Soft x-ray photoemission study of the Heusler-type $Fe_2VAl_{1-z}Ge_z$ alloys

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Abstracts

The valence-band electronic structures of the Heusler-type alloys $Fe_2VAl_{1-z}Ge_z$ (z = 0 - 0.10) have been investigated with high-resolution soft x-ray photoemission spectroscopy. The overall photoelectron spectral feature of $Fe_2VAl_{1-z}Ge_z$ with the Ge content z up to 0.10 is not so much changed, except for the main $3d$ band in the region from the Fermi level E_F to the binding energy $E_B \cong 1$ eV. For z = 0.05, the leading edge of the main band is shifted by ~ 0.07 eV, but the shift is much smaller than expected within a rigid band model for a calculated band structure. For z = 0.10, a band at $E_B \cong 0.5$ eV becomes prominent and the intensity of the Fermi edge is increased. The change in the valence band spectrum near E_F suggests the rigid-band-like shift of the $3d$ bands and the appearance of new $3d$ states in the pseudogap, which may qualitatively explain the z-dependence of the thermoelectric properties. As z increases, the V $2p$ spectra show a shift towards the high binding energy and the evolution of a shoulder structure on the low binding energy side of the main line. The shoulder structure is attributed to the charge transfer to the V site induced by the Ge substitution as well as the surface effect. The change in the valence-band electronic structure is discussed in terms of the interaction between the substituted Ge and its surrounding constituent atoms.

Key words: soft x-ray photoemission spectroscopy, valence band electronic structure, V $2p$ core level, $Fe_2VAl_{1-z}Ge_z$, Heusler-type alloys, thermoelectric properties

1. Introduction

The Heusler-type ($L2_1$-type) intermetallic compound Fe_2VAl and related alloys have been

received much attention because of their potential application for thermoelectric materials [1].

Theoretical and experimental studies [2,3] show that Fe_2VAl has a semi-metallic electronic

structure with a sharp pseudogap across the Fermi energy E_F.　According to Mott and Jones

[4], the thermoelectric power S at temperature T may be given in terms of the density of states

(DOS) $N(E)$ and its energy derivative as follows:

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

Thus large thermoelectric power will be obtained if the valence electron concentration, and

hence the Fermi energy, can be changed by substitution of a fourth element without altering

the electronic structure.　In fact, $Fe_2VAl_{1-z}Si_z$ exhibits considerable enhancement of its

thermoelectric power for $z = 0.05$: its power factor becomes comparable to that of the

conventional thermoelectric Bi-Te semiconductors [5,6].　However, the enhancement takes

place at the substitution $z = 0.05$ lower than expected in a rigid band model with use of the

theoretical electronic structure, $z \cong 0.2$.　In order to develop new thermoelectric materials

related to the Heusler-type alloy, it is important to clarify the detailed change in the electronic

structure on the substitution.

　In this study, we have investigated the electronic structures of $Fe_2VAl_{1-z}Ge_z$ by means of

high-resolution soft X-ray photoemission spectroscopy.　As in $Fe_2VAl_{1-z}Si_z$, the

thermoelectric power is enhanced by the substitution in $Fe_2VAl_{1-z}Ge_z$: its thermoelectric power shows a maximum of 132 $\mu V\ K^{-1}$ at $z = 0.05$ and slightly decreases at $z = 0.10$. The thermoelectric properties will be reported in detail elsewhere [7].

2. Experimental

The photoemission measurement using highly monochromatic circularly polarized soft x-ray photons as an excitation source was carried out at the BL25SU beamline of the 8 GeV electron storage ring, SPring-8, at the Japan Synchrotron Radiation Research Institute [8]. The spectra were recorded at 20 K with a total energy resolution of 0.132 eV at the excitation photon energy $h\nu$ of 900 eV by a hemispherical analyzer (SCIENTA SES200) in the angle integration mode. The origin of the binding energy E_B, i.e., the Fermi energy E_F, was determined by measuring the Fermi edge of a Au film evaporated onto a sample holder.

