The Effects of Element Substitution on Electronic Structure, Electron Transport Properties, and Lattice Thermal Conductivity of Fe$_2$VAl Thermoelectric Material

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By using the first principles cluster calculation together with the band calculation, we identified that (a) Ru or Rh substitution for Fe and (b) Zr, Nb and Mo substitution for V are presumably useful for decreasing the lattice thermal conductivity without greatly affecting the electron transport properties. The Fe$_2$V$_{1-x}$Zr$_x$Al$_{0.99}$Si$_{0.01}$ alloys indeed possessed the effective reduction in lattice thermal conductivity with increasing Zr concentration while the Seebeck coefficient showed very weak Zr concentration dependence. The Fe$_2$V$_{1-y}$Ir$_y$V$_{0.99}$Si$_{0.01}$ alloys, on the other hand, possessed drastic reduction of Seebeck coefficient most likely due to the newly introduced Ir 5d states. These experimental facts agree with the present theoretical-prediction, and it was clearly proved that the combinational use of cluster calculation and band calculation is very useful in developing new thermoelectric material.

Keywords: electronic structure, thermoelectric properties, pseudogap, thermal conductivity

1. Introduction

Development of thermoelectric materials possessing a large value of dimension-less figure of merit $ZT = S^2\sigma T/\kappa$ at low temperatures below 500 K is strongly required for recovering the energy from the wasted heat, partly because the efficiency of the energy conversion in thermoelectric generators increases with increasing magnitude of $ZT$, and partly because most of the wasted heat is released into environment at low temperature below 500 K. The currently existing practical thermoelectric materials usable at the low temperatures contain expensive, toxic, rare elements, such as tellurium, lead, bismuth, and selenium. We need to develop, therefore, new materials possessing a large $ZT$-value at temperatures below 500 K in the alloy systems consisting solely of cheap, environment-friendly elements.

The Heusler-type Fe$_2$VAl, which possesses a large power factor $PF = S^2\sigma$ exceeding $3 \times 10^{-3}$ Wm$^{-1}$K$^{-2}$, is one of the most plausible materials obtainable in the environment-friendly system. Unfortunately, however, its large magnitude of lattice thermal conductivity $\kappa_{\text{lat}}$ prevents us from obtaining a large $ZT$-value. If the magnitude of $\kappa_{\text{lat}}$ were effectively reduced without greatly affecting the power factor, the Heusler-type Fe$_2$VAl could be used as the environment-friendly, practical thermoelectric material.

In this study, therefore, we try to identify the elements that are capable of being partially substituted for the constituent elements of Fe$_2$VAl alloy and effectively reduce the lattice thermal conductivity without greatly affecting the power factor. We selected 4$d$ and 5$d$ transition metal elements as substitutes for Fe or V in Fe$_2$VAl because the substitution of heavy atoms generally leads to a reduction of group velocity of phonons, an enhancement in umklapp scatterings of phonons, and an increase of scattering probability. In order to find the 4$d$ and 5$d$ transition metal elements that hardly affect the electron transport properties at the partial substitution, we calculated the cluster levels of the coordination clusters persisting in the crystal structure of Fe$_2$VAl by replacing the center atoms of cluster with one of the 4$d$ or 5$d$ transition metal elements. After optimizing the inter-atomic distances by calculating the total energy of the cluster, we obtained the cluster levels that are supposed to be produced by the newly introduced elements in the system.

From the obtained cluster levels, we identified the several elements that do not greatly affect the electron transport properties of the mother phase but effectively reduce the lattice thermal conductivity. Besides, we experimentally prepared samples using the identified elements as the substitute for the constituent elements of Fe$_2$VAl, and measured their thermoelectric properties to prove the validity of our strategy.

2. Calculation and Experimental Procedures

We employed, in this study, the first principles cluster-calculation of the distributed package programs named as Discrete Variational Xa Potential Method (DVXa). This package program uses the Xa potential for electron correlation and the wave functions obtained by the linear combination of atomic orbital method. We intentionally employed, in this study, the cluster calculation rather than band calculations, because the characteristic electronic structure in the objective phases is brought about mainly by the d-bands and the energy eigenvalue of d-bands is dominantly determined by the local atomic arrangements about the transition metal elements. Since we investigate the effects of an element that is partially substituted for the constituent elements of Fe$_2$VAl, the band calculations could
not be very useful for this purpose because the periodic arrangement of the unit cell required for the band calculation is destroyed by the partial substitution of the other elements. Cluster calculations, on the other hand, are appropriate for investigating the energy eigenvalue of the localized states produced by the impurity elements.

