

Thermoelectric properties of the Heusler-type off-stoichiometric $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys

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Abstract. We report the thermoelectric properties of Heusler-type off-stoichiometric $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys. Due to the off-stoichiometric effect, which is the substitution of V/Al atoms with Al/V atoms, semiconductor-like electric resistivity behavior in Fe_2VAl is changed to metallic behavior in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys and both positive and negative absolute Seebeck coefficients are drastically increased. The maximum thermoelectric power factor of $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys was 4.3×10^{-3} ($x = -0.03$: p-type) and 6.8×10^{-3} W/mK^2 ($x = 0.05$: n-type) with a peak temperature in the range of 300 - 600 K, exceeding the values of previously reported Fe-based Heusler alloys as well as those of available thermoelectric materials such as Bi-Te semiconductors. Based on X-ray diffraction and photoemission spectroscopy results, it is thought that the maintenance of the Heusler-type ($L2_1$) crystal structure and the modification of the electronic structure due to the off-stoichiometry could explain the large thermoelectric power factor and high peak temperature in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys.

1. Introduction

The Heusler-type intermetallic compound Fe_2VAl has attracted strong attention because of the semiconductor-like temperature dependence of its electrical resistivity over a wide temperature range up to 1200 K and beyond [1]. Band structure calculations have predicted that a pseudo-gap is formed around the Fermi level (E_F) [2-7]. In fact, the existence of such a pseudo-gap has been experimentally demonstrated by both infrared spectroscopy [8,9] and photoemission spectroscopy [10,11]. The origin of the anomalous physical properties of Fe_2VAl is connected to the existence of the pseudo-gap. Because of the possession of a sharp pseudo-gap across the E_F , Fe_2VAl -based alloys have attracted a great deal of interest as potential candidates for next-generation thermoelectric materials. In metallic systems, the Seebeck coefficient S at temperature T is often discussed using the following formula [12]:

$$S(T) = \frac{\pi^2 k_B^2}{3 - e} T \left(\frac{\partial \ln \sigma(E)}{\partial E} \right)_{E=E_F},$$

where $\sigma(E)$ and $N(E)$ denote the electrical conductivity and the density of states (DOS), respectively. Since $\sigma(E)$ is proportional to $N(E)$, the above formula is given as

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

It is argued that the large value and sign of S are brought about by a low $N(E)$ coupled with a steep slope, $\partial N(E)/\partial E$, at the E_F . Since the DOS rises sharply on both sides of the pseudo-gap, we expect the absolute value of S to be well enhanced and its sign to be controlled by carrier doping, such as off-stoichiometry [13] or doping element [14]. In fact, the hole- and electron-doping case, such as in $\text{Fe}_2\text{V}_{1-y}\text{Ti}_y\text{Al}$ [15] and $\text{Fe}_2\text{VAl}_{1-y}\text{Si}_y$ alloys [16], exhibits large S from 70 $\mu\text{V/K}$ for the p-type to -130 $\mu\text{V/K}$ for the n-type. These results are consistent with the behavior of S evaluated from a band structure calculation with a rigid band model, where the E_F is shifted to the lower or higher binding energy side without a change in the electronic structure due to hole- or electron-doping, respectively [17]. In particular, the thermoelectric power factor, $P = \sigma S^2$, of $\text{Fe}_2\text{VAl}_{1-y}\text{Si}_y$ reaches as much as $5.4 \times 10^{-3} \text{ W/mK}^2$ at 320 K [16], a value comparable to that of conventional thermoelectric Bi-Te semiconductors [18].

The peak temperature of the n-type thermoelectric power factor of previous Fe-based Heusler alloys is around 300 - 400 K [16, 19-24]. For the application of thermoelectric materials to power generation, it is desirable that the peak temperature of both the n- and p-type be increased to 400-600 K. From an analysis of the theoretical electronic structure by the Boltzmann transport theory in Fe_2VAl , it has been reported that an increase in the electron and hole concentration contributes to the optimization of S and leads to a shift of the peak temperature of the thermoelectric power factor to the higher temperature side [17]. However, a too large quantity of doping elements lead to the formation of an impurity phase and deteriorate the thermoelectric power factor as well as decrease in its peak temperature. To improve the thermoelectric power factor and its peak temperature, it is important to explore possible substitution elements to maintain the Heusler-type ($L2_1$) crystal structure and dope a large number of holes and electrons.