Specimens used in this study were polycrystals of the Heusler-type $Fe_2VAl_{1-z}Ge_z$, whose preparation procedure is described in detail elsewhere [1,3,6,7]. Chemical composition was determined within an accuracy of ±0.2 atomic % by inductively coupled argon plasma atomic emission spectroscopy. Clean surfaces of the specimens for the photoemission measurement were prepared by in situ fracturing them with a knife edge at 20 K under a pressure lower than 1 x 10^{-8} Pa, and were confirmed by measuring the photoelectron spectra in a wide energy range, particularly in a range of the O $1s$ and V $2p$ lines. These spectra indicate no carbon

and oxygen contamination just after the surface preparation and a very small evolution of the O $1s$ line in 4 hours, but no change in the spectra shape of the valence band during the photoemission measurement.

3. Results and discussion

Figures 1 and 2 show typical valence-band photoelectron spectra and their details near E_F of $Fe_2VAl_{1-z}Ge_z$ recorded at $h\nu = 900$ eV, respectively.   In the figures, we also show a DOS calculated by an all-electron full-potential linearized augmented plane wave (FLAPW) method with the WIEN2k code [9] using the experimental lattice constant $a = 0.5761$ nm [1]. The calculated DOS is consistent with so far reported results [2].   Here, the DOS is convoluted by a Fermi-Dirac distribution function at 20 K and a Gaussian function representing the experimental energy resolution of 0.132 eV in order to compare it with the experimental spectra.   The experimental spectra are normalized with respect to their integrated intensity of the whole valence band up to $E_B = 11$ eV.   As already reported [3], the overall feature of the spectrum for Fe_2VAl agrees well with the predicted DOS.   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 structure corresponding to the DOS features : the main peak at $E_B = 0.8$ eV and the third one around $E_B = 3$ eV are attributed to the Fe $3d$ bands, the second peak at $E_B = 1.5$ eV to the V $3d$ states

hybridized with the Fe 3d ones, a shoulder at E_B = 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.

As the Ge substitution is increased from z = 0 to 0.05, the overall spectrum does not change so much except for the features in the region from E_F to $E_B \cong$ 1 eV. As clearly seen in Fig. 2, the leading edge of the main d-band shifts towards high binding energy, and the shoulder structure related to the pseudogap and the Fermi edge becomes clearer, although the shift of the first peak is relatively small. These spectral changes may indicate the rigid-band-like band shift due to the increase in the metallic free electrons by the Ge substitution. The band shift ΔE_B is estimated from the leading edge and the first and second 3d band peaks to be 0.07, 0.05 and 0.08 eV, respectively, but these values are much smaller than those expected from the rigid band model: the increase in the valence electron concentration would cause ΔE_B = 0.25 eV for the calculated DOS. As the substitution is further increased to z = 0.10, the structure around E_B = 0.5 eV is enhanced and the intensity at E_F is increased. The Ge substitution at z = 0.10 affects the electronic structure so that new states appear in the pseudogap.

The spectral change near E_F qualitatively explain the z-dependence of the thermoelectric power with the help of Eq.(1), as follows. In Fe$_2$VAl, the Fermi level may be located near the bottom of the pseudogap, where the energy derivative of DOS is nearly zero and hence the thermoelectric power is small. The positive sign of the thermoelectric power implies the

negative energy derivative of DOS at E_F near the bottom of the pseudogap, which is consistent with the calculated DOS. As the Ge substitution is increased to $z = 0.05$, the Fermi energy is shifted towards the low binding energy side of the sharp pseudogap and then the energy derivative of DOS at E_F will become positive and steeply increased in comparison to the DOS at E_F. Accordingly, the thermoelectric power is expected to turn negative and increase at $z = 0.05$. For $z = 0.10$, new states emerge in the pseudogap and the DOS at E_F is increased, which may decrease the thermoelectric power.