For the cluster calculation, we employed the coordination clusters in which the center atom was surrounded by the eight nearest-neighbor atoms and six second-nearest-neighbor atoms. The employed clusters are schematically drawn in Fig. 1 together with the unit cell of Fe atoms. The employed clusters are schematically drawn in nearest-neighbor atoms and six second-nearest-neighbor clusters in which the center atom was surrounded by the eight produced by the impurity elements.

Fig. 1. Schematic illustrations of (a) the unit cell of Fe$_2$VAl, (b) Fe centered coordination cluster, and (c) V centered coordination cluster. Dark black balls, light gray balls, and white balls indicate V, Fe, and Al, respectively.

We considered that the partial density of states for the d-component of atom persisting at the center should have the same characteristics of the d-band in the crystals because of the rather small transfer integrals about the d-orbital. We calculated, therefore, the cluster levels for the clusters possessing a transition metal atom at its center, and extracted the energy and the fraction of d-components of the transition metal atom persisting at the center of cluster. By multiplying the Gauss function of 50 meV in FWHM by all the fractional cluster levels, we obtained the partial density of states for the d-components of the transition metal atom.

In sharp contrast to the d-band, the s,p-band is rather difficult to be investigated by the cluster calculations especially when the size of cluster is small. Besides the cluster orbitals consisting mainly of s,p-components are supposed to be less important for the formation of pseudogap of Fe$_2$VAl. Therefore we did not calculate the cluster-levels in the cluster with Al in its center.

In addition to the theoretical calculations, we experimentally prepared two series of samples, Fe$_2$V$_{1-x}$Zr$_x$Al$_{0.98-2x}$Si$_{0.1+x}$ ($x = 0, 0.02, 0.04, 0.06$, and $0.1$) and Fe$_2$V$_{0.98-x}$Ir$_x$Al$_{0.1+x}$ ($x = 0, 0.02, 0.04, 0.06$, and $0.1$), and measured their thermoelectric properties. In the former samples, Zr atoms are partially substituted for V. Since Zr is located in the left column of V in the periodic table, the substitution of Zr for V does not only increase the mean atomic weight but also decrease the number of electrons in the system. In order to compensate the reduction of electron concentration caused by the Zr substitution, the same amount of Al is simultaneously replaced with Si. In the same manner as V with Zr, Fe is partially replaced with Ir in the latter series of samples, and the increase of valence electrons was simultaneously compensated by the Ti substitution for V.

The mother ingots were prepared from the elements of 99.9% purity by using the arc-melting in a pressurized argon-gas atmosphere, followed by annealing at 1273 K for 24 h in a vacuum atmosphere. The ingots were crushed into powders and sintered at 1373 K for 1–3 min under a pressure of 40 MPa in vacuum by the pulse current sintering (PCS) technique. The phases involved in the samples were identified by the conventional powder X-ray diffraction measurements with Cu-Kα radiation source and a Bragg-Brentano-type diffractometer set in RIGAKU RINT2000.

The electrical resistivity, Seebeck coefficient, and thermal conductivity were measured at room temperature for the sintered samples. We used the conventional four-probe method for the electrical resistivity measurement. The Seebeck coefficient was determined with the steady state method by measuring the thermoelectric voltage generated from the given temperature gradient in a furnace. The thermal conductivity was determined from the specific heat and the thermal diffusivity by using the laser flash method.

3. Results

3.1 Reduction of thermal conductivity caused by the heavier atoms

Figures 2(a) and (b) show the powder XRD patterns of the sintered samples. We confirmed that the samples consist almost solely of the objective phase, which is known as the L2$_1$-phase or the Heusler-phase. The packing density of the samples, which was deduced from the experimentally determined lattice-parameter and the sample weight by using the Archimedean method, was almost constant at 96–98% of the theoretical value. This density is comparable with 98% observed for the Fe$_2$VAl ingots prepared by arc-melting. The very small reduction of density from the theoretical value definitely indicates that the macroscopic voids, which are capable of greatly affecting the physical properties of samples, were effectively removed from the present samples.

