi level, the orbital hybridizations of P-3p and Si-3p electrons emerge obviously. The contribution of Mg-2p and Mg-3s electrons can not be ignored. So there was bonding effect between Mg, Si and P atoms. Although the peak value of P-3p electrons decreases in the conduction band interval, the hybridization with the s and p orbitals of Mg and Si still exist.
However, the bonding characteristics and orbital hybridization of Mg$_8$Si$_4$P are more complex. In comparison, the energy state density of each sublayer of Mg atoms do not change much, and the energy values of Si and P atoms in the valence band are very high. The density of electronic states between 10 and 12 eV below the Fermi level is dominated by the contribution from the P-3s and Si-3s electrons. The P-3s and Si-3s electrons show orbital hybridization and bond forming characteristics. The density of electronic states between 7 and 9 eV below the Fermi level is dominated by the contribution from the Si-3s and Si-3p electrons, and between 1 and 6 eV below the Fermi level, it is dominated by the contribution from the Si-3s, Si-3p and P-3p electrons. The bonding electrons in the conduction band are mainly contributed by Si-3s and Si-3p electrons. The Mg-2p, Mg-3s and the P-3p electrons contribute less, but there are still significant orbital hybridization between the bonding electrons.

As can be seen from figure 5(a), there are a band gap of 0.224 eV in the conduction band and valence band of Mg$_2$Si. Since the minimum value at the bottom of conduction band and the maximum value at the top of valence band of Mg$_2$Si are at two different positions in the k-spaces respectively, $X_1$ and $G_1$, it indicates that the intrinsic Mg$_2$Si phase is an indirect bandgap semiconductor. According to figure 5(b), the Fermi energy level of Mg$_6$Si$_3$P phase is in the conduction band, showing n-type semiconductor characteristics. It is caused by the increase of conductive carriers which are caused by the doping of P element. At the same time, the band density of Mg$_6$Si$_3$P and Mg$_6$Si$_4$P increases in different bands and the orbital overlap of impurity levels increases. These indicate that the interaction between different electron states is stronger and the localized carriers on each energy level are weakened. These results are also confirmed by the analysis of state density in figure 4. Results of our calculations clearly show reduction of the band gap from 0.224 to 0.184 eV for Mg$_2$Si with P dopants at the substitutional Si-sites and the band gap closure in the system with interstitial P-impurities. Both band gap narrowing and its disappearance, the latter indicating transformation of the P-doped Mg$_2$Si from its semiconducting to metallic state, arise from an appearance of additional energy levels due to the P-impurities. This results in reduction of the energy required for electron transition to the conduction band and enhances conductivity of the P-doped Mg$_2$Si. In some extent, the electrical properties of Mg$_2$Si alloy are improved. These will provide a certain reference for the application of Mg$_2$Si alloy in semiconductor materials and medium temperature thermoelectric materials.
3.4.2. Electron density difference

In order to understand the bonding between atoms in Mg$_2$Si-P system more intuitively, the differential charge density of each phase before and after doping are drawn in this work. The (110) planes of the super unit cell before and after the substitution of the P atom for the Si atom position and the body-to-center gap position are calculated and analyzed. Among them, the vacuum layer of Mg$_2$Si (110) surface is selected as 15 Å. The differential charge density diagrams are shown in figure 7 (the contour lines in the figure are drawn from $-2.701 \times 10^{-2}$ Å to $2.315 \times 10^{-2}$ Å, blue represents the absence of electrons, and red represents the electron enrichment).

It can be seen from figure 7 that the differential charge density changes caused by P atoms doped into Mg$_2$Si system at different positions are different. The high-density charge regions showed in the figure correspond to Mg, Si and P atoms. When Mg$_2$Si system undoped with P atoms (figure 7(a)), the electron density of Mg$_2$Si is localized around Si atoms. There is a significant charge accumulation between the Si atoms and the nearest Mg atoms, indicating that the bonding between the Si atoms and the Mg atoms is mainly based on a shared electron pair, forming a Mg–Si covalent bond. There are many free electrons between the Mg atoms and the nearest Mg atoms, indicating that the metallic bond is formed between the Mg atoms and the Mg atoms. In addition, due to the high charge density and strong bonding ability around Si atoms, the Si–Si covalent bonds would be formed between adjacent Si and Si atoms.

