

High-resolution soft x-ray photoelectron study of density of states and thermoelectric properties of the Heusler-type alloys $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$

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The high-resolution soft x-ray photoelectron study of Heusler($L2_1$)-type $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ ($y=23.8-25.8$) alloys directly confirms the correlation between their thermoelectric properties and the electronic structures near the Fermi level. It shows the rigid-band-like shift of the main $3d$ bands and the increase of the photoelectron intensity at the Fermi edge with the small deviation of the Al content from stoichiometry, i.e., $y=25.0$. This implies the existence of the pseudogap across the Fermi level in Fe_2VAl . The Seebeck coefficients evaluated from the present spectroscopic data agree well with the experimental ones as well as the values estimated from a theoretical density of states in a rigid-band model, while the shift is much smaller than what is expected in the rigid-band model. The small modification of the electronic structure in the off-stoichiometric $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys may be attributed to the lower contribution of Al to the electronic states near E_F .

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I. INTRODUCTION

The Heusler-type ($L2_1$ -type) intermetallic compound Fe_2VAl and related off-stoichiometric alloys, such as $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ and $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$, have attracted much attention because of their fascinating electrical, magnetic, and transport properties from not only interest in basic science but also potential application for thermoelectric materials.¹⁻⁴ The stoichiometric compound Fe_2VAl shows a semiconductorlike resistivity behavior over a wide temperature range between 2 K and 1200 K, the enhancement of the effective electron mass at low temperatures, and a marginally magnetic nature between the ferromagnetic and nonmagnetic (or paramagnetic) states, which is reminiscent of the heavy fermion system.^{1,2} On the other hand, the off-stoichiometric alloys exhibit remarkable enhancement of their Seebeck coefficient (thermoelectric power).^{3,5}

Most band structure calculations have predicted that Fe_2VAl is a nonmagnetic semimetal with a pronounced pseudogap of 0.5 eV width right at the Fermi level E_F .⁶⁻¹² The semimetallic electronic structure has been supported indirectly by a nuclear magnetic resonance study, revealing a semiconducting gap of 0.27 eV at high temperatures and a low density of carriers,¹³ and by an optical conductivity mea-

surement, indicating a 0.2 eV wide optical gap with a small Drude-like contribution for Fe_2VAl .¹⁴ The density of carriers estimated from the optical conductivity data is consistent with the results of the Hall effect measurement.¹⁵ On the basis of the predicted semimetallic band structure, the origin of the fascinating low-temperature properties of Fe_2VAl has been discussed in terms of the spin fluctuations^{1,6,7} or the excitonic correlations.⁸

The enhancement of the Seebeck coefficient in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ has been qualitatively explained also in terms of the semimetallic band structure predicted for Fe_2VAl in a rigid-band picture,³ but not in $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$.⁵ Since the Seebeck coefficient S at temperature T may be given in terms of the density of states $N(E)$ by¹⁶

$$S = - \frac{\pi^2 k_B^2 T}{3 e} \left[\frac{1}{N(E)} \frac{\partial N(E)}{\partial E} \right]_{E=E_F}, \quad (1)$$

the predicted band structure with the sharp pseudogap at E_F may bring the enhancement of the Seebeck coefficient accompanied by the change in its sign, which depends on the energy location of E_F relative to the minimum of the pseudogap. For $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$, the increase Δy in the Al content y from the stoichiometric one, i.e., $y=25.0$, may lead

to the decrease in the number of the valence electrons $\Delta n = -0.16\Delta y$, and hence the Seebeck coefficient would be enhanced with the positive sign for $\Delta y > 0$ and with the negative sign for $\Delta y < 0$ in the rigid-band model, which is indeed observed.³ However, the thermoelectric power of $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ becomes negative (positive) with the V content x increased (decreased),⁵ which is inconsistent with the rigid-band model and implies the remarkable modification of the electronic structure. In fact, several experimental and theoretical investigations^{12,17-22} have suggested that the electronic structure of Fe_2VAl may be strongly affected by the chemical deviation, in particular, in the $3d$ transition elements, and by the structural modification, such as an antisite defect, i.e., an Fe atom occupying at the nominal V site in the Heusler structure of Fe_2VAl , for instance. The evolution of the $3d$ -derived midgap states due to the antisite defects has been recently predicted by a supercell approach,^{12,17} expected to bring the unusual low-temperature properties.