Theoretical calculations have shown that the Fe sub-lattice plays an important role in determining the physical and crystalline properties of Fe_2VAl [2,6]. Therefore, the substitution of V or Al atoms with Al or V, respectively, without affecting the Fe sub-lattice, is expected to effectively bring a large number of doping carriers without modifying the Heusler-type crystal structure in any essential manner. Based on this concept, we fabricated off-stoichiometric Heusler-type $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys, in which some of the Al or V atoms surrounded by the Fe sub-lattice were substituted by V or Al atoms, respectively. However, as in the case of off-stoichiometric $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ alloys [25,26], it is difficult to predict the change of the thermoelectric properties due to the off-stoichiometric effect. The purpose of the present study is to investigate the thermoelectric properties of the off-stoichiometric $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys and to clarify their off-stoichiometric effect on the thermoelectric properties in comparison with other Fe-based Heusler alloys.

2. Experiment

Ingots of $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ 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. The ingots were homogenized at 1273 K for 48 hours in a vacuum. Samples were cut from the ingots with a SiC blade saw to the size of $1 \times 1 \times 15 \text{ mm}^3$ for resistivity measurements, $0.5 \times 0.5 \times 6 \text{ mm}^3$ for thermoelectric measurements and $3.5 \times 3.5 \times 4 \text{ mm}^3$ for thermal conductivity measurements. Each sample was sealed in an evacuated quartz capsule and annealed at 1273 K for 1 hour and then at 673 K for 4 hours followed by furnace cooling. The electrical resistivity was measured by a standard dc four-terminal method with a current of 100 mA over the temperature range of 4.2 - 800 K rising at the rate of 0.05 K/s; the measurements above room temperature were carried out in a vacuum of $4.0 \times 10^{-4} \text{ Pa}$. The Seebeck coefficient was measured with a commercially available apparatus (SB-100, MMR Technologies, Inc.) in the temperature range of 100 - 700 K. The thermal conductivity was measured in a vacuum of $5 \times 10^{-4} \text{ Pa}$ by the longitudinal steady-state method with Al_2O_3 as a standard sample [27]. The temperature difference was controlled to be less than 2 K to minimize the heat loss through radiation. Photoemission spectroscopy measurements were performed at BL25SU [28] and BL27SU [29]

beamlines of SPring-8, Japan Synchrotron Radiation Research Institute (JASRI). The photoemission spectroscopy spectra were recorded at 10 K with a total energy resolutions of 0.10 eV at BL25SU and 0.16 eV at BL27SU at the excitation photon energy at $h\nu = 900$ eV.

