Angle-Resolved Photoemission Analysis of Electronic Structures for Thermoelectric Properties of Off-Stoichiometric Fe$_{2-x}$V$_{1+x}$Al Alloys

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The electronic states of Heusler (L$_2$)$_2$-type off-stoichiometric Fe$_2$V$_{1+x}$Al alloys have been investigated by soft x-ray angle-resolved photoelectron spectroscopy (ARPES) to clarify the origin of the remarkable increase in thermoelectric power, which cannot be explained by the rigid-band model. In off-normal and normal ARPES, Fe$_{2.09}$V$_{0.91}$Al shows weakly dispersive bulk bands from the binding energy of 0.3 eV at the Γ point in the Γ–X and Γ–L directions, and an almost dispersionless one around 0.3 eV in the gap of dispersive bulk bands in the Γ–L direction, which is attributed to antisite Fe defects. The Fermi level $E_F$ is found at the X point. The antisite Fe defect states near $E_F$ might push up the band at the X point and cause p-type thermoelectric properties, which is unexpected for the rigid-band model. The change in electronic structures and thermoelectric properties for the off-stoichiometry and substitution by a forth element is discussed.

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1. Introduction

Heusler (L$_2$)$_2$-type Fe$_2$VAl-based alloys have attracted much attention as new thermoelectric materials, because small off-stoichiometry and partial substitution by a forth element can cause remarkable increase in the thermoelectric properties. These alloys have excellent mechanical strength, low environmental load and low cost compared to commercial available thermoelectric materials of highly doped semiconductors$^{3-5}$). It has been inferred that their thermoelectric properties are highly sensitive to the nanoscale atomic arrangement.

To date, theoretical and experimental studies$^{6-9}$) have shown that Fe$_2$VAl possesses a nonmagnetic semimetallic electronic band structure with a sharp pseudogap around the Fermi energy $E_F$, as observed in Fig. 1, where the electronic band structure and density of states (DOS) are calculated using the WIEN2k code$^{10,11}$). The thermoelectric power $S(T)$ at temperature $T$ may be given by the DOS $N(E)$ at energy $E$ and the Fermi–Dirac distribution function $f(E;T)$ as follows$^{12,13}$:

$$S(T) \equiv \frac{1}{eT} \int \sigma(E)(E-\mu) \frac{\partial f(E;T)}{\partial E} dE - \int \sigma(E) \frac{\partial f(E;T)}{\partial E} dE + \int N(E) \frac{\partial f(E;T)}{\partial E} dE,$$  

(1)

where $\mu$ and $\sigma(E)$ are the chemical potential ($\mu = E_F$ at low temperatures for metals) and spectral conductivity at $E$, respectively. In the second expression of eq. (1), the electron group velocity $v(E)$ and scattering time $\tau(E)$ are assumed independent of $E$. As the energy derivative of the Fermi–Dirac function may be regarded as the window function of $\pm 2k_BT$ width around $\mu$, the second formula suggests that the thermoelectric power is proportional to the moment of $N(E)$ around $\mu$. The change in electronic structures and thermoelectric properties for the off-stoichiometry and substitution by a forth element is discussed.

Fig. 1 Electronic band structure (right panel) and density of states (DOS; left panel) for Fe$_2$VAl. Total DOS and projected DOS onto the sphere at each constituent site are calculated using WIEN2k code$^{10}$ and the experimental lattice constant $a = 0.5761$ nm in the full potential linearized augmented plane wave (FLAPW) scheme and the generalized gradient approximation by Perdew, Burke and Ernzerhof (GGA-PBE)$^{12}$. The first Brillouin zone for the L$_2$ lattice of Fe$_2$VAl is shown in Figs. 4 and 5.

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and the averaged valence electron concentration (VEC) per constituent atom. The gray curve (DOS) stands for the thermoelectric power estimated from the theoretical density of states for Fe2VAI within the rigid-band model.

\[ \mu, \text{i.e., the difference in DOS below and above } E_F \text{ within the energy range of } \pm 2k_B T. \] Hence, the increase in the n- or p-type thermoelectric power is expected with changing \( \mu \) or \( E_F \) induced by minor substitution and off-stoichiometry in the rigid-band model, wherein the electronic band structure with sharp pseudogap is assumed unaltered by such negligible content change. In fact, Nishino et al. have found a universal relation between the thermoelectric power at 300 K \( (300 \text{ K}) \) and the averaged valence electron concentration (VEC) per atom \( n \) for substituted alloys \( 1^4-1^8 \), as shown in Fig. 2. On the substitution by a forth element, the \( n \)-dependence of the thermoelectric power fairly agrees with the estimated thermoelectric power (gray curve; DOS) using the calculated band structure and eq. (1).

