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

Kazuo Soda^{1,2,*2}, Shota Harada^{1,*3}, Toshimitsu Hayashi^{1,*4}, Masahiko Kato¹, Fumihiko Ishikawa³, Yuh Yamada³, Shin-ichi Fujimori⁴ and Yuji Saitoh⁴

¹Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan

²Synchrotron Radiation Research Center, Nagoya University, Nagoya 464-8603, Japan

³Department of Physics, Faculty of Science, Niigata University, Niigata 950-2181, Japan

⁴Quantum Beam Science Center, Japan Atomic Energy Agency, Hyogo 679-5148, Japan

The electronic states of Heusler ($L2_1$)-type off-stoichiometric $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ 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, $\text{Fe}_{2.05}\text{V}_{0.95}\text{Al}$ 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. At the Γ point, the bulk bands do not appear to cross the Fermi level E_F , which is consistent with the rigid-band model for excess Fe content, but no band crossing 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. [doi:10.2320/matertrans.MF201603]

(Received December 11, 2015; Accepted February 2, 2016; Published April 1, 2016)

Keywords: angle-resolved photoelectron spectroscopy, electronic structure, antisite defect state, thermoelectric properties, off-stoichiometric iron-based Heusler-type alloys

1. Introduction

Heusler ($L2_1$)-type Fe_2VAl -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 commercially available thermoelectric materials of highly doped semiconductors^{1,2}. Based on measurements of magnetization, thermoelectric power, and electric conductivity of specimens after thermal treatment³⁻⁵, it has been inferred that their thermoelectric properties are highly sensitive to the nanoscale atomic arrangement.

To date, theoretical and experimental studies⁶⁻⁹ have shown that Fe_2VAl 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}:

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

Fig. 1 Electronic band structure (right panel) and density of states (DOS; left panel) for Fe_2VAl . Total DOS and projected DOS onto the sphere at each constituent site are calculated using WIEN2k code¹⁰ and the experimental lattice constant $a = 0.5761 \text{ nm}^3$ in the full potential linearized augmented plane wave (FLAPW) scheme and the generalized gradient approximation by Perdew, Burke and Ernzerhof (GGA-PBE)¹¹. The first Brillouin zone for the $L2_1$ lattice of Fe_2VAl is shown in Figs. 4 and 5.

where μ and $\sigma(E)$ are the chemical potential ($\mu \sim E_F$ 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 $\pm 2k_B T$ width around μ , the second formula suggests that the thermoelectric power is proportional to the moment of $N(E)$ around

^{*1}This Paper was Originally Published in Japanese in J. Japan Inst. Met. Mater. **79** (2015) 607–612.

^{*2}Corresponding author, E-mail: j45880a@cc.nagoya-u.ac.jp

^{*3}Graduate Student, Nagoya University, Present address: DENSO Corp.

^{*4}Graduate Student, Nagoya University

Fig. 2 Thermoelectric power at 300 K for various Fe_2VAl -based alloys^{14–18)} and the present single-crystal specimen. The abscissa is 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 Fe_2VAl within the rigid-band model.

μ , i.e., the difference in DOS below and above E_F within the energy range of $\pm 2k_B T$. Hence, the increase in the n- or p-type thermoelectric power is expected with changing μ 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 $S(300\text{ K})$ and the averaged valence electron concentration (VEC) per atom n for substituted alloys^{1,2,14–18)}, 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 $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ ^{17–21)}, 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^{17,18,22–24)}, which shows rigid-band-like dependence on the substitution from the non-rigid-band-like value of the off-stoichiometric alloy as a starting point (broken curve in Fig. 2)¹⁸⁾. In contrast, Fe_2VAl is marginally ferromagnetic and nonmagnetic with peculiar electronic transport properties, such as semiconductor-like electric conductivity over a wide temperature range and electron-mass enhancement at low temperatures that is similar to a heavy electron system³⁾. It has been recently posited that $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ has a ferromagnetic quantum critical point at $x \sim -0.05$ ²⁵⁾. 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 $\text{Fe}_{2-x}\text{VAl}_{1+x}$ ²⁶⁾.