The photoemission intensity at E_F slightly increases at $z = 0.05$, in comparison to Fe$_2$VAl ($z = 0$), and further increases at $z = 0.10$, being about twice more than that of Fe$_2$VAl. This increase may also partly explain the z-dependence of the electric conductivity at 300 K, which monotonically increases with the Ge substitution z: 0.13, 0.24, and 0.40 $\mu\Omega^{-1}m^{-1}$ at $z = 0$, 0.05, and 0.10, respectively [7]. However, the present experimental DOS at E_F is not so much reduced at $z = 0$ as the electric conductivity decreases. The low conductivity at $z = 0$ could be ascribed to the contribution of the spin fluctuation expected at low temperatures in Fe$_2$VAl [1-3], although there might be surface states within the pseudogap [10].

The change in the valence band electronic states can be seen also in the core level spectrum. Figure 3 shows the V $2p_{3/2}$ core level spectra of Fe$_2$VAl$_{1-z}$Ge$_z$. These spectra are normalized with respect to their integrated intensity. A shoulder structure is seen in the low binding energy side of the $2p_{3/2}$ main peak, and its fraction increases with the Ge substitution.

Although the shoulder structure for Fe_2VAl is attributed to the surface component [10], the increase of its fraction suggests that there is a third component associated with the Ge substitution. In order to estimate the fraction and chemical shift of the components, we have decomposed the experimental core level spectra into two V $2p$ components and a background by a least square fitting procedure, regarding one of the components (#1) as the bulk V not affected by Ge and the other (#2) as the sum of the surface V and the bulk V affected by Ge. Here, we have represented the components by Voigt functions, whose Gaussian widths are fixed to the experimental energy resolution of 0.132 eV and whose Lorentzian widths, intensities and peak binding energies are treated as the fitting parameters, and have estimated the background by integrating the primary electrons [11]. For $z = 0$, the Lorentzian width of the surface component was assumed to be the same as the bulk one, and the energy separation between the peaks of two components for $z = 0.05$ and 0.10 was also fixed to that at $z = 0$ for convenience of the calculation, which will not affect the present discussion. The obtained parameters are listed in Table 1.

As the Ge substitution is increased from $z = 0$ to 0.05, the V $2p$ core levels are shifted as a whole by 0.073 eV towards high binding energy, which is consistent with the rigid-band-like behavior of the valence band. The Lorentzian width of the shoulder structure becomes wider and its fraction is increased. This is attributed to the third component associated with Ge as well as the surface component, as mentioned above. The shoulder structure is further

increased with z increasing to 0.10, while the bulk V $2p$ levels show further small shift of 0.014 eV. This is also compatible with the change in the valence band structure, which shows the appearance of new states and almost no shift of the valence band. These spectral findings suggest the existence of at least two different bulk V sites, at one of which the valence electrons are increased and hence the change in the (local) electronic structure may be induced by the Ge substitution.

A local coordination cluster around the substituted Ge may be a bcc-like $GeFe_8V_6$ one, because the $L2_1$ cubic Heusler lattice is composed of four interpenetrating fcc sublattices, two of which are occupied by Fe, one by V, and the other by Al, and its unit cell can be regarded as consisting of eight bcc unit cells without distinguishing those elements. Around the V site, in turn, one type of cluster, VFe_8Al_5Ge, is expected for the substitution of Ge for Al up to $z = 0.03125$ ($= 1/32$), and a cluster of $VFe_8Al_4Ge_2$ for $z = 0.25$ ($= 1/4$). Thus, between $z = 0.03$ and 0.25, a crossover will take place from the rigid-band-like behavior induced by Ge, substituted as an impurity, to the rearrangement of the electronic structure with new electronic states derived from Ge incorporated into the crystal structure. The fraction of the (next) nearest neighbor V atoms around Ge may be $6/32 \cong 0.2$ at $z = 0.03125$, which seems larger than expected from the experimental fraction of the V $2p$ shoulder component (~ 0.1). This might be caused by the anisotropic V-Ge interaction or the anisotropic local deformation of the lattice around Ge.