The electrical resistivity, thermal conductivity, and Seebeck coefficient of these samples were plotted in Fig. 3. The thermal conductivity of both series of samples was reduced drastically with increasing amount of substituted element. By roughly estimating the electron contribution of the thermal conductivity using the Wiedemann-Franz law, we confirmed that the reduction in thermal conductivity was mostly caused by the reduction in lattice thermal conductivity. One may notice that the substitution of Ir for Fe definitely provided us with more significant reduction of thermal conductivity than that of Zr for V. This difference in reduction of lattice thermal conductivity was presumably brought about by the difference in atomic weight between Ir.
and Zr. Note here that Ir is one of the 5d transition metal elements and its atomic mass is 192.22 which is much larger than 91.224 of the 4d transition metal Zr. Despite that the reduction of lattice thermal conductivity caused by the heavy atom substitution is preferable for the thermoelectric materials, the magnitude of Seebeck coefficient of Fe$_2$V$_{1-x}$Ir$_x$Al$_{0.9-y}$Si$_{0.1+y}$ (y = 0, 0.02, 0.04, 0.06, and 0.1) became smaller with increasing Ir concentration and, therefore, its power factor and dimension less figure of merit drastically decreased. The magnitude of Seebeck coefficient of Fe$_2$V$_{1-x}$Zr$_x$Al$_{0.9-y}$Si$_{0.1+y}$ (x = 0, 0.02, 0.04, 0.06, and 0.1) was also slightly decreased with increasing Zr concentration, but its reduction was less obvious than that of Fe$_2$V$_{1-x}$Ir$_x$Al$_{0.9-y}$Si$_{0.1+y}$. Since we kept the carrier concentration in both sets of samples constant, the significant reduction in the Seebeck coefficient observed only at the partial substitution Ir for Fe indicates that the electronic structure varies with the substitution. We investigate, therefore, the variation of electronic structure that is caused by the partial substitution of heavier elements for the constituent elements of Fe$_2$VAI.

### 3.2 Electronic structure

The Fe 3d and V 3d partial density of states of Fe$_2$VAI calculated by using the DVXcm method were plotted in Fig. 4 together with the density of states calculated by the band calculation on the basis of Full-potential Linearized Augmented Plane Wave Method with Generalized Gradient Approximation. Fig. 2 Powder X-ray diffraction patterns measured for (a) Fe$_2$V$_{1-x}$Zr$_x$Al$_{0.9-y}$Si$_{0.1+y}$ (x = 0, 0.02, 0.04, 0.06, and 0.1) and (b) Fe$_2$V$_{1-x}$Ir$_x$Al$_{0.9-y}$Si$_{0.1+y}$ (y = 0, 0.02, 0.04, 0.06, and 0.1). The samples consist almost solely of the objective phase known as the L2$_1$-phase or the Heusler-phase.

### Fig. 2

Powder X-ray diffraction patterns measured for (a) Fe$_2$V$_{1-x}$Zr$_x$Al$_{0.9-y}$Si$_{0.1+y}$ (x = 0, 0.02, 0.04, 0.06, and 0.1) and (b) Fe$_2$V$_{1-x}$Ir$_x$Al$_{0.9-y}$Si$_{0.1+y}$ (y = 0, 0.02, 0.04, 0.06, and 0.1). The samples consist almost solely of the objective phase known as the L2$_1$-phase or the Heusler-phase.
Approximation (FLAPW-GGA). The atomic distances in the original clusters persisting in the unit cell of Fe$_2$VAl were taken from the literature. The energy eigenvalue used in a first principle cluster calculation is different from that of other calculations, because the origin of energy in each package program is not generally identical. Besides, Fermi energy is not identical between cluster calculations and band calculations, because the carrier concentration of the cluster is generally different from that of the crystal. Therefore we slightly moved all the obtained cluster levels with the same amount so as the pseudogap in the cluster calculation to overlap with that of the band calculation, despite that an ambiguity remained in the absolute value of the energy eigenvalue. Nevertheless one can confirm in Fig. 4 that the DVXox partial density of states obtained by the method described above reproduced well the FLAPW-GGA density of states.

It is confidently argued, from the results shown in Fig. 4, that the cluster calculation is capable of providing us with important information about the $d$-orbitals, which is directly related with the pseudogap formation in Fe$_2$VAl. Therefore we calculated, as the second step, the cluster levels by replacing the center atom, Fe or V, with the 4$d$ or 5$d$ transition metal elements. In the present calculation, we selected Ru, Rh, Re, Os, or Ir as the substitute for Fe, while Zr, Nb, Mo, Hf, Ta, or W as that for V. The cluster levels in association with the 4$d$- or 5$d$-orbitals of center atom were transformed into the partial density of states, and the resulting partial density of states was plotted in Figs. 5(a) and (b).