3. Results and discussion

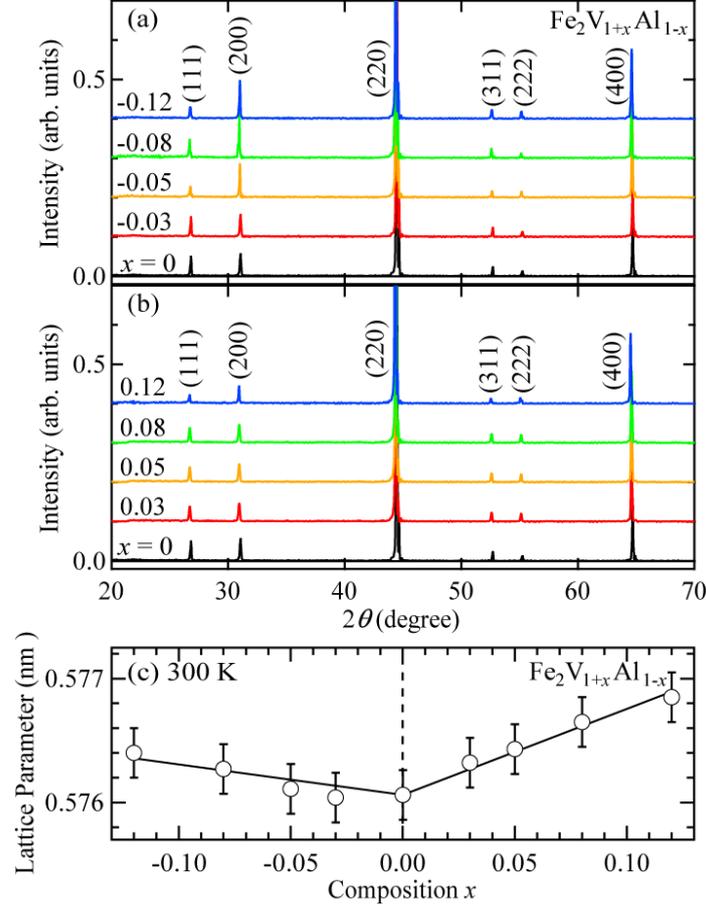


Figure 1. XRD patterns of powdered $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys with compositions of $-0.12 \leq x \leq 0$ (a) and $0 \leq x \leq 0.12$ (b). (c) Lattice parameters of $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ with compositions of $-0.12 \leq x \leq 0.12$ determined from the XRD patterns (open circles). The lines show the fitting results of these lattice parameters using a linear function.

Figures 1(a) and (b) show the powder X-ray diffraction (XRD) patterns obtained using $\text{Cu } K\alpha$ radiation for the off-stoichiometric $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys with compositions of $-0.12 \leq x \leq 0$ (Al-rich) and $0 \leq x \leq 0.12$ (V-rich), respectively. The overall XRD patterns were identified as a single-phase Heusler-type ($L2_1$) structure. Figure 1(c) shows the lattice parameter as a function of the composition x . The error bar of the lattice parameter was evaluated from the accuracy of the XRD measurements. Although the atomic radius of the V atom is larger than that of the Al atom [30], the lattice parameter slightly and monotonically increases with increasing $|x|$. This behavior is similar to that of other off-stoichiometric cases, such as $(\text{Fe}_{1-x}\text{V}_x)_3\text{Al}$ alloys [1]. This result indicates that the substitutions of V or Al for Al or V, respectively, have appropriate site selection without disturbance of Fe sub-lattice. In the case of $|x| > 0.12$, an impurity phase appears in the XRD patterns. Therefore, the solubility limit of $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys is around $|x| = 0.12$.

