Study on the electronic structures and optical properties of β-$FeSi_2$ using the pseudopotential method

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Abstract. Electronic structures and optical properties of bulk β-$FeSi_2$ are investigated in detail by first principles pseudo-potential methods based on the density function theory. The calculated results show that β-$FeSi_2$ is a quasidirect band gap material with gap value of 0.74eV. The density of states is mainly composed of Fe 3d and Si 3p states. The dielectric constant, absorption coefficient, and the conductivity are also given. The results are compared with previous theoretical calculation and the available experimental data.

Introduction

Transition-metal disilisides have recently attracted much interest due to their fundamental physics in structural materials and potential microelectronic application [1–5]. Several band structure calculations and various spectroscopic methods have been applied to probe their electronic structure [6–8]. Amongst those materials, the β-$FeSi_2$ with orthorhombic structure has become one of the most used materials in the optoelectronic technology [1–8]. The electronic structure of β-$FeSi_2$ has been well established by several authors using various density-functional methods [1-3]. β-$FeSi_2$ films have been prepared using many methods such as the SPE method in an ultrahigh vacuum (UHV) system and RF sputter deposition, and the structural and electronic structure were investigated experimentally [6-7].

Extensive theoretical and experimental studies have been investigated on β-$FeSi_2$. However, the question of whether it is a material with direct band gap or indirect one continued to be a topic of discussion for β-$FeSi_2$. The vast majority of people believe that theβ-$FeSi_2$ has a direct band gap, while others consider it is a material with indirect band gap using the first principle calculation or other theoretical methods, whose band gap energy was tens milli electron volts lower than the direct band gap. Furthermore, there are few reports about its luminescence mechanism, and few theoretical papers are reported about the optical properties.

First-principles simulation based on density functional theory is one of the most promising methods for predicting properties of materials[9-18]. This work uses the pseudo potential energy to calculate the band structure, the dielectric constant, absorption coefficient, refractive index, reflectivity and energy loss function of theβ-$FeSi_2$. The relationship between the band structure and luminescence mechanism are also discussed.

Models and methods

β-$FeSi_2$ are crystallized in the orthorhombic structure. The space group is Cmca. Each cell contains 48 atoms which includes 16 Fe and 32 Si atoms. According to the previous experimental results, the lattice constant for a, b, and c is 0.9863nm, 0.7791nm, and 0.7833nm, respectively. The Fe and Si atoms all have two kinds of different atomic environments, that is, two set of inequivalent Fe and Si atoms constitute the entire cell by symmetry transform, as shown in Figure 1.

Total-energy calculations and full geometry optimizations were performed employing the generalized gradient approximation (GGA) and the first-principles pseudopotential approach, using density functional theory as implemented in the code VASP(Vienna ab initio simulation package) that is based on pseudopotential and planewave basis functions. The cut-off energy for the basis function is 400 eV. Besides, we used the tetrahedron method with Blöchl corrections (ISMEAR = -5) which

gives a good account for the electronic density of states (DOS), and also it can get a more accurate result. The self-consistent calculations are considered to be converged when the total energy of the