In Fe/V off-stoichiometric \( \text{Fe}_2-x\text{V}_{1+x}\text{Al} \) \( (17^2-2^1) \), however, the dependence of thermoelectric power \( S \) on excess V content \( x \) cannot even be qualitatively explained in terms of the rigid-band model, as shown by the open circles in Fig. 2. It has been also found that the simultaneous substitution by a forth element in off-stoichiometric specimens leads to increased thermoelectric power over a wide temperature range and electron-mass enhancement at low temperatures that is similar to a heavy electron system \( 3^2 \). It has been recently posited that \( \text{Fe}_{2-x}\text{V}_{1+x}\text{Al} \) has a ferromagnetic quantum critical point at \( x \sim -0.05^2^5 \). It has also been proposed that the weak localization through the mid-gap defect state may be responsible for the semiconducting electric conductivity observed at low temperatures in Fe/Al off-stoichiometric \( \text{Fe}_{2-x}\text{V}_{1+x}\text{Al} \).

It is speculated that these peculiar electric, magnetic, and thermoelectric properties arise from the in-pseudogap \( d \) states of magnetic nanoclusters formed around an antisite defect pair, comprising V and Fe atoms at the Fe and V sites, respectively, or an antisite defect of excess Fe (or V) occupying the V (or Fe) site. Such states and formation of magnetic clusters have already been predicted using first principles calculations by various methods \( 27^2-3^1 \). Instead of a pseudogap, the opening of the full gap of 0.3–0.6 eV has also been predicted by the on-site coulomb interaction \( U \) combined with the generalized gradient approximation GGA (GGA + \( U \)).

Angle-resolved photoemission measurements were performed at approximately 20 K at the BL23SU beamline of the 8-GeV electron storage ring at SPring-8 in the Japan Synchrotron Radiation Research Institute (JASRI). In this beamline, the excitation soft x-ray from an APPLE-2-type undulator with variable light polarization was monochromatized with a variable line spacing plane grating monochromator and was focused onto the specimen \( 32^2,3^3 \). Angle-resolved spectra were obtained with a high-resolution hemispherical electron analyzer (GAMMADATA SCIENTA SES-2002) with the input electron lens at 45° to the incident excitation soft x-ray. The excitation photon energy \( h\nu \), total energy resolution \( \Delta E \), and the origin of the binding energy \( E_B \) (the Fermi energy \( E_F \)) were estimated by measuring the Fermi edge of a Au film evaporated onto the sample holder. Furthermore, the

![Fig. 2](image-url)
temporal change in the excitation photon energy was corrected by frequently measuring the Au 4f core-level spectra. The total energy resolution was 0.16 eV at $h\nu = 800$ eV including the thermal broadening. The angle resolution (acceptance angle) was 0.6° and 0.36° for the surface-normal and surface-parallel (off-normal) measurements, respectively. Thus, the wave vector resolution was estimated at approximately 0.6 nm$^{-1}$ for the off-normal direction and 1 nm$^{-1}$ at most for the normal direction. This is because the photoelectron mean free path (photoelectron escape depth) in Fe may be at 1 nm for electron kinetic energy of 500 eV ($h\nu \sim 500$ eV$^{34}$). The normal direction was set so that the first peak near $E_F$ has the smallest binding energy (the $\Gamma$ point) by measuring the ARPES spectra as the specimen was rotated in the plane spanned by the input electron lens axis and the excitation photon incidence directions.

Single crystals of Fe$_{2-x}$V$_{1+x}$Al were prepared by the Czochralski pulling method in a tetra-arc furnace under Ar atmosphere$^{35}$. A mixture of appropriate amounts of 99.9% pure Fe and V, and 99.9999% pure Al was premelted in an Ar mono-arc furnace. The pulling speed was 10 mm h$^{-1}$. The single-crystallinity and crystal axis directions of the specimens were determined by the back-reflection Laue method. The specimens were cut into rods of approximately 3 mm in length and 1 mm$^2$ in cross-sectional area along the [001] and [111] directions. The thermoelectric power at 300 K of the single crystal specimens (closed circle in Fig. 2) was in good agreement with that of polycrystalline specimens (open circles in Fig. 2)$^{17,18}$; thus, we believe that the real content agrees with the expected one. Clean (001) and (111) surfaces were prepared by fracturing the specimen rods with a knife edge under 2×10$^{-8}$ Pa at 20 K, and were confirmed by a fact that only signals of the constituent elements were observed in the wide-energy-range of the photoelectron spectra just after the fracture, and no O 1s signals before and after the ARPES measurements.

3. Results and Discussion

The obtained photoelectron spectra are shown in Fig. 3. Figure 3 (a) and (c) show the normal photoemission spectra recorded in the directions normal to the (001) and (111) surfaces, respectively. In Fig. 3, the excitation photon energies $h\nu$ and the symmetry points of the Brillouin zone are shown on the right-hand side of each normal spectrum and is 645 eV for the off-normal photoemission measurement. The weak features discussed in the text are marked by the vertical bars.

![Fig. 3](image-url) Angle-resolved photoelectron spectra of single crystal Fe$_{2.05}$V$_{0.95}$Al: (a) normal and (b) off-normal photoemission of the (001) surface, and (c) normal to the (111) surface. The excitation photon energy $h\nu$ is shown in the right-hand side of each normal spectrum and is 645 eV for the off-normal photoemission measurement. The weak features discussed in the text are marked by the vertical bars.