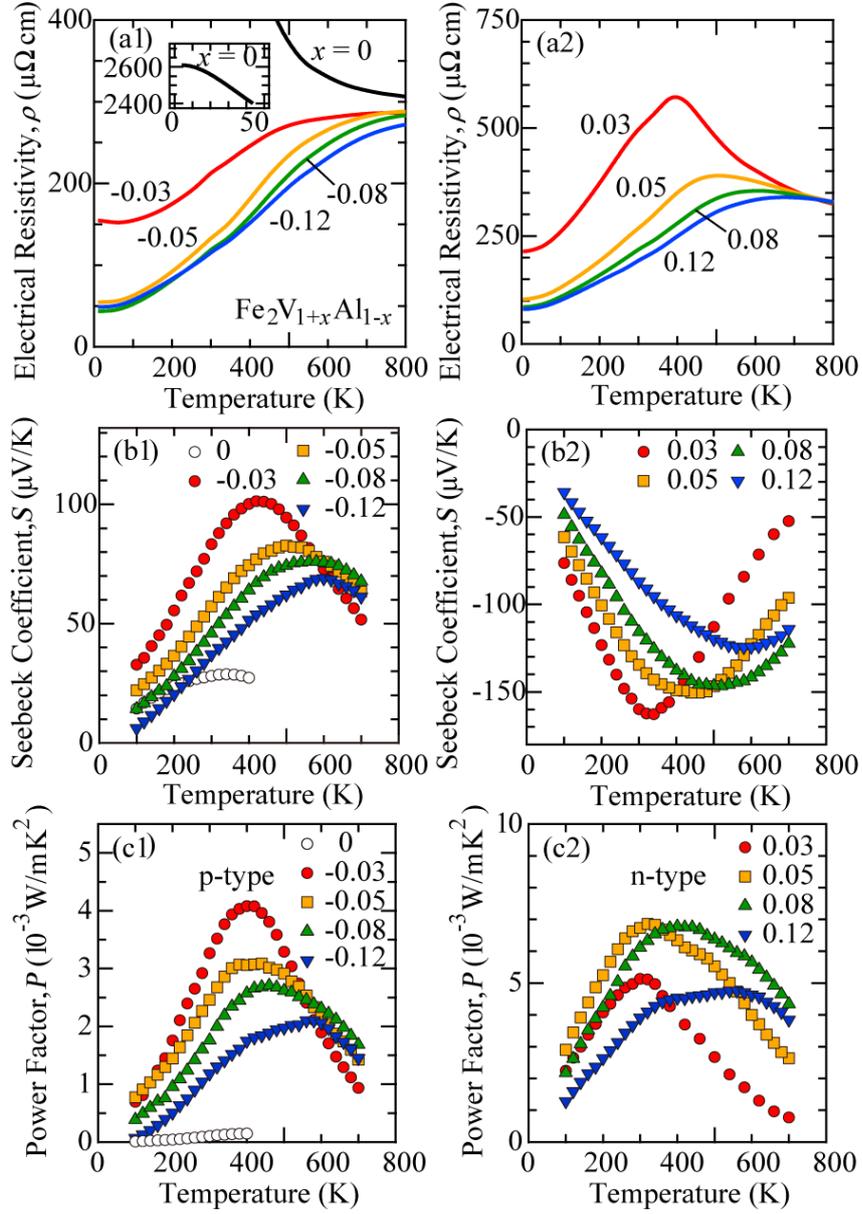


Figure 2. Temperature dependence of the electrical resistivity, ρ , Seebeck coefficient, S , and thermoelectric power factor, P , in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys with compositions of $-0.12 \leq x \leq 0$ (a1, b1, c1) and $0 < x \leq 0.12$ (a2, b2, c2). The inset shows the ρ of Fe_2VAl in the low-temperature region.

Figure 2 shows the temperature dependence of the electrical resistivity, ρ , Seebeck coefficient, S , and thermoelectric power factor, P , in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys with compositions of $-0.12 \leq x \leq 0$ (a1, b1, c1) and $0 < x \leq 0.12$ (a2, b2, c2). The ρ of the stoichiometric Fe_2VAl ($x = 0$) shows a semiconductor-like temperature-dependent behavior and reaches $2600 \mu\Omega\text{cm}$ at 4.2 K . The ρ of the off-stoichiometric case, namely, the Al-rich and V-rich alloys, gradually decreases with increasing $|x|$ and the peak position shifts to the higher temperature side for larger values of $|x|$. The substantial reduction in ρ above room temperature is favorable for the development of thermoelectric materials.

The Al-rich and V-rich alloys correspond to the hole- and electron-doping types, respectively, because the number of valence electrons of the V atom is larger than that of the Al atom. According to the band structure calculation, in the stoichiometric Fe_2VAl case, the E_F is located at the center of the pseudo-gap [2-7]. Due to the hole- and electron-doping, for $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys, the E_F is shifted to the

lower or higher energy side from the center of the pseudo-gap, respectively. Consequently, the sign of S in the Al-rich and V-rich alloys in Figs. 2(b1) and (b2) becomes positive and negative, respectively. The maximum value of $|S|$ in the Al-rich and V-rich alloys are 101 and 163 $\mu\text{V/K}$ for $x = -0.03$ and 0.03, respectively, which is larger than in typical p-type $\text{Fe}_2\text{V}_{1-y}\text{Ti}_y\text{Al}$ [15] and n-type $\text{Fe}_2\text{VAl}_{1-y}\text{Si}_y$ alloys [16]. The peak temperature of $|S|$ gradually shifts to the higher temperature side, about 300 - 600 K. In previous studies on n-type $\text{Fe}_2\text{VAl}_{1-y}\text{Si}_y$ alloys, the peak temperature of $|S|$ was about 300 - 400 K [16]. The $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ system shows the highest peak temperature among both n- and p-type Fe-based Heusler alloys.

The maximum P value of the Al-rich and V-rich alloys in Figs. 2(c1) and (c2) reaches 4.3×10^{-3} ($x = -0.03$: p-type) and 6.8×10^{-3} W/mK^2 ($x = 0.05$: n-type), respectively. These values are superior to those of conventional thermoelectric Bi-Te semiconductors [18].