It is important to study their electronic structures directly by the photoelectron spectroscopy in order to clarify the mechanism of the fascinating transport properties of Fe_2VAl and related Heusler-type alloys. In the early photoelectron measurements,^{1,23} a clear Fermi edge with large intensity was observed even at the high-excitation photon energy. Recently, however, we have successfully obtained the spectra representing the bulk electronic structure with use of the high-resolution soft x-ray photoelectron spectroscopy (HRXPS) for clean surfaces prepared by *in situ* fracturing specimens instead of scraping them,²⁴ which adequately preserves the bulk electronic structure and suppresses the surface effects. The Fe and V $L_{2,3}$ x-ray absorption spectra also reveal sharp and clear features for the *in situ* fractured specimens of Fe_2VAl in contrast to the scraped ones.²⁵

In this paper, we will report results of the HRXPS measurement for the Heusler-type alloys, stoichiometric Fe_2VAl and slightly off-stoichiometric $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$, and discuss their electronic structure and thermoelectric power.

II. EXPERIMENTAL

The Heusler-type Fe_2VAl and $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys were prepared by repeated arc-melting of appropriate mixtures of 99.99% pure Fe and Al, and 99.9% pure V in an argon atmosphere and subsequent homogenization at 1273 K for more than 48 hr in vacuum.^{1,2} Specimens were cut from the ingots with a SiC blade saw to a size of $2 \times 2 \times 5$ mm³, and annealed in an evacuated quartz capsule at 1273 K for 1 hr and at 673 K for 4 hr for the $L2_1$ ordering followed by furnace cooling. Chemical composition was determined within the accuracy of ± 0.2 at. % by inductively coupled argon plasma atomic-emission spectroscopy. Their single-phase Heusler-type $L2_1$ structure was confirmed with use of x-ray-diffraction analysis and transmission electron microscopy.¹¹

The photoelectron measurement was carried out at the high-resolution photoelectron spectroscopy station of the beamline BL25SU of an 8 GeV electron storage ring, SPring-8 at the Japan Synchrotron Radiation Research Institute.²⁶ The HRXPS spectra were measured at 20 K with

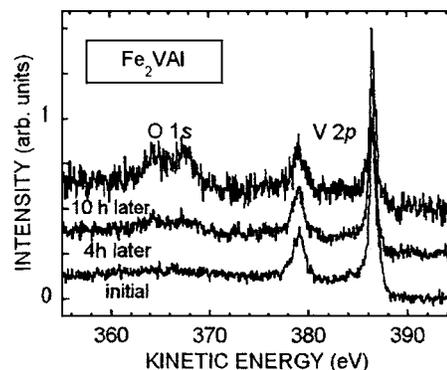


FIG. 1. V $2p$ and O $1s$ photoelectron spectra of Fe_2VAl .

a total energy resolution of 0.10 eV at $\hbar\omega = 900$ eV by use of highly monochromatic soft x ray from a twin helical undulator and a high-resolution hemispherical analyzer (SIENTA SES200). The angle between the incident-exciting photon beam and the lens axis of the electron analyzer was 45° . The angle acceptance of the analyzer were set to about $\pm 8^\circ$. The excitation photon energy was chosen because the higher output intensity was obtained with the better energy resolution and the photoionization cross sections for the s and p electrons become comparable to those for transition metals d electrons.²⁷ The origin of the binding energy, the Fermi energy E_F , was determined by measuring the Fermi edges of the Au film evaporated onto a sample holding plate or the scraped surface of a Pd metal plate attached on the sample holder. The Au $4f$ lines were also frequently measured for the rapid calibration and confirmation of the excitation energy.

Clean surfaces of the polycrystalline specimens were prepared for photoelectron measurement by *in situ* fracturing the specimens with a knife edge at 20 K under a pressure of 4×10^{-9} Pa, and they were confirmed by measuring the photoelectron spectra in a wide energy range, particularly, in a region of the O $1s$ and V $2p$ lines. As an example, some of the spectra in the range of the O $1s$ and V $2p$ lines are presented in Fig. 1 for the fractured surface of Fe_2VAl . We note no oxygen contamination just after fracturing but a little oxygen adsorption or oxidization in 4 hr after the fracture. This oxygen contamination is found to result in the spectral change in the valence band; the intensity of the d band around the Fermi level decreases relatively, whereas the bands around the binding energy $E_b = 4-5$ eV increase. However, the spectral profile near the Fermi level, below $E_b \approx 2$ eV, is not affected in a several-hour measurement. Thus we will present the spectra taken within a few hours after fracturing the specimens and discuss them hereafter.

