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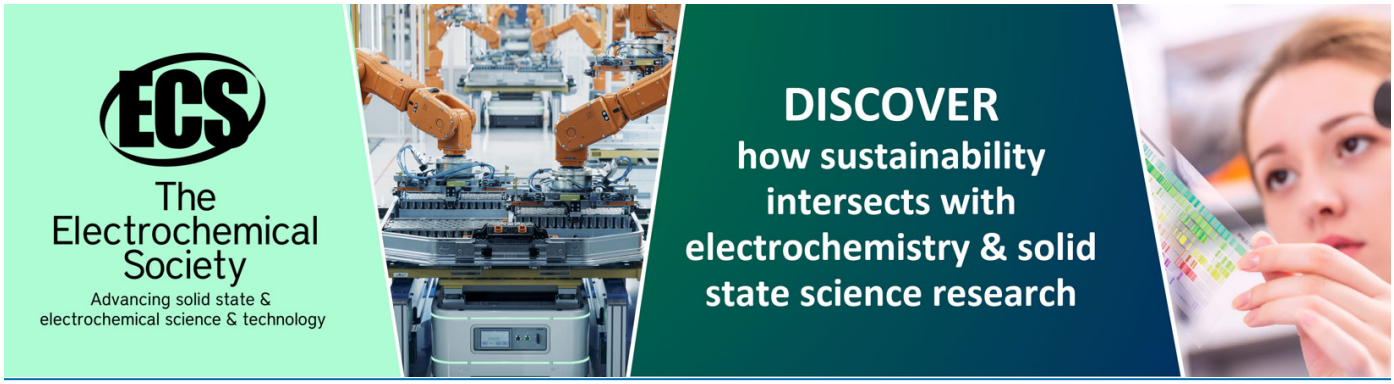

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Development of thermoelectric materials based on Fe_2VAl Heusler compound for energy harvesting applications

Y Nishino

Department of Frontier Materials, Nagoya Institute of Technology,
Showa-ku, Nagoya 466-8555, Japan

E-mail: nishino@nitech.ac.jp

Abstract. The Heusler-type Fe_2VAl compound is a nonmagnetic semimetal with a sharp pseudogap at the Fermi level. Doping of quaternary elements causes a large enhancement in the Seebeck coefficient, in parallel with a significant decrease in the electrical resistivity. Since the Seebeck coefficient varies systematically with the valence electron concentration (VEC), irrespective of doping elements, the net effect of doping is most likely to cause a rigid-band-like shift of the Fermi level from the central region in the pseudogap. Further increase in the Seebeck coefficient can be expected for the off-stoichiometric $Fe_{2-x}V_{1+x}Al$ alloys due to tuning of the Fermi level by doping. The Fe_2VAl-based compounds are a promising candidate for thermoelectric power generation near room temperature, because of the possession of higher thermoelectric power factor than that of Bi-Te system.

1. Introduction

The Heusler-type intermetallic compound Fe_2VAl has received intense attention because of the occurrence of a semiconductor-like resistivity behaviour over a wide temperature range up to 1200 K and above, an enhancement of the effective electron mass at low temperatures and a marginally magnetic nature, which is reminiscent of heavy fermion system [1]. Band structure calculations [2,3] consistently predicted the presence of a deep pseudogap at the Fermi level due to the hybridization effects. Optical conductivity [4] and photoelectron spectroscopy [5] measurements clearly manifested the existence of a pseudogap of 0.1-0.2 eV in width.

Because of the possession of a sharp pseudogap across the Fermi level, Fe_2VAl-based compounds have attracted a great deal of interest as a potential candidate for new thermoelectric materials [6]. In the metallic systems, the Seebeck coefficient S at a temperature T is often discussed using the well-known formula [7],

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

where $\sigma(E)$ is the electrical conductivity and E_F represents the Fermi energy. Provided $\sigma(E)$ is proportional to the density of states (DOS), $N(E)$, it is argued that a large Seebeck coefficient is brought about by a low $N(E)$ coupled with its steep slope, $\partial N(E)/\partial E$, near E_F. Thus we expect the Seebeck coefficient of Fe_2VAl to be well enhanced by doping or off-stoichiometry, since the DOS rises sharply in both sides of the pseudogap. If E_F shifts to a sharply rising portion of the conduction band DOS, $S(T)$ becomes negative because of a positive value of $\partial N(E)/\partial E$ at E_F, and vice versa.

