First principles study on electronic structure, ferromagnetism and dielectric properties of α-Fe, FeSiAl and Fe₃Si

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Based on the plane-wave pseudo-potential theory, the first principle calculation was used to study the electronic structure, ferromagnetism and dielectric properties of α-Fe, FeSiAl and Fe₃Si alloys. Results indicate that the Fe₃Si has the strongest hybridization and covalent bond. And α-Fe has the most stable system structure. The PDOS shown that the peak for the imaginary part of dielectric constant in the low-energy region is due to the electronic transitions of the hybridized 3d spin-down Fe states above and below the Fermi level, and the high-energy peak of it is formed by the transitions from the broad 3d spin-down band in the valence band to the unoccupied 3d spin-down states. Compared with α-Fe and FeSiAl, the imaginary part of the dielectric constant of Fe₃Si is larger, and the magnetic moment of Fe₃Si alloy is the largest according to the electronic structure and magnetic analysis. Therefore, Fe₃Si has better absorbing properties.

1. Introduction

With the continuous development of microwave communication and electronic technology, electromagnetic interference and electromagnetic pollution are becoming more and more serious. Microwave absorbing materials are usually used to convert unwanted electromagnetic waves into heat energy, so as to suppress electromagnetic interference and reduce the harm caused by electromagnetic pollution [1-3]. Fe based magnetic metal powder has the advantages of high initial permeability, high natural resonance frequency and high saturation magnetization. The microwave absorbing material prepared by Fe based magnetic metal powder has high absorbing strength, wide absorption band and easy processing, so it is the most important electromagnetic wave absorber. Compared with carbonyl iron powder (CIP), FeNi system, FeCo system, and FeSi system has stronger corrosion resistance and higher permeability, which makes its impedance matching ability stronger, and is more conducive to reduce the reflection of incident electromagnetic wave on the material surface [4-6]. At present, a lot of experiments have been carried out on the microwave absorbing properties of FeSi, FeSiAl and Fe₃Si alloys [7-13]. The effects of phase composition, grain size and phase morphology on the microstructure of the alloy were investigated by XRD, SEM and Raman spectroscopy. However, the electronic structure of the alloy, the type and strength of the bonding bond, and the electron transfer are the key factors affecting the microwave absorbing properties of the alloy. Therefore, it is very important to study the influence of the electronic structure and chemical bond of the alloy. In the present work, the relationship...
between the electronic structures and dielectric and ferrimagnetic properties of $\alpha$-Fe, FeSiAl and Fe$_3$Si are characterized using first principles methods on the plane-wave pseudo-potential theory.

2. Another section of your paper Calculation method and model

The $\alpha$-Fe belongs to the BCC structure, and FeSiAl and Fe$_3$Si has the BiF$_3$-type structure. The initial calculation model was established by the experimental structure. Figure 1 shown the calculation model of $\alpha$-Fe, FeSiAl and Fe$_3$Si structure. According to the energy convergence and lattice constant convergence, we choose and set the calculation parameters. All calculations were used by Cambridge Serial Total Energy Package (CASTEP) based on density functional theory (DFT). The exchange and correlation function were treated by the generalized gradient approximation (GGA-PBE). The K-point mesh is set to 7×7×7, and the cutoff energy of the plane wave is 330 eV. The tolerance for self-consistent-field (SCF), maximum force, and stress was $2.0 \times 10^{-6}$ eV/atom, 0.05 eV/nm, and 0.05 GPa, respectively.

![Figure 1](image)

3. Results

The partial densities of states (PDOS) and total densities of states (TDOS) diagrams of $\alpha$-Fe, FeSiAl and Fe$_3$Si are shown in Figure 2. The calculated results shown that the $\alpha$-Fe, FeSiAl and Fe$_3$Si all presents the characteristic of metal. The TDOS of $\alpha$-Fe is due to Fe 3$d$ states (Figure 2(a) and (b)). For FeSiAl, the TDOS between -5 eV and 5 eV is due to Fe 3$d$ States, Si 3$p$ states, and Al 3$s$ states. The lower region (-10~−5 eV) and the upper region (5~10 eV) is contributed by Fe 4$s$ sates, Si 3$p$ states, Al 3$s$ states and Al 3$p$ states. The TDOS of Fe$_3$Si from -7.2 eV to -2.5 eV is contributed by Fe 3$d$ states and Si 3$p$ states, and the region between -2.5 eV and 2 eV is due to Fe 3$d$ states. There are two peaks located on both sides of Fermi level, and the TDOS are all main dominated by Fe 3$d$ states. These indicate that covalent electron orbit hybridization happened in these energy ranges. At the same time, a pseudo gap exists in the Fermi level, and the pseudo-gap width decides the intensity of the electron orbital overlapping action. The Fe$_3$Si has the widest energy range near the Fermi level, then Fe$_3$Si has the strongest hybridization and covalent bond. The distance from the bottom of the pseudo-gap for $\alpha$-Fe is the shortest, which means that the system structure is the most stable. These could be dominated by the strong interactions between $d$-electrons, and the strong interactions strengthen the metallic character.

