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# Electronic structure of $\beta$ -FeSi<sub>2</sub> obtained by maximum entropy method and photoemission spectroscopy

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## Abstract

The electronic structure of  $\beta$ -FeSi<sub>2</sub> was investigated by maximum entropy method (MEM) and photoemission spectroscopy. The electronic structure obtained by MEM using X-ray diffraction data at room temperature (RT) showed covalent bonds of Fe–Si and Si–Si electrons. The photoemission spectra of  $\beta$ -FeSi<sub>2</sub> at RT were changed by incidence photon energies. For photon energies between 50 and 100 eV, resonant photoemission spectra caused by a super Coster–Kronig transition were observed. In order to reduce resonant effect about Fe(3d) for obtained photoemission spectra, difference spectrum between 53 and 57 eV was calculated, and it was compared with ab-initio band calculation and spectra function.

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## 1. Introduction

$\beta$ -FeSi<sub>2</sub> ( $a = 9.863 \text{ \AA}$ ,  $b = 7.791 \text{ \AA}$ ,  $c = 7.833 \text{ \AA}$ ) is an unusual semiconductor having energy band gap of 0.85 eV, which is caused from lattice distortion (Jahn–Teller distortion) of unstable metallic  $\gamma$ -FeSi<sub>2</sub> [1]. Recently,  $\beta$ -FeSi<sub>2</sub> is attracted for optical devices such as light emitting diode and

solar cell because of showing a highly optical absorption coefficient larger than  $10^5 \text{ cm}^{-1}$  [2]. Hence, various preparation techniques have been selected for  $\beta$ -FeSi<sub>2</sub> [3–6,8]. In addition, physical properties of  $\beta$ -FeSi<sub>2</sub> have been investigated by structural, electrical and optical measurements. In transport properties, the electrical condition is firstly accounted for small polaronic one from theoretical calculation, which is caused from electron and phonon interaction. Kondo has investigated electron-longitudinal acoustic (LA) phonon interaction using Mössbauer spectroscopy and deformation potential [9]. In addition, electron-longitudinal

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optical (LO) phonon interaction have been investigated based on Fröhlich's model [4].

$\beta$ -FeSi<sub>2</sub> has been developed using various preparation and characterization technique, however advantages for optical devices will be refused until investigating several unknown factor, such as nature of energy band gap and/or Jahn–Teller distortion. Hence, nature of physical properties, namely, electronic structure in  $\beta$ -FeSi<sub>2</sub> should be investigated. The electronic structure of  $\beta$ -FeSi<sub>2</sub> is reported by theoretical calculations [10,11]. However, only a few of experimental investigation about electronic structure for  $\beta$ -FeSi<sub>2</sub> have been reported. Therefore, the electronic structures were

obtained by maximum entropy method (MEM) using  $\beta$ -FeSi<sub>2</sub> single crystal and its X-ray diffraction data, and photoemission spectroscopy was measured at room temperature (RT) using  $\beta$ -FeSi<sub>2</sub> polycrystal. We report on here electronic structure of  $\beta$ -FeSi<sub>2</sub> obtained by MEM and photoemission spectroscopy.

## 2. Experimental

$\beta$ -FeSi<sub>2</sub> polycrystal and single crystal were prepared by normal freezing method and chemical vapor transport method, respectively [4,5]. Using  $\beta$ -FeSi<sub>2</sub> polycrystal, valence band spectra were

