Origin of large thermoelectric power in off-stoichiometric Fe$_2$VAl-based alloys

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Abstract. The valence-band and core-level soft x-ray photoelectron spectroscopy has been applied to investigate the origin of the large thermoelectric power in the off-stoichiometric and partially-substituted Fe-based Heusler-type alloys Fe$_{2-x-y}$Ir$_y$V$_{1+x}$Al and Fe$_{2-x}$V$_{1+x-y}$Ti$_y$Al. The non-rigid-band-like change in the valence-band electronic structure near the Fermi level E_F is found for the off-stoichiometric change x in Fe and V concentrations, whereas the rigid-band-like shift of E_F is recognized on the Ir or Ti substitution y. The non-rigid-band-like change may be induced by the excess-V or Fe (anti-site defects)-derived states in the pseudogap of Fe$_2$VAl, while the rigid-band-like shift may be caused by a common band formation, where the d states of the substituted elements are incorporated into the main Fe-V $3d$ bands. The V2p core-level spectra consistently show the satellite structure due to the excess V as the anti-site defect. A model electronic structure is presented for explaining the observed enhancement of their thermoelectric power.

1. Introduction

Recently it has been found that the thermoelectric power is remarkably enhanced by partial substitution of Ir for Fe (or of Ti for V) together with off-stoichiometric change of Fe/V concentration ratio; the thermoelectric power becomes -0.17 mVK^{-1} in the n-type Ir-substituted off-stoichiometric alloys Fe$_{2-x-y}$Ir$_y$V$_{1+x}$Al [1] and to +0.11 mVK^{-1} in the p-type Ti-substituted ones Fe$_{2-x}$V$_{1+x-y}$Ti$_y$Al [2], respectively. Theoretical and experimental studies [3, 4] show that an intermetallic compound Fe$_2$VAl possesses a sharp pseudogap across the Fermi energy E_F, which may lead to the enhancement of the thermoelectric power by changing E_F position on partial substitution of the forth element with more or less valence electrons than the original constituent elements without altering the valence-band electronic structure (so-called rigid band model) [5], because the thermoelectric power $S(T)$ at temperature T may depend on the electronic density of states $N(E)$ as follows [6];

$$S(T) \cong \frac{1}{eT} \frac{\int N(E)(E - E_F)\frac{\partial f(E;T)}{\partial E} dE}{\int N(E)\frac{\partial f(E;T)}{\partial E} dE}. \tag{1}$$

Here, $f(E;T)$ stands for the Fermi-Dirac distribution function at T. Indeed thermoelectric powers of the substituted alloys are on a universal curve when they are plotted as a function of averaged valence

electron counts per constituent atom (VEC) [5], which can be semi-quantitatively explained by equation (1) [4,6]. However, the off-stoichiometric Fe/V change results in quite different dependence of the thermoelectric power on VEC in a non-rigid-band-like manner and its further enhancement [1,2].

In this study, we will present model electronic structures to clarify the origin of the remarkable enhancement of thermoelectric power in the partially substituted alloys with the off-stoichiometric Fe/V ratio, based on recent valence-band and core-level photoelectron measurements, which have been partly reported elsewhere [2,7]. According to equation (1), thermoelectric power is determined by $N(E)$ around E_F within the energy range of $\sim 4k_BT$, where k_B is the Boltzmann constant, and its sign becomes positive (p-type) and negative (n-type) for large and small contributions, respectively, of the density of valence-band states $N(E<E_F)$ compared to the conduction-band one $N(E>E_F)$.

2. Experimental

Photoelectron measurements were carried out at BL27SU of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI). Linearly polarized and monochromatized soft x-rays from an undulator were used as an excitation photon source and photoelectrons from samples cooled down to ~ 10 K were analyzed in the angle-integrated mode with a hemispherical analyzer [8]. Total energy resolution was estimated as 0.16 eV at the excitation photon energy of ~ 1000 eV. Samples were polycrystalline of $Fe_{2-x-y}Ir_yV_{1+x}Al$ and $Fe_{2-x}V_{1+x-y}Ti_yAl$ and their clean surfaces for the photoelectron measurement were prepared by in situ fracturing. Details of the measurement and sample preparation are described elsewhere [1,2,7].