According to the band calculation for Fe$_2$VAl [12], the $3d$ band around $E_B = 1.5$ eV consists of the V $3d$ t_{2g} states bonding with the Fe $3d$ states, while the anti-bonding V $3d$ t_{2g} states and the V $3d$ e_g states are located at ~ 1 eV above E_F, forming the conduction d band with the Fe $3d$ e_g and t_{2g} states.   The $3d$ bands in the region from E_B ~ 1 eV to E_F are mainly composed of the Fe $3d$ t_{2g} states.   The lowest conduction band comprises only the V e_g states at the X point, while the highest valence band at the Γ point is composed of the Fe $3d$ t_{2g} and V $3d$ e_g states.   Since it is expected that the V $3d$ t_{2g} states are not hybridized with the Al and Ge sp states, the V t_{2g} band may be simply shifted by the increase in the number of conduction electrons by the Ge substitution, while new states derived from the V $3d$ e_g states and the Fe t_{2g} and e_g ones may appear due to the interactions between Ge and the surrounding Fe and V.

4. Conclusion

We have investigated the electronic structure of the Heusler-type Fe$_2$VAl$_{1-z}$Ge$_z$ alloys by soft x-ray photoemission spectroscopy, in particular, for the valence band and V $2p$ core level regions; we have found a correlation between their thermoelectric properties and electronic structures near the E_F.   We have also observed the interaction between Ge and its surrounding elements, which may increase the valence electrons at the V site and might cause the appearance of new $3d$ states within the pseudogap.   We intend further experimental study of the effect on the electronic structure of the substitution with various promising elements,

and theoretical investigation of the electronic structure by a super cell method in order to understand the detailed changes in the electronic structure and thermoelectric properties.

Acknowledgements

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Figure Captions

Fig.1 Valence band spectra of $Fe_2VAl_{1-z}Ge_z$ recorded at $h\nu = 900$ eV.   A theoretical density of

states (DOS) is also shown for comparison.

Fig. 2 Valence band spectra near the Fermi level of $Fe_2VAl_{1-z}Ge_z$ recorded at $h\nu = 900$ eV.   A

theoretical density of states (DOS) is also shown for comparison.

Fig. 3 V $2p_{3/2}$ core level spectra of $Fe_2VAl_{1-z}Ge_z$ recorded at $h\nu = 900$ eV.   Curves show the

decomposition of the spectra into two components and a background.

Table 1. Parameters for the decomposed main bulk band (#1) and the shoulder one (#2) of the

