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First Principle Study on the Electric Structure of β-FeSi₂ with Native Point Defects

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ABSTRACT

The projector-augmented plane wave potentials method under the density functional theory (DFT) was used to calculate the electronic structure of perfect and native point defective β-FeSi2 crystal. The calculated band structure shows that the band gap of perfect crystal is about 0.74eV, which is a little smaller than the experimental of about 0.9eV. The density of states results predicts that β-FeSi2 with Fe vacancies behaves n-type, and that with Si vacancies will shows p-type, which is in accordant with the experimental results.

Keywords: β-FeSi₂; First Principle Calculation; Electronic Structure

1. Introduction

In recent years there has been an increasing effort in the development of new silicon based optoelectronic materials due to their possible implementation in integrated opto- and micro-electronic devices. Due to its luminescent properties corresponding to a direct band gap of about 0.875eV and strong optical absorption ($\alpha=10^5 cm^{-1}$), β-FeSi₂ is an attractive silicon based optoelectronic materials expected for use in optoelectronic device applications such as infrared detectors or light emitters integrated in silicon technology [1-3]. More over high abundance of its non-toxic constituents Fe and Si. This opens new fields of applications, namely, high efficient solar cells, photo-detectors, and thermoelectric devices. On the other hand, β-FeSi₂ has been studied as a material for the thermoelectric conversion application due to its superior features such as its larger Seebeck coefficient, low electrical resistivity, and chemical stability. The quality of a good thermoelectric material is usually characterized by the dimensionless figure of merit *ZT* [4], which is defined as

$$ZT = \frac{S^2 \sigma T}{\kappa} \qquad (1)$$

where κ, σ, and S represent the thermal conductivity, electrical conductivity, and Seebeck coefficient, respectively, and $S^2\sigma$ is generally defined as the power factor. To achieve higher *ZT*, it is required to increase S and/or σ, and/ or decrease κ. But for simple material, κ, σ, and S are dependent on one another, a simple effective method

is to improve the transport properties of the material. The transport properties of the materials depend on structural properties such as the microstructure and defects as well as the kinds of dopants. For β-FeSi₂, there are always some point defects in the crystal, which was suggested to affect the semiconductor types and the transport properties of carrier significantly [5-6].

In this work, we performed first-principle density function calculations to get the information on the electronic structure of the perfect and native point defective β-FeSi₂. The aim is to investigate the effect of point defect of Fe and Si on the electrical properties of β-FeSi₂ crystal.

2. Computational Method

Our calculations are performed based on the density functional theory (DFT) within the generalized gradient approximation implemented in the VIENNA AB INITIO SIMULATION PACKAGE. The projector-augmented plane wave potentials are used to represent the electron-ion interactions. Atomic coordinates were fully optimized by using the conjugate gradient technique. A kinetic energy cutoff of 520 eV is used to ensure a convergence better than 1 meV for total energy per atom. We constructed a conventional unites containing 48 atoms (8 FeⅠ, 8 FeⅡ, 32 SiⅠ and 32 SiⅡ) with the space group Cmca and the lattice constants length A=9.8632 Å, length B= 7.7916 Å, length C= 7.8278 Å for β-FeSi2, and the structure is shown in Fig.1. For the calculation of electronic structure of perfect and defec-

tive β-FeSi2 crystal, a supercell containing 172 atoms were used. All supercells adoped are of vacuum layer of 15 Å in order to guarantee negligible interactions between the neighboring atoms. We replace one of the 172 site of Fe Ⅰ, Fe Ⅱ, Si Ⅰ and Si Ⅱ atom by vacancy, and signed as VFe Ⅰ, VFe Ⅱ, VSi Ⅰ, and VFe Ⅱ, respectively.
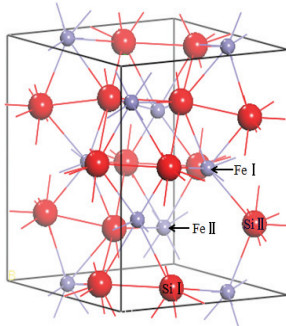

Fig.1. Unite cell of β-FeSi$_2$.