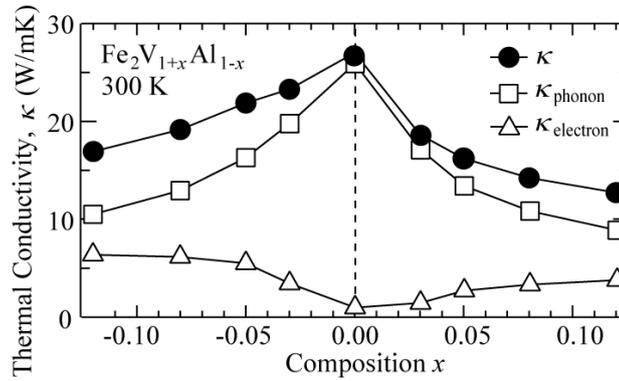


Figure 3. Thermal conductivity (filled circles), κ , of $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys with compositions of $-0.12 \leq x \leq 0.12$ at 300 K. The open squares and triangles indicate the phonon and electron component of the κ determined by the Wiedemann-Franz law, respectively.

Figure 3 shows the thermal conductivity, κ , at 300 K in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys with composition of $-0.12 \leq x \leq 0.12$. The value of κ is 27 W/mK for the stoichiometric Fe_2VAl and gradually decreases with increasing $|x|$. The decrease in κ in the n-type V-rich alloys is comparable to that of $\text{Fe}_2\text{VAl}_{1-y}\text{Ge}_y$ alloys [20] but larger than that of off-stoichiometric $\text{Fe}_{2-x}\text{V}_{1+x}\text{Al}$ alloys [26]. κ in ordinary metals and semimetals can be expressed by the sum of the electronic component (κ_{electron}) and the lattice component (κ_{phonon}). κ_{electron} is evaluated from the electrical resistivity, ρ , through the Wiedemann-Franz law: $\kappa_{\text{electron}}\rho/T=L_0$, where L_0 is the Lorenz number, *i.e.*, $L_0 = 2.45 \times 10^{-8}$ $\text{W}\Omega/\text{K}^2$. In Fig. 3, it is seen that κ_{electron} is almost saturated above $|x| \sim 0.05$. The main contribution of the decrease in κ arises from the decrease in κ_{phonon} , which is similar in the Al-rich and V-rich alloys. Therefore, the origin of this decrease is the increasing scattering by phonons due to the increasing mass difference between the stoichiometric and off-stoichiometric samples.

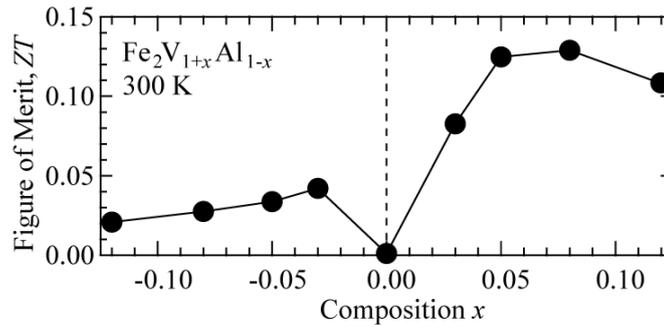


Figure 4. Figure of merit, ZT , in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys with compositions of $-0.12 \leq x \leq 0.12$ at 300 K.

The dimensionless figure of merit, ZT , given by $ZT=S^2T/\rho\kappa$, is the factor of potential for thermoelectric materials. The calculated ZT in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys with compositions of $-0.12 \leq x \leq 0.12$ at 300 K is shown in Fig. 4. The ZT value reaches 0.04 and 0.13 for p-type, $x = -0.03$, and n-type, $x = 0.08$, respectively. Surprisingly, these values are larger than those reported for $\text{Fe}_2\text{V}_{1-y}\text{Ti}_y\text{Al}$ [15] and $\text{Fe}_2\text{VAl}_{1-y}\text{Si}_y$ alloys [16] and are comparable to those of $\text{Fe}_2\text{VAl}_{1-y}\text{Ge}_y$ alloys [20], but without fourth element doping. Consequently, the off-stoichiometric effect on the substitution of V or Al atoms with Al or V atoms allows a well-balanced improvement of thermoelectric properties, such as electrical resistivity, Seebeck coefficient and thermal conductivity.