V $2p_{3/2}$ core level spectrum

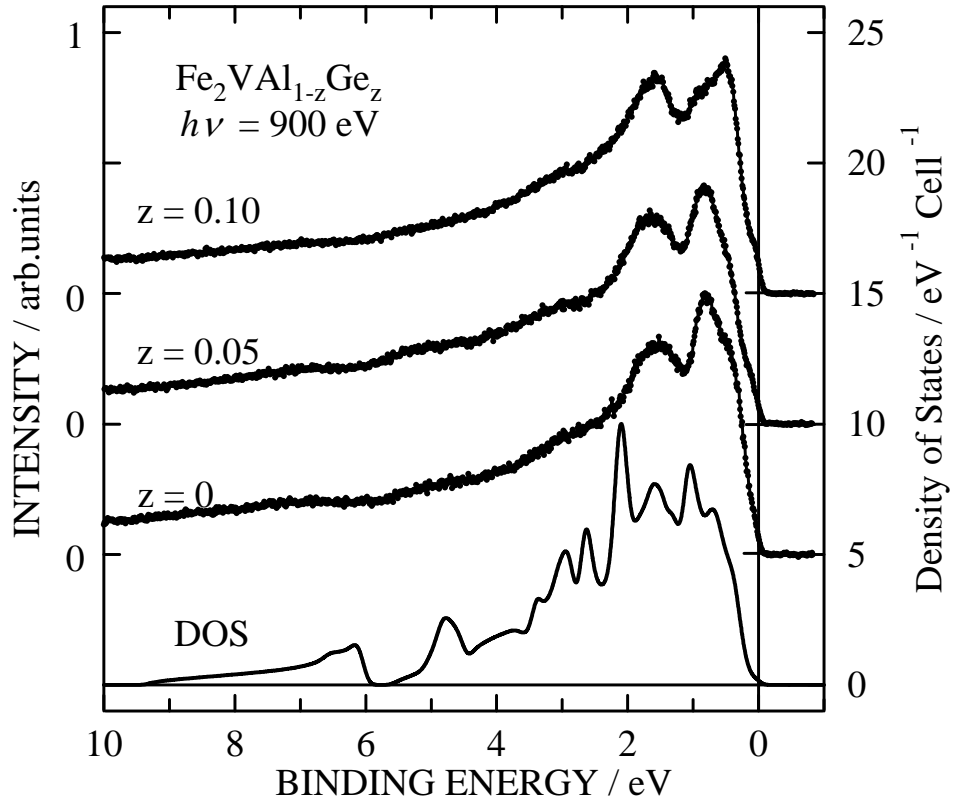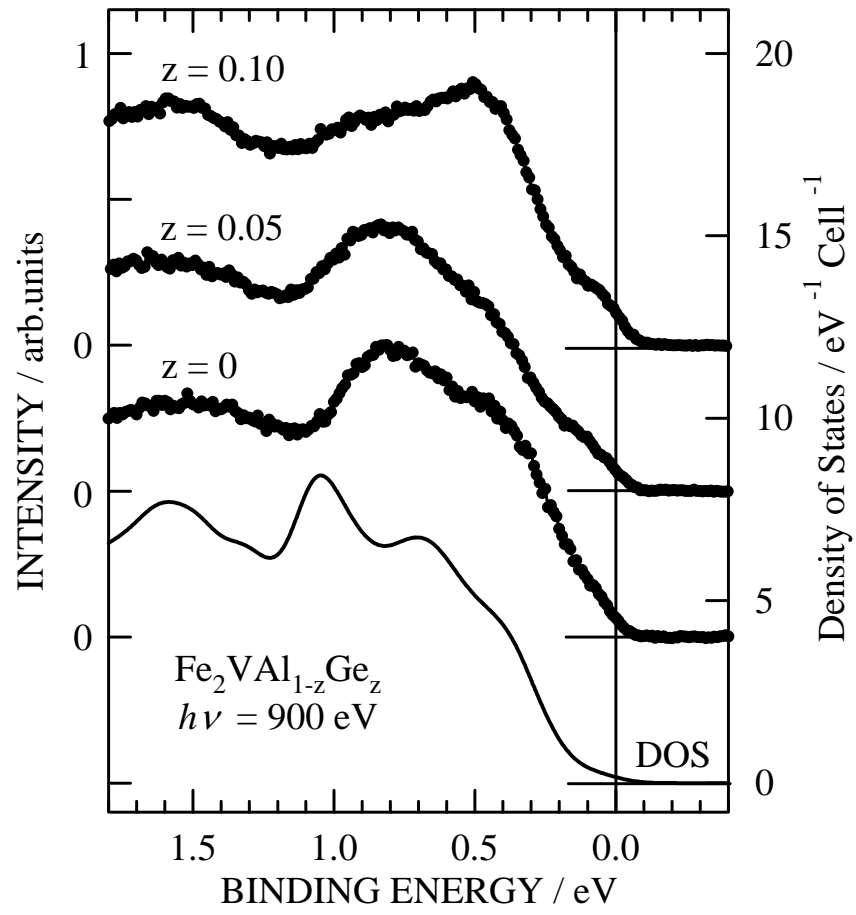|	Ge content z	0	0.05	0.10
	Peak Position / eV	513.180	513.253	513.267
#1	Band Width / eV	0.276	0.276	0.276
	Intensity Fraction	0.850	0.782	0.642
	Peak Position / eV	512.518	512.591	512.605
#2	Band Width / eV	0.276	0.307	0.374
	Intensity Fraction	0.150	0.218	0.358

Fig.1 Miyazaki et al.