3. Results and discussion

Figure 1 compares typical valence-band spectra of some of studied alloys. The stoichiometric alloy Fe_2VAl with small but positive thermoelectric power shows a small shoulder structure at E_F in the photoelectron spectrum, indicating the pseudogap predicted for the alloy as having a semimetallic band structure [6]. A small shoulder structure around E_F, indicative of the pseudogap, is also recognized for the n-type thermoelectric alloys with the excess V ($x > 0$). This shoulder structure for the n-type alloys suggests that the conduction-band density of states may be increased just above E_F, although unoccupied electronic states cannot be directly proved by photoelectron spectroscopy. On the other hand, a monotonic steep increase of the main d band is clearly seen from E_F to $E_B \sim 0.3$ eV for the p-type alloys with the excess Fe ($x < 0$), showing the valence-band edge which may lead to the
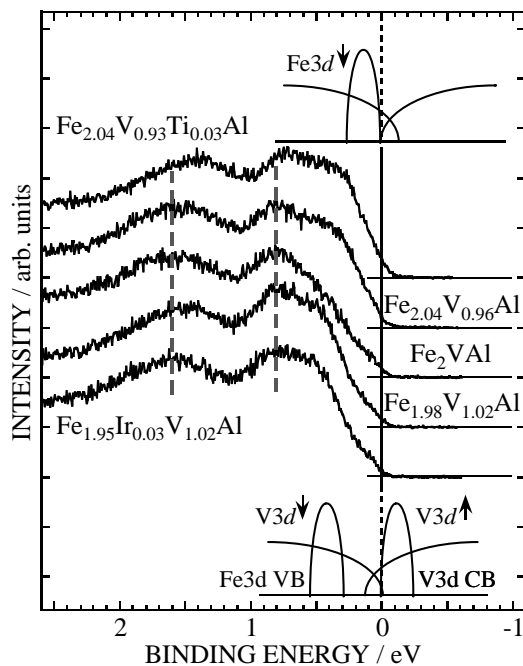

Figure 1. Valence-band electronic structures of Fe_2VAl-based off-stoichiometric alloys. Model electronic structures are shown in the bottom and top for anti-site V and Fe defects, respectively, where majority (down) spin $3d$ states of V and Fe appear below the Fermi energy E_F (thin vertical lines) in a semimetallic pseudogap with Fe$3d$ valence band (Fe$3d$ VB) and V$3d$ conduction band (V$3d$ CB), and unoccupied minority (up) spin V$3d$ states are located just above E_F. Thick broken lines are drawn as a guide for eyes.

positive thermoelectric power. Thus the spectral findings confirm the relation between the thermoelectric power and the density of states.

In $Fe_{2-x}V_{1+x}Al$, the off-stoichiometric change in the Fe/V ratio causes no rigid-band-like shift of the valence-band structures. Instead, a band at the binding energy E_B of about 0.5 eV is enhanced for the excess V concentration $x > 0$, and a new band appears at $E_B \sim 0.3$ eV for the excess Fe concentration $x < 0$. These new bands can be attributed to the anti-site V and Fe defects, which may be formed around the excess V and Fe occupying at the Fe and V sites, respectively, in the Heusler($L2_1$)-type Fe_2VAl lattice structure. According to Bansil *et al.* [9], $3d$ states of the transition-metal elements in the octahedral site (the V site in Fe_2VAl) form a pair of bonding and anti-bonding bands for each spin sub-bands, while those in the tetrahedral site (the Fe site in Fe_2VAl) show a triple-band structure consisting of bonding and anti-bonding bands and an extra band between them. For the anti-site Fe defect, its body-centered-cubic-like local cluster brings such anti-bonding majority (down) spin Fe$3d$ states below E_F [9], as shown in the top of figure 1. This may correspond to the 0.3-eV band observed for the Fe-rich ($x < 0$) alloys. On the other hand, spin-projected densities of states calculated for V_2FeAl [10] suggests that the anti-site V in the tetrahedral site may induce a majority (down) spin V$3d$ band below E_F and a minority (up) spin V$3d$ band above E_F in the pseudogap, as drawn in the bottom of figure 1. This is supported by a band structure calculation with a supercell method for $Fe_{2-x}V_{1+x}Al$ [11]. The 0.5-eV band for the V-rich ($x > 0$) alloys may be attributed to such a majority spin V$3d$ state.