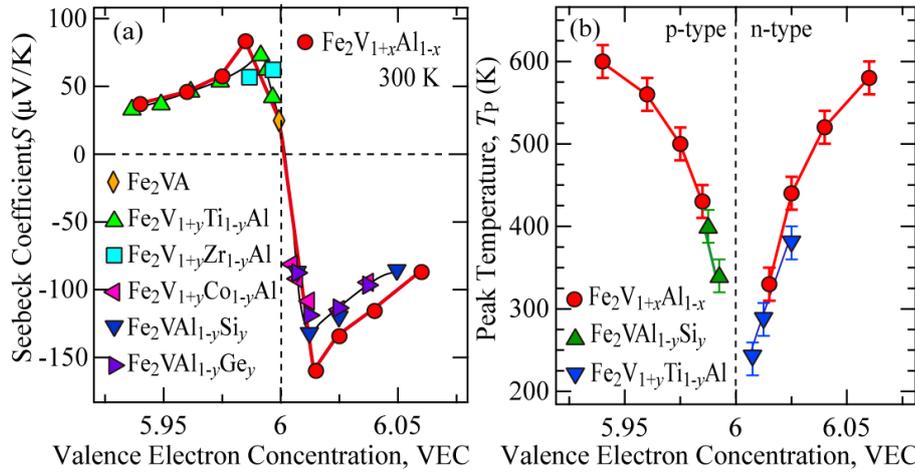


Figure 5. Valence electron concentration (VEC) dependence of the experimental Seebeck coefficient, S , at 300 K (a) and peak temperature, T_p , determined by S (b) in typical Fe-based Heusler and $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys.

Figure 5(a) shows the valence electron concentration (VEC) dependence of S in previously [14] and presently reported Fe-based Heusler alloys. The previous results fall on a universal curve irrespective of the doping element. However, the values of $|S|$ in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys are enhanced. One possible reason for the enhanced $|S|$ could be a modification of the electronic structure due to the off-stoichiometric effect.

Figure 5(b) shows the VEC dependence of the peak temperature of $|S|$ in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys and typical Fe-based Heusler alloys, such as $\text{Fe}_2\text{V}_{1-y}\text{Ti}_y\text{Al}$ (hole-doping) [15] and $\text{Fe}_2\text{VAl}_{1-y}\text{Si}_y$ (electron-doping) alloys [16]. The peak temperature for $\text{Fe}_2\text{V}_{1-y}\text{Ti}_y\text{Al}$ and $\text{Fe}_2\text{VAl}_{1-y}\text{Si}_y$ follows the same trend as in the $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ case, but is limited to 250 - 400 K. Indeed, in the case of a larger number of doping carriers, there is the degradation of the thermoelectric power factor and its peak temperature due to the appearance of an impurity phase. However, the peak temperature in $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys is higher than the former, reaching 600 K. Therefore, we believe that the $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys are promising as practical thermoelectric materials for future power generation.