Fe$_2$VAl$_{1-z}$Ge$_z$
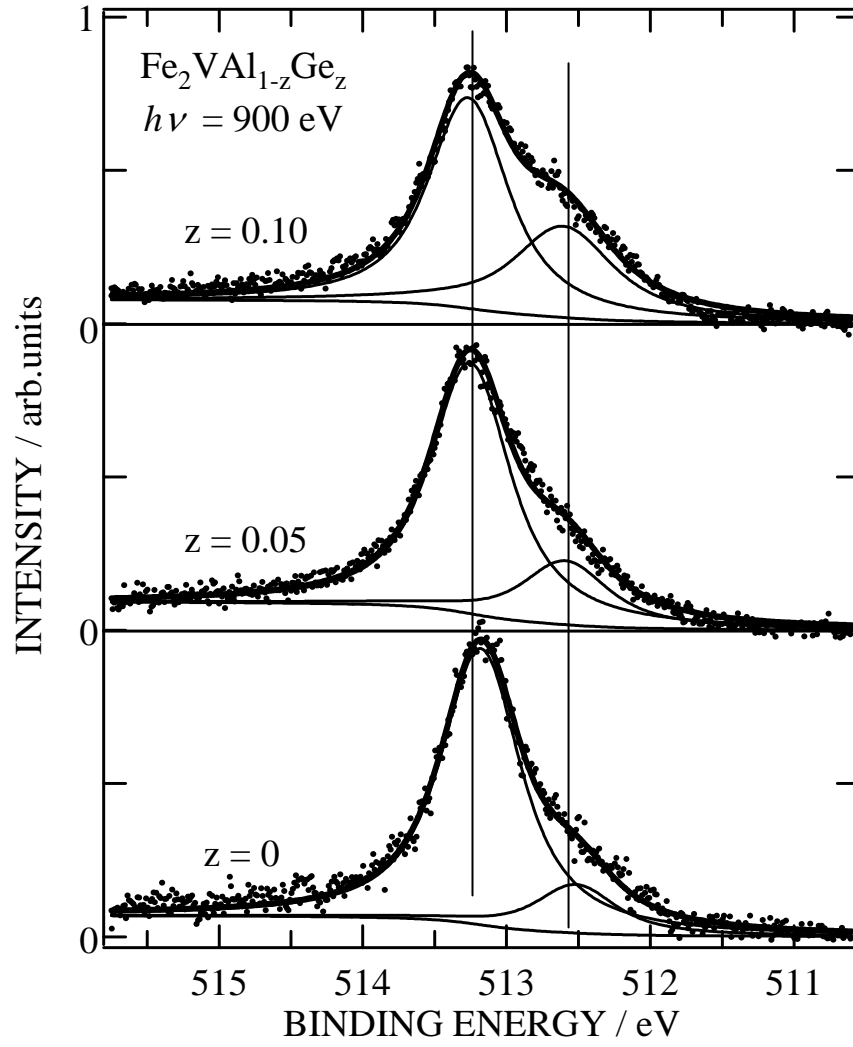$h\nu = 900$ eV

Fig.2 Miyazaki et al.

INTENSITY / arb.units

$Fe_2VAl_{1-z}Ge_z$
$h\nu = 900$ eV

z = 0.10

z = 0.05

z = 0

1

0

0

0

515   514   513   512   511

BINDING ENERGY / eV

Fig. 3 Miyazaki et al.