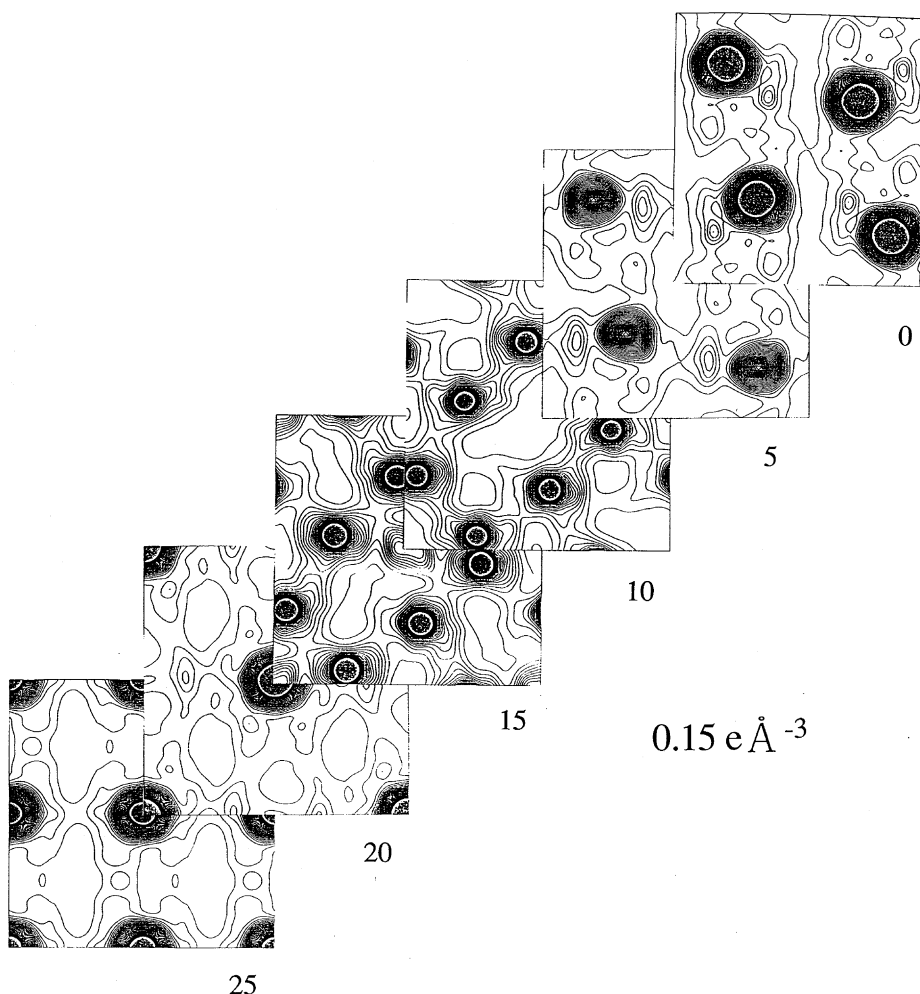


Fig. 1. Electronic density distribution map of  $\beta$ -FeSi<sub>2</sub> calculated by MEM using X-ray diffraction data at RT.

measured by photoemission method, and  $\beta$ -FeSi<sub>2</sub> single crystal was analyzed by four-axis X-ray diffraction method.

The electron density distribution maps were calculated by MEM using X-ray diffraction data. The light source of photoemission spectroscopy was selected for synchrotron radiation. Synchrotron radiation was monochromatized using a grazing incidence spherical grating monochromator. The kinetic energy of the photoelectron was measured with a double cylindrical mirror analyzer. The total resolution of the experimental system was about 0.3 eV.

### 3. Results and discussion

The electron density distribution maps were calculated by MEM using X-ray diffraction data.

The entropy  $S_e$  for information theory is written by

$$S_e = - \sum_r \rho_1(\mathbf{r}) [\rho_1(\mathbf{r}) / \tau_1(\mathbf{r})], \quad (1)$$

where the probability  $\rho_1(r)$  and the prior probability  $\tau_1(r)$  are related to the actual electron density expressed by  $\rho_1(\mathbf{r}) = \rho_1(\mathbf{r}) / \sum_r \rho_0(\mathbf{r})$  and  $\tau_1(\mathbf{r}) = \tau_0(\mathbf{r}) / \sum_r \tau_0(\mathbf{r})$  [7]. The  $\rho_1(\mathbf{r})$  is the electron density at a certain pixel located at  $\mathbf{r}$  and  $\tau_0(\mathbf{r})$  is the prior density for  $\rho_0(\mathbf{r})$ . Fig. 1 shows the cross-sectional (perpendicular to  $a$  axis) electron density distribution map of  $\beta$ -FeSi<sub>2</sub>. Large atom is Fe, and small one is Si. The electrons distribute with isotropic shapes. The contour lines are drawn at densities of  $n \times 0.15 \text{ \AA}^{-3}$ . The mirror reflections in  $\beta$ -FeSi<sub>2</sub> crystal structure are