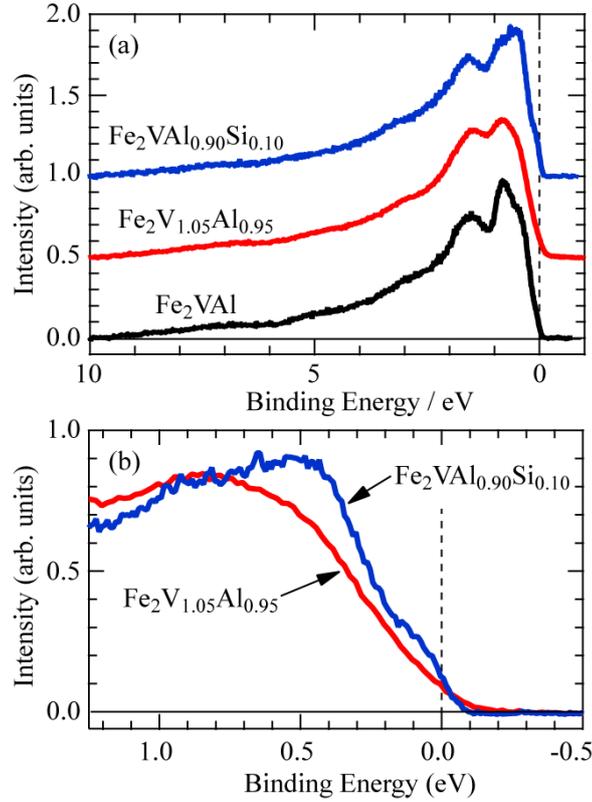


Figure 6. The valence band photoemission spectra of wide energy range (a) and near the Fermi level (b) of Fe₂VAl, Fe₂V_{1.05}Al_{0.95} and Fe₂VAl_{0.90}Si_{0.10} recorded at $h\nu = 900$ eV.

To discuss the origin of the improvement of S and its peak temperature in Fe₂V_{1+x}Al_{1-x} alloys, we measured the valence band photoemission spectra of the wide energy range and near the E_F in Fe₂VAl, Fe₂V_{1.05}Al_{0.95} and Fe₂VAl_{0.90}Si_{0.10} alloys, as shown in Figs. 6(a) and (b), respectively. These spectrum intensities are normalized with their area between -1 and 10 eV.

In Fig. 6(a), while the peak width of Fe₂V_{1.05}Al_{0.95} alloy becomes broader than that of Fe₂VAl alloy, the spectral shapes are almost similar to each other. The peak of Fe₂V_{1.05}Al_{0.95} alloy around 0.9 eV is shifted by 0.05 eV to the higher binding energy side compared to that of Fe₂VAl alloy. This behavior can be explained by the rigid band model, that is to say, due to the increasing electrons by the V atom substitution to Al atom, the E_F is shifted without significant change in the electronic structure.

When comparing the spectra of the Fe₂V_{1.05}Al_{0.95} alloy and a typical electron doping case of the same VEC, such as Fe₂VAl_{0.90}Si_{0.10} alloy, as shown in Fig. 6(b), it is seen that a new state appears around 0.5 eV in the pseudo-gap for the Fe₂VAl_{0.90}Si_{0.10}, while it does not for the Fe₂V_{1.05}Al_{0.95} alloy. It indicates that the doping carrier does not affect the local electronic and crystal structure for the off-stoichiometric Fe₂V_{1+x}Al_{1-x} alloys. Furthermore, the leading-edge near E_F in the Fe₂V_{1.05}Al_{0.95} alloy shifts to the higher binding energy side compared to that of Fe₂VAl_{0.90}Si_{0.10}. This means that the width of pseudo-gap in the off-stoichiometric alloy become wider than in the stoichiometric alloy. From band structure calculation, a wider pseudo-gap leads to a shift in the peak temperature of maximum thermoelectric power to the higher temperature side [17]. This is coherent with the present experimental results. Therefore, it is thought that the origin of the improvement of S and its peak temperature should be attributed to the maintenance of the $L2_1$ crystal structure and the modification of the electronic structure with a rigid band like shift due to the off-stoichiometries effect.

4. Conclusion

In conclusion, we have simultaneously succeeded in improving the thermoelectric power and peak temperature by fabricating Heusler-type ($L2_1$) off-stoichiometric $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys. The maximum thermoelectric power factor of the $\text{Fe}_2\text{V}_{1+x}\text{Al}_{1-x}$ alloys is about 4.3×10^{-3} ($x = -0.03$: p-type) and 6.8×10^{-3} W/mK^2 ($x = 0.05$: n-type) and the peak temperature is in the range of 300 - 600 K, exceeding the values for previously reported n- and p-type Fe-based Heusler alloys. The off-stoichiometric effect of substituting V/Al atoms with Al/V atoms is an effective way of improving of the thermoelectric properties of Fe-based Heusler alloys.

