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# Magnetic property and electronic structure of β-$FeSi_2$

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**Abstract**

The magnetic and photoemission spectroscopy measurements were used to characterize β-$FeSi_2$ crystal. The magnetic susceptibility of β-$FeSi_2$ showed a minimum at 90 K. The electronic structure of β-$FeSi_2$ was studied by photoemission spectroscopy. The valence-band spectra showed a strong photon energy dependence. The electron–electron interaction was discussed by comparing experimental data with ab initio band calculation. 

*Keywords:* β-$FeSi_2$; Magnetic susceptibility; Electronic structure

Recently, renewed interests about ε-FeSi appear from uncommon behavior of optical conductivity measurements at low temperatures [1]. Temperature dependence of resistivity ($\rho(T)$) of ε-FeSi shows semiconducting thermal activation features at low temperatures. It, however, behaves as a metal above room temperature (RT). Temperature dependence of magnetic susceptibility ($\chi(T)$) of ε-FeSi follows Curie law below 90 K, and shows Curie–Weiss behavior above 500 K. At first, they were accounted for by a simple semiconducting model having very narrow energy band gap ($E_g$) and bandwidth [2]. Schlesinger et al. presented a picture of ε-FeSi as a Kondo insulator [1].

In this context, it would be of interest to substitute Fe in ε-FeSi with Si in view of bandwidth control using excess Si for ε-FeSi. Therefore, Si-rich stoichiometry compounds: β-$FeSi_2$ and α-$Fe_2Si_5$ are of great interest in view of the change of their physical properties from those of ε-FeSi. Quenched high-temperature structural phase (α-$Fe_2Si_5$) shows a resistivity minimum (Kondo effect), and β-$FeSi_2$ shows semiconducting features with $E_g$ of about 0.85 eV reflecting Jahn–Teller distortion [3]. Therefore, it is of great importance to investigate physical properties of β-$FeSi_2$ in order to compare them with those of ε-FeSi. In this paper, we present the investigations of magnetic properties and electronic structure about β-$FeSi_2$.

The $\chi(T)$ was measured in the temperature range between 4.2 and 400 K at a magnetic field of $1.257 \times 10^6$ Oe ($1.0 \times 10^4$ G) using a superconducting quantum interference device (SQUID). 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.

Temperature dependence of $\chi(T)$ for the sample is displayed in Fig. 1. Below 90 K, $\chi(T)$ increases with decreasing temperature, i.e., $\chi(T)$ follows Curie law. Jaccarino et al. pointed out that large excess Si for ε-FeSi results in a decrease in the value of $\chi(T)$ [2]. Although

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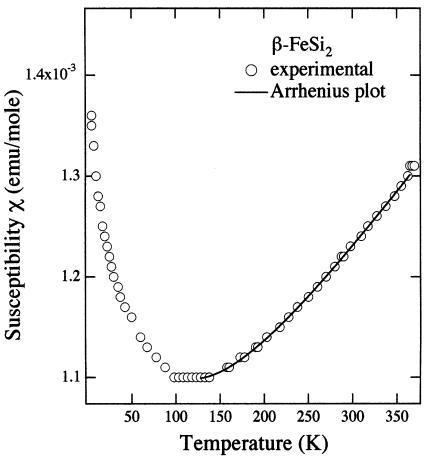


Fig. 1. The temperature dependence of magnetic susceptibility $\chi(T)$ of the sample. Below 90 K, $\chi(T)$ follows Curie law and increases with decreasing temperature. Above 90 K, $\chi(T)$ increases with increasing temperature, and spin gap $\Delta g$ of the sample is found to be 0.056 eV from Arrhenius plot.