![Fig. 4](image-url) Experimental band structure; (a) parallel and (b) normal to the (001) surface of Fe$_{2.05}$V$_{0.95}$Al. Part of the calculated bands for stoichiometric Fe$_2$VAl is shown by the white curves. The first Brillouin zone for the $L_2$ lattice of Fe$_2$VAl is also shown.

$$\hbar k_{//} = \sqrt{2m(E_i + h\nu - \phi)} \sin \theta - \hbar G_{//},$$

(2)
The inner potential energy $E_\text{F}$ increases relative to the rigid-band model; however, the increase in the density of the occupied states implies the increase in the p-type thermoelectric power, which is in qualitative agreement with the experimental $x$-dependence of the thermoelectric power (Fig. 2).

None of abovementioned bulk bands cross $E_F$ at the $\Gamma$ point, as expected from the Fe-rich content of Fe$_{2.05}$V$_{0.95}$Al in the rigid band model, whereas no electron pocket predicted at the $X$ point for Fe$_{2.05}$V$_{0.95}$Al is clearly observed; the defect states near $E_F$ might push up the band. Thus, there is the possibility of opening a full gap owing to the antisite defects. Although the intensity near $E_F$ increases at the $\Gamma$ point, it is not presently clear whether the antisite-induced states exist near the $\Gamma$ point and whether they cross $E_F$. The possibility of full gap and narrower band width than that calculated for Fe$_{2.05}$V$_{0.95}$Al point to the importance of the correlation effect.

It is important to compare the experimental results with the band structure calculations including the antisite defects. We have already compared the angle-integrated photoelectron spectra with the calculated total and partial DOS of the antisite defects [17]. According to the calculations by the linear muffin-tin orbital atomic sphere approximation (LMT-ASA) method using a supercell for Fe$_{2.04}$V$_{0.96}$Al ($x = 0.04$) [25,27], it was predicted that localized majority spin states appear at $E_F$ and the band located at $E_F \sim 0.1$ eV disperses by approximately 0.3 eV toward the high binding energy. Although there are no large features clearly observed near $E_F$ in the angle-resolved spectra, the intensity near $E_F$ increases in the angle-integrated spectrum. The calculations also predict a weak dispersive band at $E_F \sim 0.3$ eV. Presently, it is unclear, because of the strong bulk band, whether the observed 0.3-eV band disperses to the $\Gamma$ point or not. The calculation by the Korringa-Kohn-Rostocker method with coherent-potential approximation (KKR-CPA) also predicts that a majority spin antisite defect-derived band appears at $E_F \sim 0.5$ eV. Thus, the band at $E_F = 0.3$ to 0.4 eV with weak dispersion in the $\Gamma$–$L$ direction is ascribed to the majority spin states of the magnetic clusters due to the excess Fe. The excess electrons caused by the increments of VEC may occupy these defect-derived states, which brings the non-rigid-band-like behavior of the change in the valence-band electronic structure and, hence, thermoelectric power.

As mentioned above, in Fe/V off-stoichiometric content, the presence of Fe (or V) in the chemically different V (or Fe) site induces the defect states within the pseudogap. For excess Fe, the DOS in the high-energy (low binding energy) region of $E_F$ will decrease as the band edge of the p-type semiconductor and, hence, p-type thermoelectric power will appear. Substitution by a forth element may cause almost no change in the electronic structure. For example, as VEC is
raised by 0.05 in Fe$_{2.04}$V$_{0.96}$Al$_{1-x}$Si$_x$, a 0.2–0.3 eV increase in $E_F$ is estimated from the band structure calculations. Then, the DOS of the unoccupied conduction band or the unoccupied minority spin band increases and, hence, n-type thermoelectric power will appear. In fact, it was observed that the valence band of Fe$_{2.04}$V$_{0.96}$Al$_{1-x}$Si$_x$ shifts towards the high binding energy side. Thus, the rigid-band-like dependence of thermoelectric power is expected on the substitution by a fourth element to the Fe/V off-stoichiometric alloy.

4. Summary

We have investigated the electronic band structure near $E_F$ of Fe$_{2.05}$V$_{0.95}$Al by angle-resolved photoelectron spectroscopy and compared it with the band structure calculations for Fe$_2$VAl. We found bulk bands with strong intensity dispersing in and out of the surface-normal and surface-parallel directions in accordance with the calculated results and less dispersive bands with weak intensity induced by the magnetic cluster around the excess Fe. It is found that the bulk band does not cross $E_F$ at the $\Gamma$ point and the electron pocket is not clearly observed at the X point. It is desirable to identify the spin states of the antisite defects by spin-resolved photoelectron spectroscopy and clarify the existence of the gap by high-resolution angle-resolved photoelectron spectroscopy. Angle-resolved photoemission analysis of single crystal specimens is useful for obtaining the information that is not available in the DOS study by angle-integrated photoelectron spectroscopy, such as the band gap, the group velocity, the localized properties, the interaction, and the life time (self-energy) by investigating the dispersion relation and spectral shape. This will also critically test theoretical results such as band structure calculations. Further systematic studies of the electronic structure of Fe$_{2-x}$V$_x$Al will clarify the mechanism for the thermoelectric power and how to control it in practice.

Acknowledgments

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