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Indeed a variety of Fe_2VAl-based thermoelectric materials have been developed, all of which exhibit a large enhancement in the Seebeck coefficient, in parallel with a sharp reduction in the electrical resistivity. The aim of this review is to survey our recent studies concerning the thermoelectric properties of the pseudogap Fe_2VAl system, focusing on the doping and off-stoichiometric effects.

2. Doping effects on thermoelectric properties

2.1. Seebeck coefficient

In figure 1, the Seebeck coefficient S for $Fe_2V(Al_{1-x}Si_x)$ with $0 \le x \le 0.20$ is shown as a function of temperature [8]. While the value of S for Fe_2VAl ($x = 0$) is positive and centered around 20 - 30 μV/K, the sign of S becomes negative by the Si substitution and the absolute value increases remarkably with increasing x, reaching $S = -130$ μV/K at 300 K for $x = 0.05$. The absolute value of S increases gradually as the temperature increases, forming a broad maximum, and then turns to decrease. The upturn in S at high temperatures could be ascribed to the contribution of thermally excited carriers across the pseudogap, as in the case for semiconductors, and the temperature at which $|S|$ reaches a maximum increases with increasing x. On the basis of the rigid band model, the Si substitution leads to an increase in the total density of valence electrons, so that an increase in the electron density is responsible for the possession of a negative sign of the Seebeck coefficient. It should be remarked that $Fe_2V(Al_{1-x}Si_x)$ with $x = 0.10$ shows a large power factor, $P = S^2/\rho$, of 5.5×10^{-3} W/m K^2 at around 300 K [8], which is substantially higher than that of a conventional thermoelectric material Bi_2Te_3.

On the basis of the site selectivity of doping elements, various Fe_2VAl-based thermoelectric materials have been developed. We believe that the variation of valence electron concentration (VEC) due to doping is the most important factor for a large enhancement in the Seebeck coefficient. Figure 2 summarizes the Seebeck coefficient measured at 300 K for various Fe_2VAl-based alloys as a function of VEC [6]: Fe_2VAl has in total 24 valence electrons per formula unit, so that VEC = 6. The sign of the Seebeck coefficient S is always positive for the alloys with VEC ≤ 6 but becomes negative for VEC > 6. Thus the value of S including its sign varies most significantly in the vicinity of VEC = 6. As can be seen, the VEC dependence of the Seebeck coefficient falls on a universal curve, irrespective of the doping elements. Therefore, a small deviation of VEC from the stoichiometric value of 6 always leads

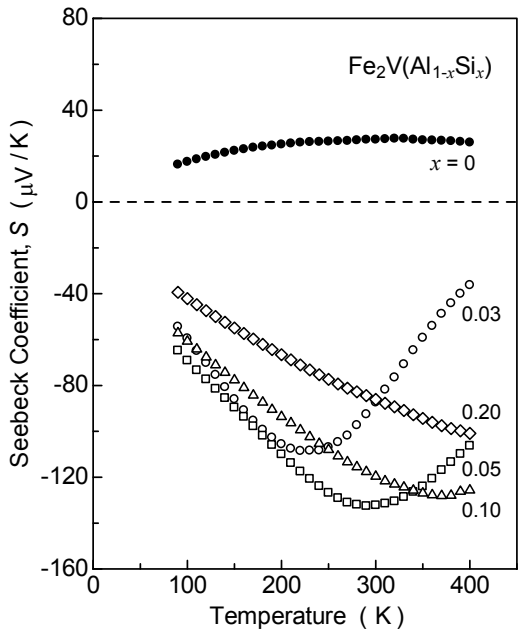

Figure 1. Temperature dependence of Seebeck coefficient in $Fe_2V(Al_{1-x}Si_x)$ with $0 \le x \le 0.20$.