III. RESULTS AND DISCUSSION

Typical valence-band photoelectron spectra recorded at the normal emission for the fractured surfaces of Fe_2VAl are shown in Fig. 2 in comparison to a theoretical spectrum, which is obtained by convolution of a predicted total density of states (DOS)¹¹ with the Fermi-Dirac distribution function at 20 K and a 0.1 eV wide Gaussian function. Here, we sub-

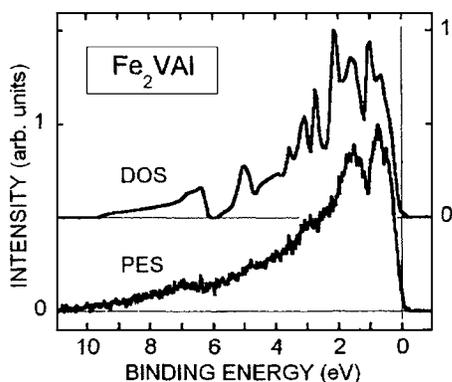


FIG. 2. Valence-band photoelectron spectrum of Fe_2VAI . The background because of the secondary electrons was subtracted from the experimental photoelectron spectrum. Theoretical density of states (DOS), convoluted with the Fermi-Dirac distribution function at 20 K and a 0.1 eV wide Gaussian function, is also shown for comparison.

tracted the background from the experimental photoelectron spectrum with an iteration method,²⁸ while we did not take account of the difference in the subshell ionization cross sections nor the lifetime broadening dependent on the binding energy of the created photohole in obtaining the theoretical spectrum. As already reported,²⁴ the overall feature of the spectrum agrees remarkably well with the predicted spectrum. In particular, the spectrum exhibits steep decrease in the intensity toward E_F , i.e., the indication of a pseudogap across E_F , as well as a 10 eV wide valence band with several fine structures corresponding to the features in the calculated spectrum. Along with the theoretical predictions,^{6–11} the main feature above the binding energy $E_b \sim 1$ eV and the third peak structure around $E_b = 3$ eV are attributed to the Fe 3d bands, the second peak at $E_b \sim 1.5$ eV to the V 3d states hybridized with the Fe 3d ones, the shoulder feature at $E_b \sim 5$ eV to the Al 3p-derived band, and a broad hump around 7 eV to the Al 3s state hybridized with the Fe and V 4s states.

These fine structures and pseudogap have not been observed in either the spectrum for the scraped surface measured at the high-excitation photon energy^{23,29} nor those recorded on the lower photon energy excitation, e.g., $\hbar\omega = 63$ eV.¹ This is probably because of the high sensitivity of the electronic structure of Fe_2VAI to the structural modification (such as the surface itself, the antisite defect, and the strain), which might be induced by scraping, and because of the high surface sensitivity of the photoelectron spectroscopy with the low photon energy excitation.³⁰ As for the surface effects, in fact, the spectra recorded at the high detection angle from the surface normal, i.e., with the shallow effective probing depth, indicate the enhancement of the spectral weight from $E_b \approx 1$ eV to E_F . However, their contribution to the normal emission spectra is estimated to be $\sim 10\%$ at most,²⁴ and will not affect the discussion below so much.

The detailed valence band spectra near E_F for $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ are presented in Figs. 3(a), the main d bands, and 3(b) the Fermi edges. Here, these spectra are normalized at the peak of the main d bands at $E_b \sim 0.7$ eV.

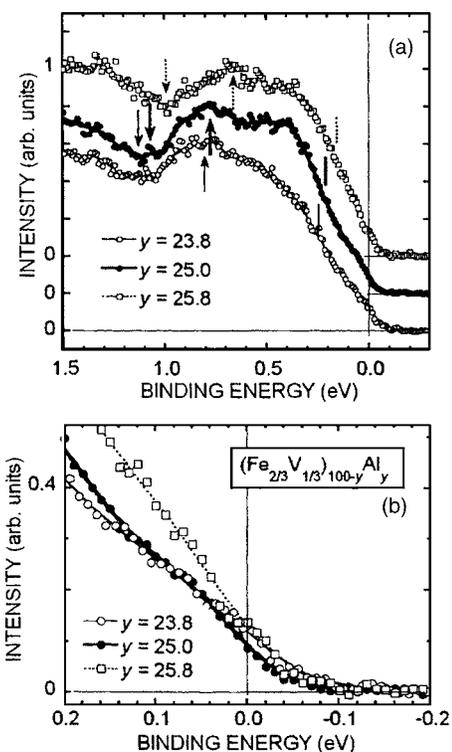


FIG. 3. Detailed valence-band photoelectron spectra of $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$. (a) the main d -bands and (b) the Fermi edges.