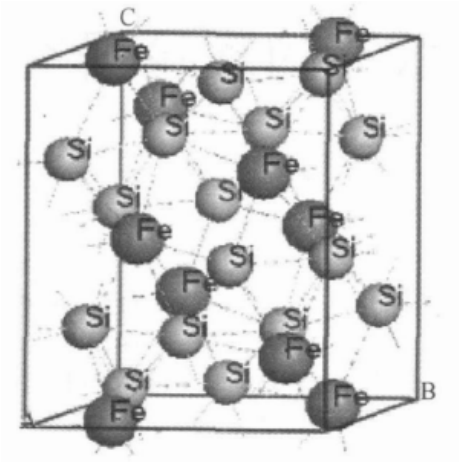

Fig.1 Primitive cell ofβ-$FeSi_2$ crystal

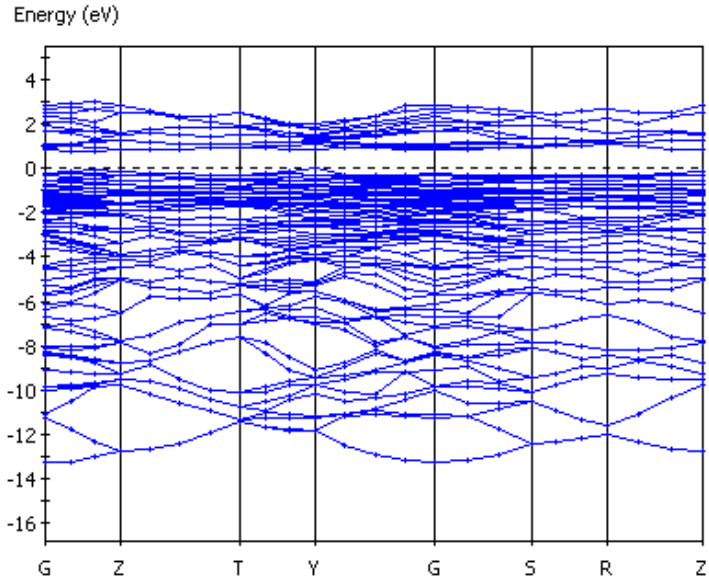

Fig.2 Energy band diagram ofβ-$FeSi_2$

Table 1 The energy values of in the first Brillouin zone in the vicinity of valence band Ev and the bottom of conduction band Ec（eV）

	∧	Z	T	Y	S
Ev	-0.065	-0.176	-0.396	0.0	-0.347
Ec	0.740	0.823	0.876	0.821	0.911

system is stable. The integrals over the Brillouin zone are performed up to 30 k-points in the irreducible Brillouin zone (IBZ), using the Monkhorst–Pack special k-points approach.

Results and discussion

The fitting of the Murnaghan equation of state [10-11] to the total energies versus lattice parameters, yields to the stable structure of β-$FeSi_2$ and the equilibrium lattice parameters. When the original cell volume is 279.79$Å^3$, the total minimum energy of the β-$FeSi_2$ is achieved. The corresponding lattice constants for a, b and c are 0.9764nm, 0.767Inm, and 0.7720nm, respectively. There is a good agreement between our results and the other theoretical investigation. Compared with the experimental value, the error is 1%-1.54%. In comparison with the experimental data we find that the lattice parameters are a little underestimated. To verify the accuracy of these results, several tests have been performed using different radius as well as different sets of special k-point to ensure the convergence.

Figure 2 shows the calculated band structure at equilibrium volume for β-$FeSi_2$ as a prototype. The important features of the band structure (main band gaps and valence band widths) are given in Table 2. The overall band profiles are in fairly good agreement with previous theoretical results [12]. The valence band maximum (VBM) of 0 eV and conduction band minimum (CBM) of 0.74eV are occurs at the Y and ∧ points, as shown in table 2. Thus the energy gap is indirect between the top of the valence band at the Y point and the bottom of conduction band at ∧ point. The width of band gap Eg is 0.74eV. It is noticed that the energy value of between valence band maximum and conduction band minimum at ∧ point is 65meV. Therefore, β-$FeSi_2$ shows a quasi direct band gap. This calculated results is consistent with other theoretical calculated results[13, 14].

Figure 3 (a), (b) and (c) show the total density of state of β-$FeSi_2$ and the partial density of states of Fe and Si. Electrons of 3d6 and 4s2 of Fe atom as well as the 3s2 and 3p2 of Si atom are used as the valence electron in calculation. It is observed that the density of states of β-$FeSi_2$ in the smaller range of electron energies (-13.7eV～5eV) is mainly composed of 3s electronic states of Si. In the energy