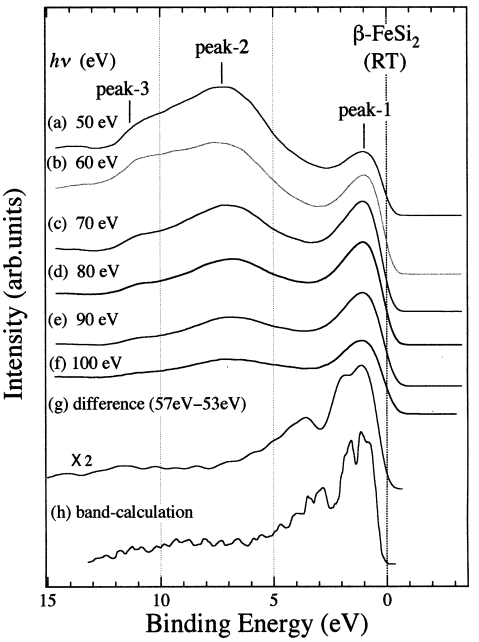


Fig. 2. The valence band photoemission spectra of β-$FeSi_2$ obtained by synchrotron radiation and ab initio band calculation. The experimental spectra (a)–(f) are taken at 50–100 eV, difference spectra (g) is obtained by 57–53 eV. Comparing experimental data with (h) ab initio band calculation, the Fe(3d) state hybridizes Si(3s) state.

excess Si for ε-FeSi, i.e. Fe/Si $= \frac{1}{2}$, composition promotes a decrease in the value of $\chi(T)$ compared with that of ε-FeSi, temperature dependence of $\chi(T)$ for the sample shows a minimum at 90 K in Fig. 1.

Above 90 K, $\chi(T)$ increases with increasing temperature [4]. The Arrhenius plot of $\chi(T)$ is demonstrated as a solid line in Fig. 1. $\chi(T)$ can be expressed as $\chi(T) = (C'/T)\exp(-\Delta g/k_B T)$, where $C'$ is Curie constant and $\Delta g$ is spin gap. We estimated that $\Delta g$ and $C'$ are 0.056 eV and 0.9 emu/mol, respectively. $C'$ can be expressed as $N(g\mu_B/3k_B)S(S+1)$, where $g$, $\mu_B$ and $S$ are $g$-value, Bohr magneton and spin tensor, respectively. The parameter $C'$ is associated with $S = 1$ and $g = 2$, hence these results suggest that valence of Fe in β-$FeSi_2$ takes an unionized $Fe^{+0}$ ($d^8$) [5]. From the above results, $E_g$ of β-$FeSi_2$ was found to be larger than that of ε-FeSi, however, $\Delta g$ is not quite different compared with that of ε-FeSi.

Fig. 2 shows energy dependence of valence-band spectra of β-$FeSi_2$ (a)–(f), difference spectrum (g) and ab initio band calculation (h) [3]. For photon energies $50 < h\nu < 100$ eV, the spectra exhibit pronounced changes as a function of $h\nu$, due to the resonant photoemission effect. In spectra (a)–(f), peak 1 has no energy dependence, however, peak 2 presents a drastic energy dependence for excitation energy between 50 and 100 eV. These features are reflected by cross-section in which photoelectrons collide with the sample. Therefore, the positions of peaks 1 and 2 indicate Fe (3d) and Si (3s) states, respectively. From the results, the bonding is expressed in terms of hybridization between the Fe(3d) and Si(3s), and in addition, the Si(3p) electrons seem to be involved in the bonding. Peak 3 is the satellite of the valence band region reflecting covalent bonding of β-$FeSi_2$ [6]. The difference spectrum ($g$) of β-$FeSi_2$ is similar to Fe (3d) and/or photoemission curve of α-$Fe_2Si_5$. Therefore, from difference spectrum reflecting elemental electronic structure, it is revealed that the appearance of the paramagnetic behaviors in β-$FeSi_2$ is attributed to Fe (3d), although crystal structure of β-$FeSi_2$ is different from that of α-$Fe_2Si_5$. Fig. 2(h) shows the ab initio band calculation of β-$FeSi_2$. It is consistent with the difference spectrum in Fig. 2(g). In comparison with spectra (a)–(f), free-electron-based model in this material can no longer fully describe electron–electron interaction and hybridization in the electron structure [7].

In conclusion, magnetic and photoemission measurements of β-$FeSi_2$ crystals were carried out. The temperature dependence of magnetic susceptibility of β-$FeSi_2$ crystal showed the unusual feature similar to that of ε-FeSi. Density of states in β-$FeSi_2$ crystal was discussed from valence-band spectra, and some parts of the spectra do not agree with band calculation. This disagreement with the band calculation suggests an effect of other interactions, such as electron correlation. Thus, this point has to be clarified in future studies.

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