5. Acknowledgement

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References

- [1] Nishino Y, Kato M, Asano S, Soda K, Hayasaki M, and Mizutani U 1997 *Phys. Rev. Lett.* **79** 1909
- [2] Guo G Y, Botton G A, and Nishino Y 1998 *J. Phys.: Condens. Matter* **10** L119
- [3] Singh D J and Mazin I I 1998 *Phys. Rev. B* **57** 14352
- [4] Weht R and Pickett W E 1998 *Phys. Rev. B* **58** 6855
- [5] Weinert M and Watson R E 1998 *Phys. Rev. B* **58** 9732
- [6] Bansil A, Kaprzyk S, Mijnaerends P E, and Tobola J 1999 *Phys. Rev. B* **60** 13396
- [7] Botton G A, Nishino Y, and Humphreys C J 2000 *Intermetallics* **8** 1209
- [8] Okamura H, Kawahara J, Nanba T, Kimura S, Soda K, Mizutani U, Nishino Y, Kato M, Shimoyama I, Miura H, Fukui K, Nakagawa K, Nakagawa H, and Kinoshita T 2000 *Phys. Rev. Lett.* **84** 3674
- [9] Feng Y, Rhee J Y, Wiener T A, Lynch D W, Hubbard B E, Sievers A J, Schlagel D L, Lograsso T A, and Miller L L 2001 *Phys. Rev. B* **63** 165109
- [10] Soda K, Mizutani T, Yoshimoto O, Yagi S, Mizutani U, Sumi H, Nishino Y, Yamada Y, Yokoya T, Shin S, Sekiyama A, and Suga S 2002 *J. Synchrotron Radiat.* **9** 2333
- [11] Miyazaki H, Soda K, Yagi S, Kato M, Takeuchi T, Mizutani U, and Nishino Y 2006 *J. Vac. Sci. Technol. A* **24** 1464
- [12] Mott N F and Jones H 1936 *The Theory of the Properties of Metals* (Oxford: Clarendon Press)
- [13] Nishino Y, Kato H, Kato M, and Mizutani U 2001 *Phys. Rev. B* **63** 233303
- [14] Nishino Y 2005 *The Science of Complex Alloy Phases* (Warrendale: TMS) p. 325
- [15] Matsuura H, Nishino Y, Mizutani U, and Asano S 2002 *J. Jpn. Inst. Met.* **66** 767
- [16] Kato H, Kato M, Nishino Y, Mizutani U, and Asano S 2001 *J. Jpn. Inst. Met.* **65** 652
- [17] Do D, Lee M, and Mahanti S D 2011 *Phys. Rev. B* **84** 125104
- [18] Scherrer H and Scherrer S 1955 *CRC Handbook of Thermoelectrics* (New York: CRC Press) p. 211
- [19] Vasundhara M, Srinivas V, and Rao V V 2005 *J. Phys.: Condens. Matter* **17** 6025
- [20] Nishino Y, Deguchi S, and Mizutani U 2006 *Phys. Rev. B* **74** 115115
- [21] Lue C S, Chen C F, Lin J Y, Yu Y T, and Kuo Y K 2007 *Phys. Rev. B* **75** 064204
- [22] Vasundhara M, Srinivas V, and Rao V V 2008 *Phys. Rev. B* **77** 224415
- [23] Mikami M, Tanaka S, and Kobayashi K 2009 *J. Alloys Compd.* **484** 444
- [24] Mikami M, Kinemuchi Y, Ozaki K, Terazawa Y, and Takeuchi T 2012 *J. Appl. Phys.* **111** 093710
- [25] Hanada Y, Suzuki R O, and Ono K 2001 *Comput. J. Alloys Compd.* **329** 63
- [26] Lue C S, and Kuo Y K 2002 *Phys. Rev. B.* **66** 085121
- [27] Scherrer H and Scherrer S 1955 *CRC Handbook of Thermoelectrics* (New York: CRC Press) p.

- [28] Saitoh Y, Kimura H, Suzuki Y, Nakatani T, Matsushita T, Muro T, Miyahara T, Fujisawa M, Soda K, Ueda S, Sekiyama A, Imada S, and Suga S 2001 *Nucl. Instrum. Methods Phys. Res. A* **467-467** 553
- [29] Ohashi H, Ishiguro E, Okumura H, Hiraya A, Senba Y, Okada K, Saito N, Suzuki I, Ueda K, Ibuki T, Nagaoka S, Koyano I, and Ishikawa T 2001 *Nucl. Instrum. Methods Phys. Res. A* **467-467** 529
- [30] Clementi E, Raimondi D L, and Reinhardt W P 1965 *J. Chem. Phys.* **38** 2686