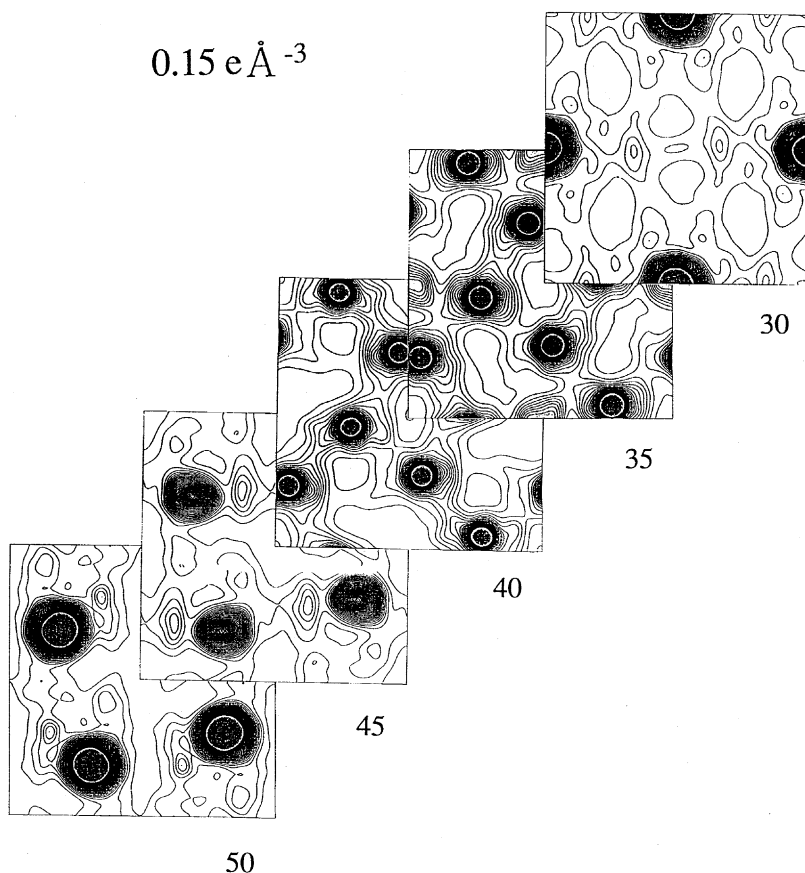


Fig. 1 (continued)

positioned in  $(a/2, b/2, c/2)$  [1]. The numbers are indicating the positions of electron density distribution plots ( $c_i a$ ), where  $c_i$  is constant ( $c_i = i/9.863 \text{ \AA}$ ,  $i = 0, 5, 10, \dots, 95, 100$ ). Along  $a$ -axis, Fe and Si layers are clearly observed. The bond between Fe and Si atoms does not formed. On the other hand, covalent bonds of Si electrons (Si-network) are observed evidently.

Fig. 2 shows the energy dependence of valence band spectra of  $\beta$ -FeSi<sub>2</sub> at RT obtained by photoemission method. For photon energies  $50 < h\nu < 100 \text{ eV}$ , spectra exhibit pronounced changes as a function of  $h\nu$ , due to the resonant photoemission effect, i.e. interference between direct photoemission  $3d^n \rightarrow 3d^{n-1} + \varepsilon l$  and a core excitation  $3p^6 3d^n \rightarrow 3p^5 3d^{n+1}$  followed by a super Coster–Kronig transition  $3p^5 3d^{n+1} \rightarrow 3p^6 3d^{n-1} + \varepsilon l$ . In spectra (a)–(f), the peak-1 has no energy dependence, however the peak-2 presents a drastic energy dependence for excitation energy between