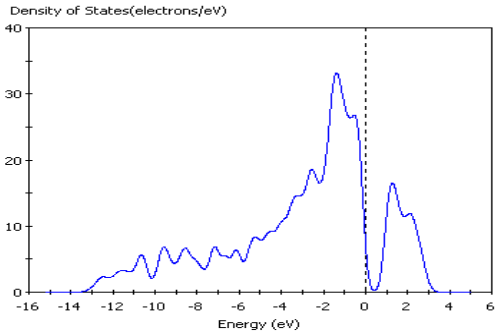

Fig. 3(a) The total density of state of β-$FeSi_2$

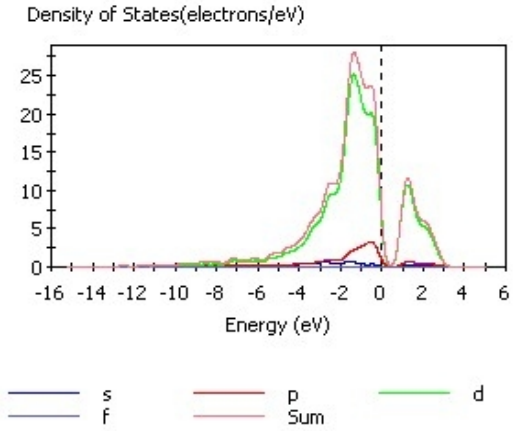

Fig.3(b) The partial density of states of Fe

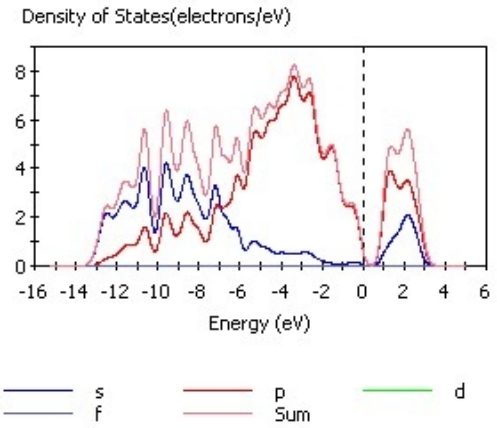

Fig.3(c) The partial density of states of Si

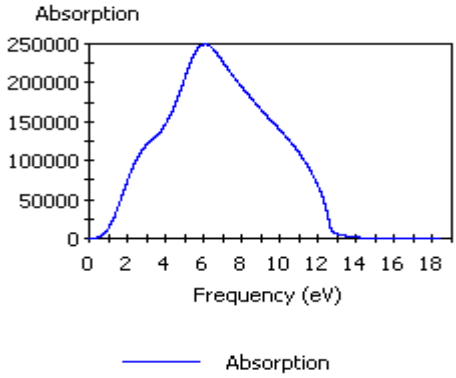

Fig.4 The absorption coefficient of β-$FeSi_2$

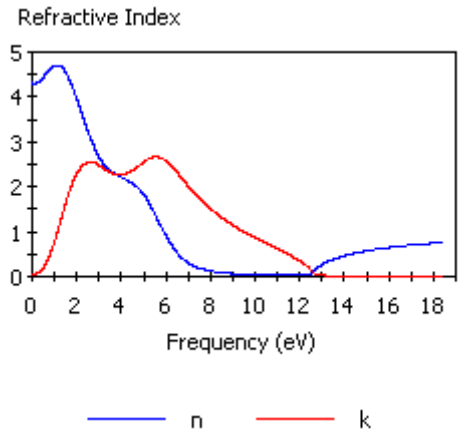

Fig.5 The complex refractive index ofβ-$FeSi_2$

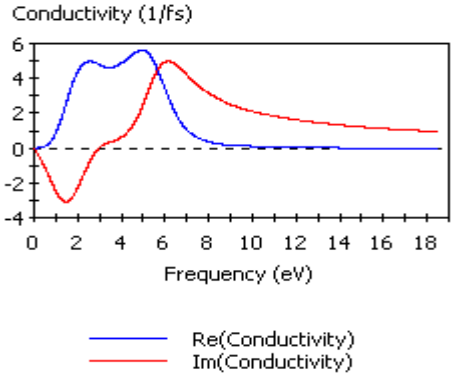

Fig.6 The complex photoconductivity of β-$FeSi_2$

range of -5eV～0eV, the density of states of β-$FeSi_2$ is mainly composed of 3d electronic states of Fe and some contributions of 3p electronic states. The contribution of Fermi level $E_f$comes mainly from the 3d electronic states of Fe and the 3p electronic states of Si. The 3s electronic states of Si have few contribution to the Fermi level and it has relatively small contributions in the whole energy range. In the range of energy bigger than zero, the density of states of β-$FeSi_2$ is mainly composed of 3d electronic states of Fe and 3p electronic states of Si. The valence band ofβ-$FeSi_2$ extends from 0 to 13.7eV whose maximum value appears at the position of 1.61eV. In the range of -15eV～-5eV, the density of states of Si in the β-$FeSi_2$ is mainly determined by the 3s state electron while to the energy larger than -5eV, the density of states of Si in the β-$FeSi_2$ are mainly determined by the 3p electron. The electronic density of states of Fe is mainly determined by the 3d electron of Fe. Thus it can be concluded that the electrical transport properties and carrier type of β-$FeSi_2$ is mainly determined by the 3p electron of Si and the 3d electron of Fe.

Absorption coefficients represent the decrement of the light waves spreading in the medium. In calculations of the optical properties, a dense mesh of uniformly distributed k-points is required. Hence, the Brillouin zone integration was performed in the irreducible part of the Brillouin zone without broadening. The absorption coefficient of β-$FeSi_2$ were obtained by the relationship $a=\omega\varepsilon 2/nc$. In figure 4, the absorption coefficient is zero when the energy is less than 0.74eV and larger than 16.3eV, indicating thatβ-$FeSi_2$ is transparent when the wavelengths are in the range of 1770nm and 761um. The absorption coefficient begins to increase when the photon energy is larger than 0.74eV, corresponding to the calculated indirect band gap of 0.74eV. The maximum peak value of $2.67x10^5cm^{-1}$ located at 6.26eV for the energy absorption coefficient. Then it decreases gradually with increasing the photon energy and it decreased to zero when the absorption coefficient increased to 16.3eV.