In other point of view, the excess Fe and V might induce so-called impurity states in the pseudogap, which is brought about by small overlap between a mainly Fe$3d$-derived valence-band top and almost purely V$3d$-derived conduction-band bottom [3,12]. Since Fe(II) is more electronegative than Fe(I) in $D0_3$-ordered Fe_3Al [9,13], which can be regarded as $L2_1$-type Fe(II)$_2$Fe(I)Al, the anti-site Fe, similar to Fe(I), may have less valence electrons than Fe at the Fe(II) site and the anti-site V may increase its valence electrons. Indeed, the V$2p$ core-level spectra show new chemically shifted components in the low binding energy side of the main line for the excess V concentration $x > 0$ [7], implying the increase in the local valence electrons of the anti-site V. Although satellite structures were not observed for the Fe and Al $2p$ core-levels at present, the anti-site Fe and V might result in Fe and V $3d$ states split off from the valence and conduction bands, respectively. Thus 0.3-eV band appearing in the Fe-rich alloys might be ascribed to such split-off Fe $3d$ states. For the V-rich alloys, the anti-site V forms a V cluster with neighboring V tetrahedrally coordinated and hence the bonding and anti-bonding states between them might appear below and above E_F, respectively. This might cause the 0.5 eV band in the V-rich alloys.

Further Ir and Ti substitutions lead to rigid-band-like shifts of the first and second peaks observed respectively at $E_B \sim 0.8$ and 1.6 eV, where thick broken lines are drawn as a guide for eyes in figure 1; the peaks are shifted towards the low and high binding energy sides for Ti and Ir substitutions, respectively. This rigid-band-like behavior can be explained in terms of a common band formation [9,14] between the Fe-V $3d$ bands and the substituted Ir $5d$ or Ti $3d$ states. The d states of Ir and V occupying at the Fe and V sites may be moderately incorporated into the main Fe-V $3d$ bands. Close inspection of the intensity at E_F indicates its increase and decrease on the Ti and Ir substitutions, respectively. Taking account of the experimental energy resolution of 0.16 eV and sample temperature of ~10 K, these changes in the intensity at E_F suggest further increasing difference between the densities of states below and above E_F, $N(E < E_F)$ and $N(E > E_F)$, on substitution, which implies further enhancement of their thermoelectric powers in $Fe_{2-x-y}Ir_yV_{1+x}Al$ and $Fe_{2-x}V_{1+x-y}Ti_yAl$.

Thus the present results show that the thermoelectric power in those alloys is enhanced by the non-rigid-band-like drastic change caused by the anti-site defects and the rigid-band-like moderate shift by the common band formation between the Fe-V $3d$ bands and the substituted Ir $5d$ or Ti $3d$ states under the presence of the pseudogap.

4. Conclusion

We have investigated the origin of the large thermoelectric power in the off-stoichiometric and partially-substituted Fe-based Heusler-type alloys $Fe_{2-x-y}Ir_yV_{1+x}Al$ and $Fe_{2-x}V_{1+x-y}Ti_yAl$ by soft x-ray

photoelectron spectroscopy. We have found the non-rigid-band-like change in the valence-band electronic structure near E_F for the off-stoichiometric change x in Fe and V concentrations, the rigid-band-like shift of E_F on the Ir or Ti substitution y, and the satellite structure due to the anti-site V in the V$2p$ core-level spectra. The non-rigid-band-like change may be induced by the anti-site defects-derived states in the pseudogap of Fe$_2$VAl, while the rigid-band-like shift is caused by a common band formation, where the d states of the substituted elements are incorporated into the main Fe-V $3d$ bands. We have proposed model electronic structures to explain the observed enhancement of the thermoelectric power, based on our experimental results and so far reported theoretical studies; the positive enhancement of thermoelectric power in the Fe-rich alloys is attributed to the increase in the density of anti-site Fe-derived majority spin states below E_F and the negative enhancement in the V-rich alloys to the increase in the density of unoccupied anti-site V-derived minority spin states above E_F. Assumed unoccupied states will be clarified by other methods such as inverse photoelectron spectroscopy.

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