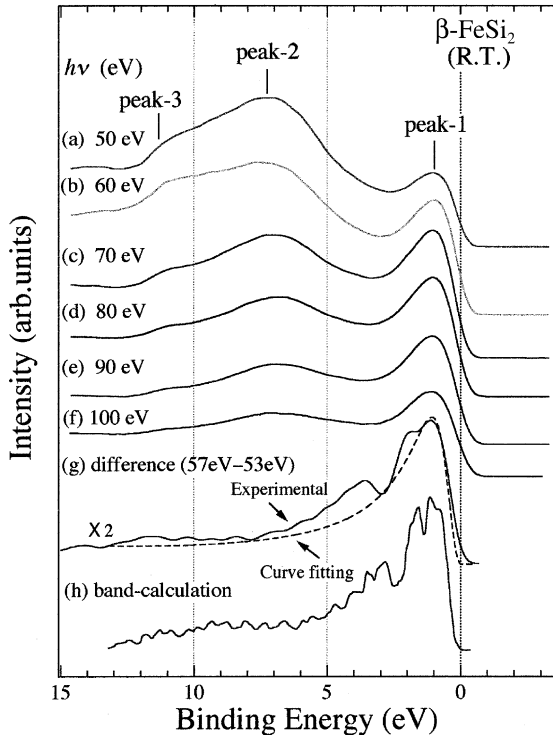


Fig. 2. The valence band photoemission spectra of  $\beta$ -FeSi<sub>2</sub> obtained by synchrotron radiation and ab initio band calculation.

50 and 100 eV. In order to reduce resonance effect, a difference spectrum between 53 and 57 eV is calculated. Fig. 2(g) shows the difference spectrum. The spectrum is similar to the result of ab initio band calculation in Fig. 2(h) [10,12].

Saitoh et al. showed the electron correlation of  $\varepsilon$ -FeSi, giving a qualitative explanation to the unusual electronic and magnetic properties using a self-energy ( $\Sigma(\omega)$ ) model,

$$\Sigma(\omega) = g'(\omega - \mu')/(\omega - \mu' + i\gamma')^2, \quad (2)$$

where  $\omega$  is the frequency of photon,  $\mu'$  is the chemical potential,  $g'$  is coefficient and  $\gamma'$  is damping constant. Using  $\Sigma(\omega)$ , we calculated the spectral function  $\rho(\omega)$ ,

$$\begin{aligned} \rho(\omega) &= -\text{Im} \frac{1}{\pi} G(\omega) \\ &= -\frac{1}{\pi} \cdot \frac{\text{Im} \Sigma(\omega)}{(\omega - \varepsilon_k^0 - \text{Re} \Sigma(\omega))^2 + \text{Im} \Sigma(\omega)^2}, \end{aligned} \quad (3)$$

where  $G(\omega)$  is Green function and  $\varepsilon_k^0$  is the energy of non-interacting electron. From above results,  $\Sigma(\omega)$  model parameters of  $\beta$ -FeSi<sub>2</sub> were found to be widely changed comparing with that of  $\varepsilon$ -FeSi ( $\mu' = 0 \text{ eV}$ ,  $g' = 13.0 \text{ eV}$  and  $\gamma' = 5.0 \text{ eV}$ ) [13,14].

#### 4. Conclusions

$\beta$ -FeSi<sub>2</sub> polycrystal and single crystal were prepared by normal freezing method and chemical vapor transport method, respectively. The electronic structure was investigated by electronic density distribution map and valence band spectra. From electronic density distribution map, Fe and Si electrons form covalent bond. In addition, Si-network are evidently observed. In photoemission spectroscopy, Fe(3d) electron is hybridized with Si(3s, 3p) electron. From above results, Fe(3d)–Si(3s, 3p) and Si(3s, 3p)–Si(3s, 3p) electrons occur Jahn–Teller distortion and band opening from metallic  $\gamma$ -FeSi<sub>2</sub>.

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