As can be seen from figure 7(b), when Si atoms are replaced by P atoms, P atoms had a higher charge density distribution as the Si atoms. There is an obvious charge accumulation between the P atoms and the nearest Mg atoms, indicating that the bonding between P atoms and Mg atoms is mainly based on sharing electron pairs, forming the Mg–P covalent bond. Due to the high charge density around Si and P atoms, Si–P covalent bonds would form between adjacent P and Si atoms. As compared to figure 7(a), when Si atoms are replaced by P atoms, the free electron density between Mg and Mg atoms increases. It indicates that the doping promotes the formation of Mg–Mg metal bond in the Mg$_2$Si system. Furthermore, the effect of the Si–P covalent bond will be

![Figure 7. Electronic charge density difference contour plots of Mg$_2$Si (a), Mg$_8$Si$_3$P (b) and Mg$_8$Si$_4$P (c).](image-url)
stronger than that of the Si–Si covalent bond because the electronegativity of P element is greater than the Si element. Therefore, the stability of the system is improved when the Si atoms are replaced by P atoms.

As shown from figure 7(c), the charge density distribution around Si and P atoms in this system is high when the P atoms are doped into the body center interstitial position of Mg$_2$Si. Among them, the free electron density between Mg and Mg atoms decreases, which weakens the ability of Mg-Mg metal bonds. However, the interaction of Si-P, Mg-P and Si-Si covalent bonds greatly improves the structural stability of the phase. These are consistent with the above analysis results of cohesive energy and density of states, which reveals the reason why the stability of the phase is improved by doping P into Mg$_2$Si. In addition, it is also verified that the conductivity of the above-mentioned doping system is enhanced by comparing the color distribution of the charge density of the doping system.

4. Conclusions

(1) According to the criteria for the mechanical stability and formation enthalpy, Mg$_2$Si, Mg$_8$Si$_3$P and Mg$_8$Si$_4$P can be stable in the system, and P atoms tend to occupy the position of Si atoms in the Mg$_2$Si lattice when P atoms are doped in Mg$_2$Si alloy systems.

(2) The results of formation enthalpy and cohesive energy studies indicate that the method of doping P atoms in Mg$_2$Si lattice can improve the forming ability and structural stability of the system.

(3) The calculation results of elastic modulus indicate that Mg$_2$Si and Mg$_8$Si$_3$P are brittle phases, and Mg$_8$Si$_4$P is ductile phase. Doping with P atoms can improve the toughness and plasticity of the Mg$_2$Si system. When the P atoms replace the position of Si atoms in the Mg$_2$Si lattice, Mg$_2$Si phase will change from brittleness phase to toughness phase.

(4) The electronic structure analysis results show that the intrinsic Mg$_2$Si phase presents semiconductor characteristics, and the bonding characteristics includes Mg-Si covalent bond, Si-Si covalent bond and Mg-Mg metallic bond in Mg$_2$Si alloy system. The method of doping P atoms changes the orbital hybridization and bonding characteristics of the system. The Mg-P and Si-P covalent bond formed by Mg$_8$Si$_3$P and Mg$_8$Si$_4$P increase the structure stability. Additionally, The incorporation of P element increases the number of conductive carriers, and narrows or even closure the forbidden band gap. It reduces the energy required for free electron transition. So the Mg$_8$Si$_3$P phase exhibit N-type semiconductor characteristics after doping, and Mg$_8$Si$_4$P phase transform from its semiconducting to metallic state. This method enhances the metallic property of the material. The conductivity of the Mg$_2$Si alloy system will be improve.

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