We have applied another reasonable normalization procedure using the integrated intensity of the whole valence band up to $E_b \sim 11$ eV, confirming the same results as obtained with the normalization procedure at the peak. In Fig. 3(a), up and down arrows indicate the energy positions of the peak and dip of the d bands, respectively, and vertical bars represent the d -band edges in the low-binding energy side, at which the intensities of the d bands become half of their peaks. These peaks, dips, and edges of the d bands show that the main d bands are shifted toward the low-binding energy side as the Al content y is increased. Furthermore, a shoulder structure at E_F (the Fermi edge) is clearly recognized for $y = 23.8$ and 25.0 but not for $y = 25.8$, and the intensity at E_F shows a minimum at $y = 25.0$, as shown in Fig. 3(b). Since the increase in the Al content y means the decrease in the number of the valence electrons, the observed shift of the main d bands and the spectral change near E_F qualitatively agree with those predicted in the rigid-band picture with the theoretical DOS for Fe_2VAI . This gives further evidence for the existence of the pseudogap. The density of states at the Fermi energy $N(E_F)$, i.e., the spectral intensity at E_F , relative to that for $y = 25.0$ and the band shift ΔE_b estimated from the d -band edges (vertical bars), are summarized in Table I.

Then we will estimate the thermoelectric power of the $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloy from the present spectroscopic data, in particular, the spectral intensity at E_F , $N(E_F)$, and the band shift ΔE_b , using Eq. (1) within the rigid-band picture. In this picture, the deviation in the Al content y would change the number of the valence electrons n and, hence, the Fermi energy position $E_F(y)$ without altering the density of states $N(E)$. Since we have only three data points as listed in Table

TABLE I. Relative density of states at the Fermi energy $N(E_F)$ and d band shift ΔE_b for $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$. ρ_y is the resistivity at 4.2 K for $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$.

| $y(\%)$ | 23.8 | 24.3 | 25.0 | 25.5 | 25.8 |
|--------------------------------|--------|------|------|------|-------|
| $N(E_F)$ | 1.27 | | 1 | | 1.41 |
| $\Delta E_b(\text{eV})$ | -0.032 | | 0 | | 0.054 |
| $\rho_y(\mu\Omega\text{cm})^a$ | | 600 | 2600 | 300 | |
| $\rho_{y=25.0}/\rho_y$ | | 4.3 | 1 | 8.7 | |

^aReference 3.

I, we have further assumed a quadratic relation for DOS versus energy $E(=-\Delta E_b)$ for Fe_2VAl as

$$N(E) = aE^2 + bE + c, \quad (2)$$

which is drawn by a broken curve with large solid diamonds in Fig. 4. In this figure we have also shown the photoelectron spectra by shifting them so that the d -band edges for $y \neq 25.0$ may coincide with that for Fe_2VAl of $y=25.0$, because the abscissa of the figure, the electron energy E , has been defined and denoted by the binding energy for Fe_2VAl . The Fermi energy positions of the spectra are represented by vertical lines. A minimum just below E_F or peak at E_F anticipated in the spectrum for $y=23.8$ in the rigid-band picture is indiscernible probably because of the insufficient instrumental energy resolution of 0.1 eV. Thus the absolute values of the Seebeck coefficients $S_y(T)$ at temperature T for $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ can be estimated as

$$S_y(T) = -\frac{\pi^2 k_B^2 T}{3e} \frac{2aE_F(y) + b}{aE_F(y)^2 + bE_F(y) + c}, \quad (3)$$

where $E_F(y) = -\Delta E_b(y)$. Estimated Seebeck coefficients at 300 K (closed circles) are shown in Fig. 5 together with those obtained by thermoelectric measurement³ (open circles) and predicted from Eq. (1) with a theoretical DOS¹¹ (open squares). They agree remarkably well with both the experimental and predicted ones in spite of this rough estimation.³¹

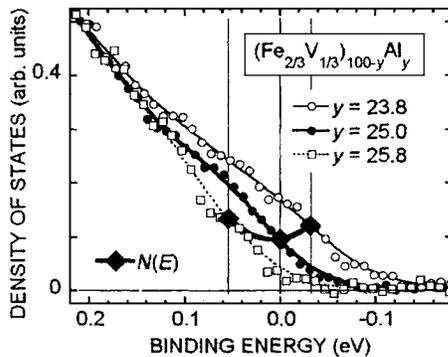


FIG. 4. Assumed density of states $N(E)$ near the Fermi level of Fe_2VAl . The $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ photoelectron spectra are also shown by shifting them so that the d -band edges for $y \neq 25.0$ may coincide with that for $y=25.0$, i.e., Fe_2VAl .