![Image](image)

The spin-projected TDOS and PDOS of $\alpha$-Fe, FeSiAl and Fe$_3$Si are shown in Figure 3. The distribution of the TDOS between spin-up and spin-down is asymmetry, so that the ferromagnetism is induced. The electrons of Fe 3$d$ states cause the ferromagnetism of all metals. The difference between spin-up and spin-down electrons at $E_{f}$ in the Fe$_3$Si is the highest.
Figure 2. PDOS and TDOS diagrams of $\alpha$-Fe ((a) and (b)), FeSiAl ((c), (d), (e) and (f)) and Fe$_3$Si ((g), (h), (i) and (j)).

Figure 3. The spin-projected TDOS and PDOS diagrams of $\alpha$-Fe ((a) and (b)), FeSiAl ((c), (d), (e) and (f)) and Fe$_3$Si ((g), (h), (i) and (j)).
Table 1 lists the overlapping populations and atomic Mulliken charges for α-Fe, FeSiAl and Fe₃Si. The atomic charge of Fe atom in α-Fe is 0, that means the valence electron transfer of α-Fe is zero. The atomic charges of Fe, Si and Al atom is -0.06, 0.06 and 0.07 for FeSiAl. And the atomic charges of Fe[B], Fe[A,C] and Si atom in Fe₃Si are 0.13, -0.09 and 0.05, respectively. Charge transfer is discovered to occur from Si and Fe[B] atoms to Fe[A,C] atoms for Fe₃Si. For FeSiAl, charge transfer occurs from Si and Al atoms to Fe atoms. The overlapping population between Fe-Fe neighbors is -0.23 eV for α-Fe. The overlapping population between Fe-Fe, Fe-Si, and Fe-Al is -0.21 eV, 0.22 eV and 0.17 eV for FeSiAl, which characterized the strong hybridization between Fe atoms and Si atoms and Al atoms, strong antibonding interaction between Fe atoms, and Fe-Si and Fe-Al bonds is covalence. In Fe₃Si, the overlap population between Fe–Si neighborhoods is 0.25 eV, which indicates that Fe[A,C] 3d orbits strongly hybridize with Si sp orbits, and Fe-Si bonds have covalency. For α-Fe, the local magnetic moment is 1 μ₀. For FeSiAl, the local magnetic moment is 0.95 μ₀, -0.06 μ₀ and -0.10 μ₀ for Fe atom, Si atom, and Al atom, respectively. And the saturation moment per unit cell is 6.96 μ₀. And for Fe₃Si, the local magnetic moment is 2.62 μ₀ for Fe[B], and 1.26 μ₀ for Fe[A,C]. They are closed to the values calculated by A. Go, i.e. 1.42 μ₀ at Fe[A,C] and 2.62 μ₀ at Fe[B] site [14]. Based on LSD, the calculation values at Fe[A,C]site and Fe[B] site is 1.36 μ₀ and 2.48 μ₀, respectively [15]. The saturation moment per unit cell is 19.92 μ₀.

**Table 1.** Overlap populations and Mulliken charges for atoms and bond length for α-Fe, FeSiAl and Fe₃Si.

| System | Atom | Electron orbit | Mulliken charge (e) | Spin (μ₀/atom) | NN bond | Overlap populations (eV) | Bond length (Å) |
|--------|------|----------------|--------------------|----------------|---------|--------------------------|----------------|
| α-Fe   | Fe   | s 0 p 7.00     | -0.06              | 0.00           | Fe-Fe   | -0.23                    | 2.4824         |
|        | Si   | 0.33 0.62 7.12 | 0.66               | 0.95           | Fe-Si   | 0.22                     | 2.4882         |
|        | Al   | 1.19 0.76 0.00 | 0.06               | -0.06          | Fe-Fe   | -0.21                    | 2.8500         |
|        | Fe[A,C] | 0.94 1.99 0.00 | 0.07               | -0.10          | Fe-Al   | 0.17                     | 2.4682         |
| FeSi   | Si   | 0.25 2.70 0.00 | 0.05               | -0.06          | Fe-Si   | 0.25                     | 2.4469         |
|        | Fe[3B] | 0.45 0.75 6.89 | -0.09              | 2.62           | Fe-Fc   | -0.07                    | 2.4469         |
|        | Fe[3C] | 0.68 0.68 6.59 | 0.13               | 1.26           | Fe-Fc   | 2.4469                    |