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^{27–31)}. 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), where GGA is frequently used as the correlation-exchange interaction in metallic electronic band structure calculations, or by a correlation approximation different from GGA owing to the strong correlation of the transition metal 3d electrons^{27,28)}. However, this remains experimentally unverified yet.

It is important to understand and control the change in the electronic structure including the magnetic nanoclusters for efficiently using the transport and thermoelectric properties of these alloy systems. We have experimentally investigated the total electronic density of states of off-stoichiometric $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ alloys with angle-integrated soft x-ray photoelectron spectroscopy to clarify their electronic structures for thermoelectric applications^{17,23,24)}. Although it is difficult to study the unoccupied states by photoelectron spectroscopy, the spectral shape near E_F of the valence band of $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ changes from a p-type semiconductor-like steep increase to a small shoulder feature representing the pseudogap as V increases, which qualitatively explains the observed change from p- to n-type thermoelectric power (see Fig. 5). On the basis of these experimental and theoretical results, we proposed a model electronic band structure explaining the x -dependence of the thermoelectric power²⁴⁾.

Herein, we discuss the experimental results of angle-resolved photoelectron spectroscopy for the off-stoichiometric alloy $\text{Fe}_{2.05}\text{V}_{0.95}\text{Al}$ to clarify its valence-band electronic structure, particularly the band structure near E_F and the states induced by the antisite defects, and discuss the effect of the Fe/V off-stoichiometry on the electronic structure and thermoelectric properties. To the best of our knowledge, there is no experimental report on the dispersion relation of the Fe_2VAl -based alloys by angle-resolved photoelectron spectroscopy owing to the difficulty to grow Fe_2VAl single crystals.

2. Experimental Procedure

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 specimens^{32,33)}. 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 ΔE , 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. 3 Angle-resolved photoelectron spectra of single crystal $\text{Fe}_{2.05}\text{V}_{0.95}\text{Al}$: (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.

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 ($h\nu \sim 500 \text{ eV}$)³⁴. The normal direction was set so that the first peak near E_F has the smallest binding energy (the Γ 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 $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ were prepared by the Czochralski pulling method in a tetra-arc furnace under Ar atmosphere³⁵. 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 x agrees with the expected one. Clean (001) and (111) surfaces were prepared by fracturing the specimen rods with a knife edge under $2 \times 10^{-8} \text{ Pa}$ 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

Fig. 4 Experimental band structure; (a) parallel and (b) normal to the (001) surface of $\text{Fe}_{2.05}\text{V}_{1.95}\text{Al}$. Part of the calculated bands for stoichiometric Fe_2VAl is shown by the white curves. The first Brillouin zone for the $L2_1$ lattice of Fe_2VAl is also shown.

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 the spectra. Figure 3 (b) shows the off-normal photoemission spectra in the Γ -X direction parallel to the (001) surface at the excitation photon energy $h\nu = 645$ eV, which corresponds to the Γ point in the normal photoemission. Several dispersive bands are recognized between $E_B = 0$ to 2 eV.

Figure 4 shows the experimental band structures of $\text{Fe}_{2.05}\text{V}_{0.95}\text{Al}$ deduced from the second energy-derivative of the spectra for the (001) surface, where Figs. 4 (a) and (b) indicate the band structures along the Γ -X direction parallel and normal, respectively, to the (001) surface. For comparison, part of the band structure calculated for Fe_2VAl is shown by the white curves (see Fig. 1). The surface-parallel component $k_{\parallel}$ and surface-perpendicular component $k_{\perp}$ of the wave vector were estimated by the following equations³⁶:

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

Fig. 5 Experimental band structure normal to the (111) surface of $\text{Fe}_{2.05}\text{V}_{1.95}\text{Al}$. Angle-integrated photoelectron spectra of polycrystalline $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ ^{17,23)} are shown in the right panel for comparison. The first Brillouin zone for the $L2_1$ lattice of Fe_2VAl is also shown.

$$\hbar k_{i\perp} = \sqrt{2m(E_i + \hbar\nu - \phi + V_0)} - \hbar G_{\perp}, \quad (3)$$

where m , E_i , ϕ , θ , $G_{\parallel}$, and $G_{\perp}$ is the electron mass, the initial state energy, the work function, the photoemission angle to the surface-normal, and the appropriate reciprocal lattice vectors parallel and perpendicular to the surface, respectively. The inner potential energy V_0 was set at 13.4 eV from the experimental work function and the lowest energy ($E_B = 9.2$ eV) of the calculated valence band. The photon momentum is neglected but partly corrected by the abovementioned procedure of adjusting the surface-normal direction.