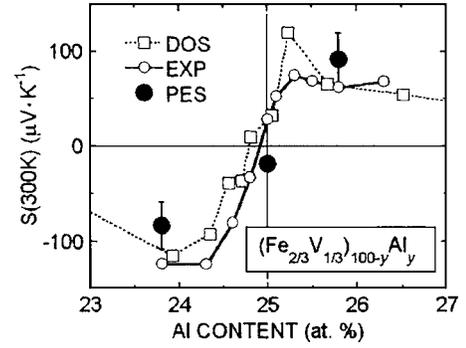


FIG. 5. Seebeck coefficients at 300 K (PES; closed circles) estimated from the present photoelectron spectra of $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$. The coefficients obtained by thermoelectric measurement (EXP; open circles) and those evaluated from a theoretical density of states (DOS; open squares) are also shown for comparison.

Observed band shift ΔE_b is, however, much smaller than expected in the rigid-band model; change in the Al content from $y=23.8$ to 25.8 would cause ~ 0.5 eV shift in the model, whereas the observed shift is 0.09–0.14 eV, the latter of which was estimated by the d -band peaks and dips in Fig. 3(a). The d -band edge for Fe_2VAl is also located at the lower-binding energy by ~ 0.1 eV than theoretically expected, as seen in Fig. 2. Furthermore, the present spectroscopic data are qualitatively compatible but quantitatively inconsistent with the dependence of the resistivity ρ at low temperatures on the Al content y ; the spectral intensity at E_F is not so much enhanced for $y \neq 25.0$ as the electric conductivity $\rho_{y=25.0}/\rho_y$ listed in Table I.

The small d -band shift and the spectral change near E_F may be ascribed to the partial destroy of the pseudogap by the substitution or depletion of Al atoms. According to a theoretical study,⁹ the pseudogap arises from the hybridization between Al and the transition metals in the BiF_3 structure. On the other hand, the antisite defects would form magnetic clusters and bring the transition-metal $3d$ -derived electronic states within the pseudogap,^{7,12,17} which may lead to the low-temperature anomalies in the thermal, magnetic, and electronic transport properties. Relatively large intensity at E_F for Fe_2VAl also suggests the existence of such midgap states for the present Fe_2VAl specimens (the nominal V content $x=0$ in $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$), since the recent study for $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ indicates the drastic reduction in both the low-temperature resistivity and the magnetization at $x=0.02$,¹⁸ implying the antisite defects included least at this V content. In $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$, although the sites of excess Al or the transition metals are not known yet, it seems that the sp states of the excess Al for $y > 25.0$ and the d states of the excess Fe and V for $y < 25.0$ act as less-effective scatterers than the d states of the Fe or V antisite defects and bring the metallic nature to the valence bands of $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$.

The rigid-band-like behavior in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ implies the small modification of their electronic structures. Indeed the theoretical investigations show that the electronic states near E_F in Fe_2VAl consist of the Fe and V $3d$ states with minor Al contribution.^{6–10,17} The present results suggest

that the substitution of the *sp*-valent elements for Al, such as $\text{Fe}_2\text{VAl}_{1-z}\text{Si}_z$, may not so much affect the electronic structure near E_F in contrast to the substitution of the transition metal elements for Fe or V, such as in $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$. The HRXPS study for $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ and $\text{Fe}_2\text{VAl}_{1-z}\text{Si}_z$ will be reported elsewhere.

IV. CONCLUSIONS

We have investigated the HRXPS valence-band spectra of the Heusler-type $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys and found the correlation between their thermoelectric properties and electronic structures near E_F . The existence of the pseudogap across E_F and its rigid-band-like behavior in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ are experimentally confirmed, and their thermoelectric powers semiquantitatively explained. The sharp pseudogap may bring the semiconductorlike resistivity behavior at high temperatures as well. The small modification of the electronic structure in the off-stoichiometric

$(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys may arise from the lower contribution of Al to the electronic states near E_F in contrast to the off-stoichiometric alloys, such as $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$. It is also found that the spectral intensity at E_F is relatively large in Fe_2VAl , suggesting the appearance of the midgap (pseudogap) states because of the imperfection in a real Fe_2VAl alloy.

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additional feature around $E_b=9.5$ eV and no fine structures due to its low energy resolution and surface preparation of the Ar sputtering.

³⁰A. Zangwill, in *Physics at Surfaces* (Cambridge University Press, New York, 1988), p. 21.

³¹Several points to be considered beyond the present analysis can be found in T. Takeuchi, T. Kondo, T. Takami, H. Takahashi, H. Ikuta, U. Mizutani, K. Soda, R. Funahashi, M. Shikano, M. Mikami, S. Tsuda, T. Yokoya, S. Shin, and T. Muro, *Phys. Rev. B* **69**, 125410 (2004).