The total charge density and difference of electronic density on the (111) plane of α-Fe, FeSiAl and Fe₃Si is presented in Figure 4. For α-Fe, the red area indicates the loss of electrons, and the blue area shows the acquisition. Fe atoms in the red part are not bonded, while the delocalized electron clouds in the blue and light blue parts indicate that there is a metal bond between Fe atoms, so the α-Fe shows metallic characteristics (Figure 4(a), (b)). Regarding FeSiAl (Figure 4(c), (d)) (The red area indicates the loss of electrons, and the blue area shows the acquisition), Fe atoms are covalently bonded with Si and Al atoms respectively, while the local electron cloud between Fe atoms and Fe atoms is metal bond. Therefore, FeSiAl alloy has the characteristics of coexistence of covalent bond and metal bond. While for Fe₃Si, blue area represents the low electron density region, and red area represents the high electron density region. The nonlocal electrons represent the metal bond formed between Fe[B] atom and Fe[A,C] atom, and the covalent bond between Fe [A,C] atom and Si atom. And these are also concurred with the analysis of DOS and Mulliken analysis.

One of the most important and basic microwave absorption parameters is a dielectric function, which is the linear response of the material to the electromagnetic radiation. Figure 5 presents the real (a) and imaginary (b) parts of the dielectric constant of α-Fe, FeSiAl and Fe₃Si, respectively. The static dielectric constant of α-Fe, FeSiAl and Fe₃Si is all close to 60. With the increase of the energy, the real part of the dielectric constant first decreases greatly and then tends to be flat. We see a sharp peak at low energy in the real part of dielectric for them, and the peak of α-Fe is the lowest. This peak is attributed to the metallic nature of the system, and the metal features of α-Fe is most obvious. The initial value of the imaginary part of the dielectric constant of α-Fe, FeSiAl and Fe₃Si is 3.63, 3.64 and 12.17, respectively. The imaginary part of dielectric constant of α-Fe and Fe₃Si increases first, then decreases, and finally tends to be flat. The imaginary part of dielectric constant (ε₂) of α-Fe and Fe₃Si reaches the maximum value at the energy of 1.5 eV, which is about 27 eV and 36.8 eV respectively. However, the imaginary...
part of the dielectric constant of FeSiAl decreases greatly with the increase of energy and then tends to be stable. At 0.54–2.32 eV range, the Fe$_3$Si has the largest $\varepsilon_2$. At 2.31–4.31 eV range and higher than 10.43 eV, the of $\varepsilon_2$ of $\alpha$-Fe is larger than FeSiAl and Fe$_3$Si. And FeSiAl has the largest $\varepsilon_2$ at 4.5–8.18 eV range. These indicate that the absorption applicability of the material depends strongly on the frequency. Moreover, the dielectric constant is dominated by the energy bands of electrons with the direction of the minority spin. Based on the intensity and energy position of PDOSs (see Figure 3), the high-energy peaks in $\varepsilon_2$ is originated by the electronic transitions from the 3$d$ spin-down band in the valence band to the unoccupied 3$d$ spin-down states. Therefore, the low-energy peak in it is resulted from the transitions between the hybridized 3$d$ spin-down Fe states above and below the Fermi level. Compared with $\alpha$-Fe and FeSiAl, the $\varepsilon_2$ of Fe$_3$Si is larger, and the magnetic moment of Fe$_3$Si alloy is the largest according to the electronic structure and magnetic analysis. Therefore, Fe$_3$Si has better absorbing properties.

**Figure 4.** The total charge density and difference of electronic density on the (111) plane of $\alpha$-Fe ((a) and (b)), FeSiAl ((c) and (d)) and Fe$_3$Si ((e) and (f)).
4. Conclusion
The first-principles calculations were carried out to investigate the electronic, ferromagnetic and dielectric properties of $\alpha$-Fe, FeSiAl and Fe$_3$Si with DFT. Results indicate that the Fe$_3$Si has the strongest covalent bond and hybridization. And $\alpha$-Fe has the most stable structure. The saturation moment per unit cell of $\alpha$-Fe, FeSiAl and Fe$_3$Si is 1.00 $\mu_B$, 6.96 $\mu_B$ and 19.92 $\mu_B$, respectively. The peak for the $\varepsilon_2$ in the low-energy region is due to the electronic transitions of the hybridized 3$d$ spin-down Fe states above and below the Fermi level, and the high-energy peak of it is formed by the transitions from the broad 3$d$ spin-down band in the valence band to the unoccupied 3$d$ spin-down states. Compared with $\alpha$-Fe and FeSiAl, the imaginary part of the dielectric constant of Fe$_3$Si is larger, and the magnetic moment of Fe$_3$Si alloy is the largest according to the electronic structure and magnetic analysis. Therefore, Fe$_3$Si has better absorbing properties.

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