There are at least three bands observed in Fig. 4. The band at $E_B \sim 1.5$ eV has weak dispersion in the surface-normal direction, whereas the bands at $E_B \sim 0.3$ eV clearly observed near the Γ point are dispersive along the surface-normal and -parallel directions, which is in relatively good correspondence with the band calculations. Hereafter, we refer to these bands as bulk bands for distinguishing them from those derived from the antisite defects. There are weak features at approximately 0.8 eV and 1.6 eV, as indicated by the vertical bars in Fig. 3, although they are not discernible in Fig. 4. These weak features seem to show almost no dispersion; thus, they are attributed to the antisite defects or the surface. The dispersion of the band at $E_B \sim 1.5$ eV near the Γ point is weak compared to the calculated result. This may be attributed to the poorer angular resolution in the surface-normal direction than that in the surface-parallel direction or to the enhancement of the signals of the overlapping localized antisite defect states.

The band structure along the Γ -L direction of $\text{Fe}_{2.05}\text{V}_{0.95}\text{Al}$ is shown together with the angle-integrated spectra of polycrystalline $\text{Fe}_{2.04}\text{V}_{0.96}\text{Al}$ (black curve) and Fe_2VAl (gray curve)^{17,23)} in Fig. 5. As in the Γ -X direction, three bands are also recognized. A largely dispersive band around $E_B = 0.3$ eV at the Γ point and a less dispersive one at $E_B \sim 1.5$ eV correspond to the bulk bands of Fe_2VAl denoted by the white curves. As seen in Fig. 3(c), the band that peaked at 1.5 eV at the Γ point broadens towards the L point, implying the presence of another band in the calculations. The bands at E_B of

0.3–0.4 eV and 0.8 eV, seen as shoulders in the angle-resolved spectra near the L and Γ points, respectively, in Fig. 3(c) are not predicted by the calculations, and are hence attributed to the states induced by the antisite defects. These bands correspond to the shoulder at $E_B \sim 0.3$ eV and the peak at $E_B \sim 0.8$ eV in the angle-integrated spectrum of polycrystalline $\text{Fe}_{2.04}\text{V}_{0.96}\text{Al}$. A close inspection of the polycrystalline spectra in Fig. 5 suggests that despite the increase in VEC in $\text{Fe}_{2.04}\text{V}_{0.96}\text{Al}$, the first peak slightly shifts toward the low binding energy and the intensity at E_F increases relative to stoichiometric Fe_2VAl . This cannot be explained with 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 Γ point, as expected from the Fe-rich content of $\text{Fe}_{2.05}\text{V}_{0.95}\text{Al}$ in the rigid band model, whereas no electron pocket predicted at the X point for Fe_2VAl 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 Γ point, it is not presently clear whether the antisite-induced states exist near the Γ point and whether they cross E_F . The possibility of full gap and narrower band width than that calculated for Fe_2VAl 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 defects¹⁷⁾. According to the calculations by the linear muffin-tin orbital atomic sphere approximation (LM-TO-ASA) method using a supercell for $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ ($x = -0.125$)^{29,37)}, it was predicted that localized majority spin states appear at E_F and the band located at $E_B \sim 0.1$ 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 $E_B \sim 0.3$ eV. Presently, it is unclear, because of the strong bulk band, whether the observed 0.3-eV band disperses to the Γ 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 $E_B \sim 0.5$ eV. Thus, the band at $E_B = 0.3$ to 0.4 eV with weak dispersion in the Γ -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 $\text{Fe}_{2.04}\text{V}_{0.96}\text{Al}_{1-z}\text{Si}_z$, 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 $\text{Fe}_{2.04}\text{V}_{0.96}\text{Al}_{0.95}\text{Si}_{0.05}$ shifts towards the high binding energy side³⁸. 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 $\text{Fe}_{2.05}\text{V}_{0.95}\text{Al}$ by angle-resolved photoelectron spectroscopy and compared it with the band structure calculations for Fe_2VAl . We found bulk bands with strong intensity dispersing in 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 Γ 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^{13,36}. This will also critically test theoretical results such as band structure calculations. Further systematic studies of the electronic structure of $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ will clarify the mechanism for the thermoelectric power and how to control it in practice.