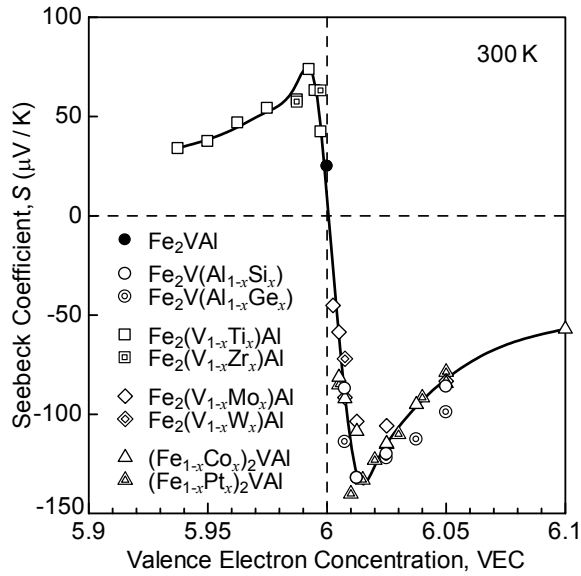

Figure 2. Seebeck coefficient at 300 K for various Fe_2VAl-based alloys as a function of valence electron concentration (VEC): VEC for Fe_2VAl is equal to 6.

to a large enhancement in the Seebeck coefficient. It is considered that, since the DOS within the pseudogap is very small, even a small compositional change due to doping would result in an appreciable shift of the Fermi level from the central region in the pseudogap without modifying the band structure in any essential manner.

The doping effects on the thermoelectric properties have hitherto been investigated for various Heusler compounds with VEC = 6, e.g., $Fe_2V(Al_{1-x}Si_x)$ [8-10], $Fe_2V(Al_{1-x}M_x)$ (M = Si, Ge) [11], (M = B, In, Si) [12] and (M = Si, Sn) [13], $Fe_2(V_{1-x}Ti_x)Al$ [14], $Fe_2(V_{1-x-y}Ti_xTa_y)Al$ [15], $Fe_2(V_{1-x}Nb_x)Al$ [16], $(Fe_{1-x}Re_x)_2VAl$ [17], $(Fe_{1-x}Co_x)_2VAl$ [18], $Fe_2V(Ga_{1-x}Ge_x)$ [19] and $(Fe_{1-x}Co_x)_2TiAl$ [20].

2.2. Electrical resistivity

Figure 3 shows the temperature dependence of the electrical resistivity in $Fe_2V(Al_{1-x}Si_x)$ with $0 \le x \le 0.20$ [8]. As soon as Al is partly replaced by Si, the semiconductor-like resistivity behavior disappears rapidly, and the low-temperature resistivity decreases with increasing x. The resistivity for $x = 0.20$ is reduced to only 35 μΩ cm at 4.2 K, which is almost two orders of magnitude lower than that for Fe_2VAl, and a positive slope in its temperature dependence appears in the region below 600 K. In spite of a significant decrease in the low-temperature resistivity, all the resistivity curves almost coincide with each other at high temperatures above 600 K.

In order to compare the doping effect, the electrical resistivity ρ measured typically at 300 K for $Fe_2V(Al_{1-x}Si_x)$ and $Fe_2V(Al_{1-x}Ge_x)$ is plotted in the inset of figure 3 as a function of the composition x [11]. It is seen that the compositional variation coincides with each other regardless of the doping elements, which is also a positive evidence for a rigid-band-like shift of the Fermi level due to doping of isoelectronic elements. We conclude that one can control both the Seebeck coefficient and the electrical resistivity in the pseudogap systems by tuning the Fermi level to an energy position at which equation (1) can be maximized without a substantial modification of the electronic structure.

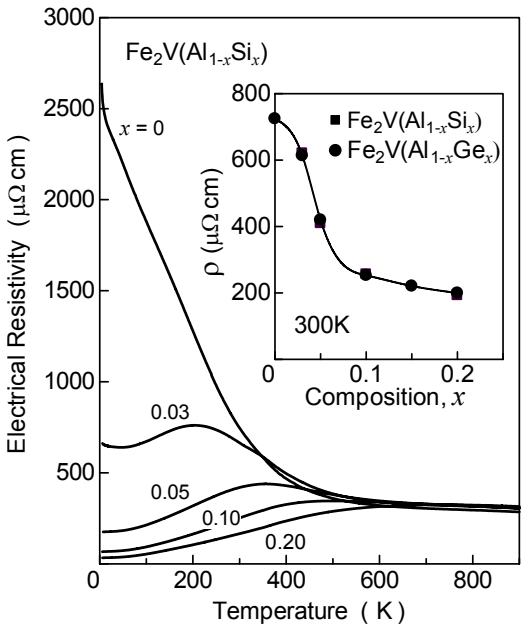

Figure 3. Temperature dependence of electrical resistivity in $Fe_2V(Al_{1-x}Si_x)$ with $0 \le x \le 0.20$. The inset shows the resistivity ρ at 300 K as a function of composition x in $Fe_2V(Al_{1-x}Si_x)$ and $Fe_2V(Al_{1-x}Ge_x)$.