3. Results and discussion

The calculated band structures of β-FeSi2 crystal are shown in Fig.2. It indicates that the valence band maximum (VBM) and the conduction band minimum (CBM) are located at G, suggesting a direct band gap semiconductor of β-FeSi2 crystal, with the calculated band gap of about 0.74eV. This result is accordant with the calculated result band gaps of Pan et al., who used Win2K [7]. But the calculated band gap is smaller than the experimental band gap of about 0.9 eV. Generally, an underestimation of the calculated band gaps is an intrinsic feature of the ab initio method due to the DFT limitations, no taking into account the discontinuity in the exchange-correlation potential.
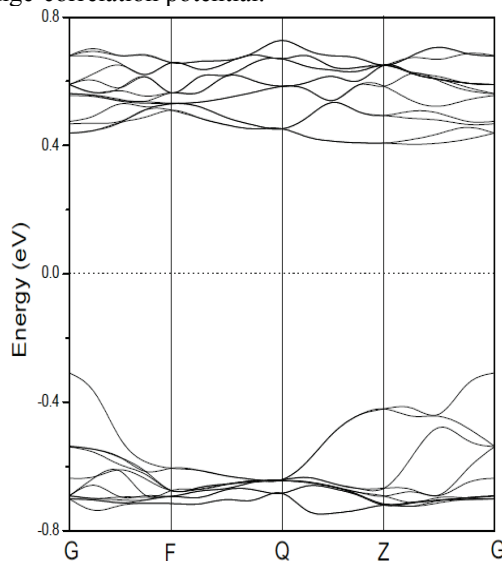

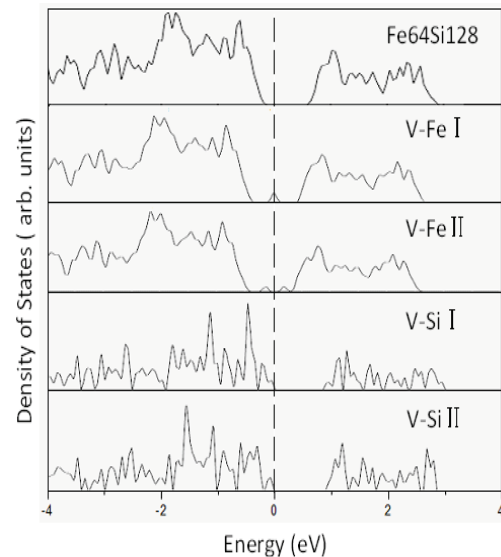**Fig.2. Calculated band structures of perfect crystal of β-FeSi$_2$**

Fig.3.Total DOS the perfect crystal and defective crystal of β-FeSi2

Fig.3 shows the calculated total DOS for the perfect and defective β-FeSi$_2$ crystal. Compared with the perfect crystal, there is some different in DOS of the defective crystal. For DOS of the defective crystal with $V_{FeⅠ}$ and $V_{FeⅡ}$, it can be seem clearly that there is sharp level produced between the valence band and the conduction band. The EF exists at the sharp defective level below the bottom of the conduction band. As a result that electrons in the levels can exists to the conduction band by thermal energy, and the electrons can be produced in the conduction band. This calculated results indicate that the defective β-FeSi$_2$ crystal with $V_{FeⅠ}$ and $V_{FeⅡ}$ will behaves as n-type semiconductor. For DOS of the defective crystal with $V_{SiⅠ}$ and $V_{SiⅡ}$, the E_F level shifts to the top of the valence band. In this condition, the electrons in the top of the valence band can excite to the defective level by thermal energy, and holes would be produced in the valence band. J.Tani et al. obtained a similar calculated results using CASTEP [8]. It suggested that the defective β-FeSi$_2$ crystal with $V_{SiⅠ}$ and $V_{SiⅡ}$ will behaves as p-type semiconductor. It is strange for compound semiconductor that the defective crystal containing metal vacancies shows n-type, while the crystal containing non-metal vacancies shows p-type. But it exists in the defective β-FeSi$_2$ crystal, and the calculated results are consistent with the experimental results [9].

4. Conclusions

The projector-augmented plane wave potentials method under the density functional theory (DFT) was used to calculate the electronic structure of perfect and native point defective β-FeSi$_2$ crystal. The calculated band structure shows that the band gap of perfect crystal is

about 0.74eV, which is a little smaller than the experimental result of about 0.9eV. The density of states results predicts that β-FeSi$_2$ with Fe vacancies behaves n-type, and that with Si vacancies will shows p-type, which is in accordant with the experimental results.

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