Acknowledgments

Photoelectron measurements were performed at the BL23SU of the Japan Atomic Energy Agency in SPring-8 with the approval of the nanotechnology network project supported by the Ministry of Education, Culture, Sports, Science and Technology (Proposal No. 2007B3872, 2008A3874, 2009B3877, and 2010A3873). We thank Prof. Yoichi Nishino and his laboratory group at Nagoya Institute of Technology for supplying the polycrystalline specimens, thermoelectric data, and valuable discussion. We also thank Dr. Shinpei Fujii of Kagoshima University for the results of the electronic band structure calculations with the LMTO-ASA method.

REFERENCES

- 1) Y. Nishino: *The Science of Complex Alloy Phases*, ed. By T. B. Massalski and P. E. Turchi (TMS, Warrendale, 2005) pp.325–344.
- 2) Y. Nishino: IOP Conf. Series: Materials Sci. and Eng. **18** (2011) 142001/1–6.
- 3) Y. Nishino, M. Kato, S. Asano, K. Soda, M. Hayasaka and U. Mizutani: *Phys. Rev. Lett.* **79** (1997) 1909–1912.
- 4) A. Matsushita, T. Naka, Y. Takano, T. Takeuchi, T. Shishido and Y. Yamada: *Phys. Rev. B* **65** (2002) 075204.
- 5) K. Soda, H. Murayama, S. Yagi, M. Kato, T. Takeuchi, U. Mizutani, S. Imada, S. Suga and Y. Saitoh, T. Muro H. Sumi and Y. Nishino: *Physica B* **351** (2004) 338–340.
- 6) G.Y. Guo, G.A. Botton and Y. Nishino: *J. Phys. Condens. Matter* **10** (1998) L119–L126.
- 7) A. Bansil, S. Kaprzyk, P.E. Mijnenrends and J. Tobola: *Phys. Rev. B* **60** (1999) 13396–13412.
- 8) K. Soda, H. Murayama, K. Shimba, S. Yagi, J. Yuhara, T. Takeuchi, U. Mizutani, H. Sumi, M. Kato, H. Kato, Y. Nishino, A. Sekiyama, S. Suga, T. Matsushita and Y. Saitoh: *Phys. Rev. B* **71** (2005) 245112.
- 9) H. Okamura, J. Kawahara, T. Namba, S. Kimura, K. Soda, U. Mizutani, Y. Nishino, M. Kato and I. Shimoyama, H. Miura, K. Fukui, K. Nakagawa, H. Nakagawa and T. Kinoshita: *Phys. Rev. Lett.* **84** (2000) 3674–3677.
- 10) P. Blaha, K. Schwarz, P. Sorantin and S.B. Trickey: *Comput. Phys. Commun.* **59** (1990) 399–415.
- 11) J.P. Perdew, K. Burke and M. Ernzerhof: *Phys. Rev. Lett.* **77** (1996) 3865–3868.
- 12) K. Soda, H. Miyazaki, K. Yamamoto, T. Mochizuki, M. Inukai, M. Kato, S. Yagi and Y. Nishino: *Adv. Synchrotron Rad.* **1** (2008) 235–243.
- 13) T. Takeuchi, T. Kondo, T. Takami, H. Takahashi, H. Ikuta, U. Mizutani, K. Soda, R. Funahashi, M. Shikano, M. Mikami, S. Tsuda, T. Yokoya and S. Shin: *Phys. Rev. B* **69** (2004) 125410.
- 14) F. Kobayashi, N. Ide and Y. Nishino: *J. Jpn. Inst. Met.* **71** (2007) 208–212.
- 15) H. Matsuura, Y. Nishino, U. Mizutani and S. Asano: *J. Japan Inst. Metals* **66** (2002) 767–771.