2.3. Thermal conductivity

Thermal conductivity is generally determined by contributions both from conduction electrons and phonons. One of the current challenges is therefore to reduce the lattice thermal conductivity while retaining the low electrical resistivity as well as the large Seebeck coefficient. Taking into account the large power factor for $Fe_2V(Al_{1-x}Si_x)$ alloys, we expect the substitution of isoelectronic elements such as heavy Ge to be beneficial for reducing the lattice thermal conductivity due to the atomic mass effect without a substantial modification of the electronic structure. In figure 4, the thermal conductivity κ

for $Fe_2V(Al_{1-x}Si_x)$ and $Fe_2V(Al_{1-x}Ge_x)$ alloys is plotted as a function of the composition x [11]. While the value of κ always decreases with increasing x for both the alloys, the Ge substitution causes a more remarkable reduction in κ down to about 11 W/m K for x = 0.20. Now we can estimate the electronic thermal conductivity by using the Wiedeman-Franz law with the measured resistivity data. As seen in figure 4, the electronic thermal conductivity κ_e, plotted by the closed symbols, is almost the same for both the alloys and is always smaller than the lattice thermal conductivity κ_{ph}. This means that the total thermal conductivity is mainly due to phonons rather than charge carriers at room temperature. By considering similar composition dependence between κ and κ_{ph}, we can safely argue that the reduction in κ is dominantly brought about by disordering due to doping. It should be remarked that κ_{ph} for the Ge substitution decreases more rapidly than that for the Si substitution. This behavior is in contrast to the Seebeck coefficient and the electrical resistivity, where the doping effect of isoelectronic elements is almost the same as each other.

In Klemens's perturbation theory [21] for phonon scattering by point defects, the perturbation energy is proportional to the difference in mass between the substitutional atom and an atom averaged over host atoms in the matrix. Reductions of the phonon mean-free-path in solid solutions may be analyzed in terms of a phonon relaxation time τ involved in the mass-difference scattering [21]:

$$\tau^{-1} = \Omega\Gamma\omega^4 / 4\pi\upsilon^3, \tag{2}$$

where Ω is the average atomic volume, ω is the phonon frequency, and υ refers to the average phonon velocity. Also Γ is a measure of the scattering strength and is given by

$$\Gamma = \sum_i c_i \left(\Delta M_i / M\right)^2, \tag{3}$$

where c_i is the fractional concentration of the impurity, whose atomic mass M_i differs from the average mass M by $\Delta M_i = M_i - M$. In figure 5, we plot the lattice thermal resistivity, i.e., the inverse of the lattice thermal conductivity, $1/\kappa_{ph}$, for $Fe_2V(Al_{1-x}Si_x)$ and $Fe_2V(Al_{1-x}Ge_x)$ alloys against the dimensionless strength of phonon scattering, Γ, evaluated by using equation (3) with $c = 0.25x$ [11]. As expected from equation (2), there is a linear relation between $1/\kappa_{ph}$ and Γ, and the data on both the alloys are found to be in line with each other. Therefore the lattice thermal resistivity can be mainly interpreted in terms of the mass-difference scattering, so that doping of heavier elements reduces more effectively the phonon mean-free-path in Fe_2VAl-based alloys. It is concluded that the substitution of heavy atoms like Ge certainly acts in favor of the development of thermoelectric materials because of a substantial reduction of κ_{ph} while retaining the low value of ρ and the large value of $|S|$.