Figure 5 shows the complex refractive index of β-$FeSi_2$. The main peak of n appears in the energy range of 1.15eV～1.64eV, where the peak are at 1.15eV and 1.38eV. The refractive index decreases gradually with increasing the photon energy when the photon energy is larger than 1.64eV. We can see from Figure 5 that $\varepsilon(\omega)$ is smaller than zero when the energy is in the range of 8.86eV to 12.87eV which means that the wave vector k is imaginary. In other words, light do not propagate in the solid in this frequency range. In this frequency range, $k(\omega)$ is larger than $n(\omega)$ and n tends to zero, which shows a metal-like reflection characteristics for β-$FeSi_2$. The extinction coefficient of β-$FeSi_2$ is zero when the energy is less than 0.74eV and larger than 12.87eV. The main peak of k appeared at 1.86eV and 6.26eV.

Figure 6 shows the complex optical conductivity of β-$FeSi_2$. The real part of photoconductivity for β-$FeSi_2$ is zero when the energy is lower than 0.74eV and greater than 16.3eV. The main peak value appeared at the energy between 1.86eV and 6.26eV, corresponding to previous peaks of absorption coefficient and the extinction coefficient. This results verify the relationship between the real part of photoconductivity and absorption coefficient.

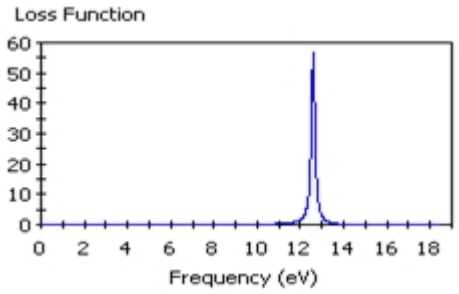

Fig. 7 Electron energy loss spectra

Figure 7 shows the electron energy loss spectra. It is zero when the energy is less than 0.74eV. The maximum energy loss peak appeared at 12.8eV which corresponds to the bulk plasma edge energy ofβ-$FeSi_2$. In addition, according to the calculation of Si and Fe partial density of states, the second

energy loss peak value locates at 11.8eV, 12.2eV, 13.5eV which come from the energy transition from Si3s to Fe3d electrons.

Summary

In our calculation we have used the density functional theory method using the core level in the PAW pseudo potential to study the structural, electronic and optical properties. Our results for the band structure and DOS, show that the calculated results show that β-$FeSi_2$ is a indirect band gap material with gap value of 0.74eV. The structural parameters and optical properties are compared with previous theoretical results and experimental data.

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