- 16) Y. Nishino, S. Deguchi and U. Mizutani: *Phys. Rev. B* **74** (2006) 115115.
- 17) K. Soda, S. Harada, M. Kato, S. Yagi, M. Inukai, H. Miyazaki, Y. Sandaiji, Y. Tamada, S. Tanaka, T. Sugiura and Y. Nishino: *J. Electron Spectrosc. Relat. Phenom.* **184** (2011) 236–239.
- 18) Y. Nishino and Y. Tamada: *J. Appl. Phys.* **115** (2014) 123707.
- 19) T. Nakama, Y. Takaesu, K. Yagasaki, T. Naka, A. Matsushita, K. Fukuda and Y. Yamada: *J. Phys. Soc. Jpn.* **74** (2005) 1378–1381.
- 20) C.S. Lue and Y.-K. Kuo: *Phys. Rev. B* **66** (2002) 085121.
- 21) Y. Hanada, R.O. Suzuki and K. Ono: *J. Alloy. Compd.* **329** (2001) 63–68.
- 22) T. Sugiura and Y. Nishino: *J. Jpn. Inst. Metals* **73** (2009) 846–851.
- 23) Y. Sandaiji, N. Ide, Y. Nishino, T. Owada, S. Harada and K. Soda: *J. Jpn. Soc. Powder Powder Metallurgy* **57** (2010) 207–212.
- 24) K. Soda, S. Harada, M. Kato, S. Yagi, Y. Sandaiji and Y. Nishino: IOP Conf. Series: Mater. Sci. and Eng. **18** (2011) 142004.
- 25) T. Naka, K. Sato, M. Taniguchi, T. Nakane, F. Ishikawa, Y. Yamada, Y. Takaesu, T. Nakama and A. Matsushita: *Phys. Rev. B* **85** (2012) 085130.
- 26) K. Soda, S. Osawa, M. Kato, H. Miyazaki, Y. Nishino: *JPS Conf. Proc.* **3** (2014) 017036.
- 27) D. Do, M.-S. Lee and S.D. Mahanti: *Phys. Rev. B* **84** (2011) 125104.
- 28) D.I. Bilc and P. Ghosez: *Phys. Rev. B* **83** (2011) 205204.
- 29) V.N. Antonov, A. Ernst, I.V. Maznichenko, A.N. Yaresko and A.P. Shpak: *Phys. Rev. B* **77** (2008) 134444.
- 30) S. Fujii, Y. Ienaga, S. Ishida and S. Asano: *J. Phys. Soc. Jpn.* **72** (2003) 698–704.
- 31) J. Deniszczak: *Acta Phys. Pol. B* **32** (2001) 529–533.
- 32) T. Nakatani, Y. Saitoh, Y. Teraoka, T. Okane and A. Yokoya: *J. Synchrotron Radiat.* **5** (1998) 536–538.
- 33) A. Yokoya, T. Sekiguchi, Y. Saitoh, T. Okane, T. Nakatani, T. Shimada, H. Kobayashi, M. Takao, Y. Teraoka, Y. Hayashi, S. Sasaki, Y. Miyahara, T. Harami and T.A. Sasaki: *J. Synchrotron Radiat.* **5** (1998) 10–16.
- 34) S. Tanuma, C.J. Powell and D.R. Penn: *Surf. Interface Anal.* **21** (1994) 165–176.
- 35) F. Ishikawa, K. Fukuda, N. Kawase, M. Mochigi, Y. Yamada and A. Matsushita: *J. Magn. Magn. Mater.* **310** (2007) e616–e617.
- 36) S. Suga and A. Sekiyama: *Photoelectron Spectroscopy – Bulk and Surface Electronic Structures*, (Springer, Berlin, 2014) Chapt. 2.
- 37) S. Fujii: *private communication*.
- 38) K. Soda, Y. Yamada, T. Nomoto, H. Kondo, K. Morita, M. Kato, Y. Tamada, R. Hamda and Y. Nishino: *unpublished* (SPring-8 User Experiment Report, No. 2011A1626).