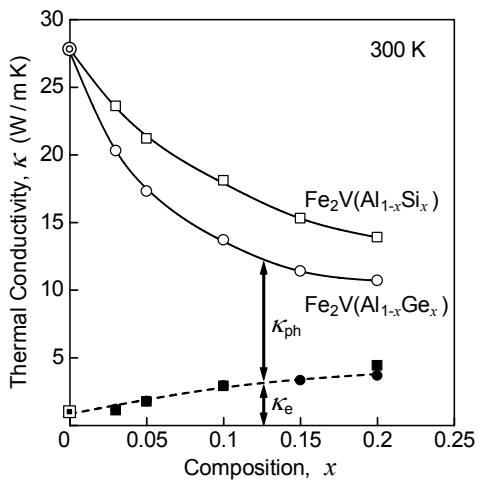

Figure 4. Thermal conductivity κ at 300 K as a function of composition x in $Fe_2V(Al_{1-x}Si_x)$ and $Fe_2V(Al_{1-x}Ge_x)$: the calculated values of κ_e are also plotted by the closed symbols.

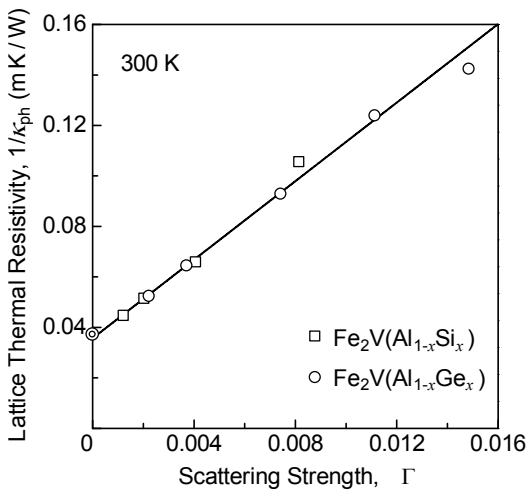

Figure 5. Lattice thermal resistivity $1/\kappa_{ph}$ at 300 K as a function of dimensionless strength of phonon scattering, Γ, in $Fe_2V(Al_{1-x}Si_x)$ and $Fe_2V(Al_{1-x}Ge_x)$.

3. Off-stoichiometric effects on thermoelectric properties

The possibility for thermoelectric applications has also been investigated for the off-stoichiometic concentration change, i.e., $(Fe_{2/3}V_{1/3})_{100-y}Al_y$ [22], $Fe_{2-x}V_{1+x}Al$ [23-25], $Fe_{2-x}V_{1+x}Ga$ [23], Fe_2VGa_{1+x} [26] and $Fe_{2-x}Ti_{1+x}Sn$ [27]. For the $Fe_{2-x}V_{1+x}Al$ system, the sign of the Seebeck coefficient S becomes negative at a slightly V-rich composition ($x > 0$), and a large enhancement in S is observed in parallel with a drastic increase in the low-temperature resistivity [23]. The occurrence of a more pronounced semiconducting behavior for the V-rich alloys with $x > 0$ is, however, very different from the $(Fe_{2/3}V_{1/3})_{100-y}Al_y$ system [22] where a small deviation of the Al content always causes a substantial reduction in the resistivity. Although the off-stoichiometric $Fe_{2-x}V_{1+x}Al$ alloys do exhibit a large Seebeck coefficient, their large values of resistivity make them rather poor thermoelectric materials [23]. We have recently found that not only a large Seebeck coefficient but also a low electrical resistivity can be expected for the off-stoichiometric alloys only by tuning the Fermi level very precisely due to doping [28,29].

Figure 6 shows the Seebeck coefficient at 300 K in $(Fe_{2-x-y}M_y)V_{1+x}Al$ with $x = 0$, 0.02 and 0.05 as a function of composition y of M = Ir and Rh [28]. While a small deviation from the stoichiometric Fe_2VAl composition causes an enhancement in the Seebeck coefficient, a slight substitution of Ir or Rh for Fe leads to a further increase in the Seebeck coefficient, reaching −170 μV/K at 300 K for $x = 0.05$ and $y = 0.03$, which is larger than that of the stoichiometric Fe_2VAl-based alloys so far reported. It is noted here that the doping effect of M = Ir and Rh is almost the same even for the off-stoichiometric alloys. A large enhancement in the Seebeck coefficient of the off-stoichiometric alloys could be due to a modification in the band structure around the Fermi level. Further, the doping of heavier atoms such as Ir reduces more effectively the thermal conductivity, reaching 7 W/m K for $y = 0.10$, while retaining the low electrical resistivity as well as the large Seebeck coefficient, thus resulting in an increased figure of merit of $Z = 8.6 \times 10^{-4}\,K^{-1}$ at 300 K.

In order to demonstrate the off-stoichiometric effect, figure 7 shows the Seebeck coefficient at 300 K in $Fe_{2-x}(V_{1+x-y}Ti_y)Al$ with $x = -0.04$ and 0.02 as a function of Ti composition y [29]. For the V-rich alloy with $x = 0.02$, the sign of the Seebeck coefficient changes from negative to positive on the Ti substitution, and the Seebeck coefficient is substantially larger than the stoichiometric alloy with $x = 0$. This change in the sign of the Seebeck coefficient for the Ti substitution could be caused by a shift of the Fermi level across the bottom of the pseudogap. It can be seen that the Seebeck coefficient for the Fe-rich alloy with $x = -0.04$ is always larger than the V-rich alloy, reaching 110 μV/K at 300 K for $y = 0.03$. According to soft X-ray photoelectron spectroscopy, the valence-band spectra near the Fermi

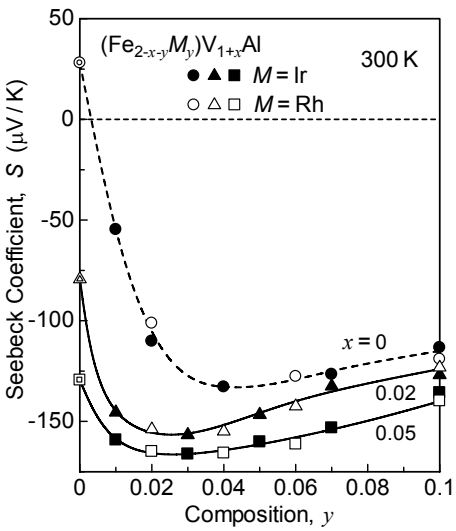

Figure 6. Seebeck coefficient at 300 K in $(Fe_{2-x-y}M_y)V_{1+x}Al$ with $x = 0$, 0.02 and 0.05 as a function of composition y of M = Ir and Rh.

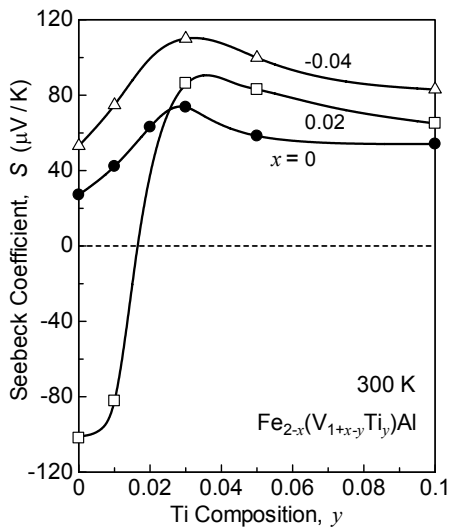

Figure 7. Seebeck coefficient at 300 K in $Fe_{2-x}(V_{1+x-y}Ti_y)Al$ with $x = -0.04$, 0 and 0.02 as a function of Ti composition y.

level E_F of the Fe-rich alloy with $x = -0.04$ is drastically changed from that of stoichiometric Fe_2VAl, so that substantial enhancements in the Seebeck coefficient could be due to a modification in the band structure on the valence band side around E_F [29]. We conclude that a larger Seebeck coefficient with a positive sign can be obtained for the Fe-rich alloys rather than the V-rich alloys, while a larger Seebeck coefficient with a negative sign is available for the V-rich alloys.

4. Concluding remarks

While the Heusler compound Fe_2VAl exhibits a semiconductor-like resistivity behavior, doping of quaternary elements causes a significant decrease in the low-temperature resistivity and a large enhancement in the Seebeck coefficient. In particular, doping of heavier atoms reduces more effectively the lattice thermal conductivity because of mass-difference scattering. The compositional variation of the Seebeck coefficient falls on a universal curve, irrespective of the doping elements, when plotted as a function of the valence electron concentration (VEC), suggesting a rigid-band-like shift of the Fermi level from the center of the pseudogap due to doping. Remarkably, doping to the off-stoichiometric $Fe_{2-x}V_{1+x}Al$ alloys leads to a further enhancement in the Seebeck coefficient, reaching −170 μV/K for the n-type V-rich alloy and 110 μV/K for the p-type Fe-rich alloy.

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