The large magnitude of Seebeck coefficient observed for Fe$_2$VAl is caused by the presence of pseudogap. If the impurity states were located in the pseudogap, the absolute value of Seebeck coefficient is supposed to be reduced. In

![Fig. 4](image)

**Fig. 4** Electronic density of states obtained by the FLAPW-GGA band calculation (solid line) and Fe 3$d$ partial density of states (dashed line) and V 3$d$ partial density of states (dotted line) obtained by the DVXox cluster calculation.

(a) Fe site substitution

![Fig. 5](image)

**Fig. 5** The partial density of states of the $d$-component of transition metal elements that is substituted for Fe or V in the coordination cluster of Fe$_2$VAl. The gray area indicates the energy range of pseudogap. Absence of the cluster orbital in this energy range is required for sustaining the good thermoelectric properties of Fe$_2$VAl.
such a case, the sample should not be used as a practical thermolectric material even if the lattice thermal conductivity is effectively reduced by the substitution. This condition was clearly observed for the present samples of Fe\textsubscript{2−\textit{x}}Ir\textsubscript{\textit{x}}V\textsubscript{0.9−\textit{y}}Ti\textsubscript{0.1+\textit{y}}Al (\textit{y} = 0, 0.02, 0.04, 0.06, and 0.1), in which the cluster orbitals in association with Ir 5\textit{d} orbitals fill the pseudogap and the magnitude of Seebeck coefficient was consequently reduced with increasing Ir concentration.

The band calculation of Fe\textsubscript{2}VAl suggests that the pseudogap is located at $-0.2 \leq \varepsilon - \varepsilon_F \leq 0.3$ eV. We identified, therefore, the elements that do not produce the cluster levels in this particular energy range. From the calculated partial density of states, we realized that Ru and Rh are usable as the substitute for Fe. We also identified that Nb and Mo are appropriate for substituting V. The substitutions of these elements for V in Fe\textsubscript{2}VAl must provide with minor effects on the pseudogap and consequently on the electron transport properties. It is also realized that Zr would be also usable as the substitute for V because the impurity states produced by the Zr 5\textit{d} orbital do not fill the whole pseudogap but the half of it. Notably we have already confirmed in the experiments shown in the previous subsection that the magnitude of Seebeck coefficient of Fe\textsubscript{2}V\textsubscript{1−\textit{x}}Zr\textsubscript{\textit{x}}Al\textsubscript{0.9−\textit{y}}Si\textsubscript{0.1+\textit{y}} (\textit{x} = 0, 0.02, 0.04, 0.06, and 0.1) was not significantly reduced with increasing Zr concentration.

The heavier elements are supposed to have more significant effects on both phonon dispersions and scattering probability to reduce lattice thermal conductivity. Unfortunately, however, all 5\textit{d} elements, Hf, Ta, W, Re, Os, and Ir employed in this study were found to possess cluster levels inside of the pseudogap, when those elements were located in the Fe or V site in Fe\textsubscript{2}VAl. In such a case, Seebeck coefficient would be greatly reduced by the substitutions. This rather negative result suggests that, in order to effectively reduce the lattice thermal conductivity of Fe\textsubscript{2}VAl, we should employ some other technique, such as the use of artificial superlattice, together with the heavy atom substitution.

4. Discussions

In order to develop the Fe\textsubscript{2}VAl-based thermolectric materials possessing a large ZT-value exceeding unity, we have to consider not only the electronic density of states but also the valence electron concentration. We predicted from the present calculation that the presence of pseudogap in the electronic density of states is not greatly affected by (a) Ru or Rh substitution for Fe nor (b) Nb or Mo substitution for V, while these substitutions cause a variation in electron concentration. Since the variation in electron concentration naturally leads to the variation of Seebeck coefficient, one cannot really understand nor control the effect of the heavy element on both the lattice thermal conductivity and electron transport properties without considering the carrier concentration.

The variation in electron concentration caused by the heavier element substitution should be compensated by the other element-substitution. If Si were partially substituted for Al in Fe\textsubscript{2}VAl, the number of electrons would be increased without a significant variation in the band structure because of the absence of \textit{d}-electrons in Al nor Si. We can, therefore, safely use the Si substitution for Al to increase the number of electrons in the sample.

We should also find other elements that could decrease the number of electron in the sample without altering the pseudogap structure. Unfortunately, however, we have not find the best element-substitution for decreasing carrier concentration. We considered that \textit{d}-band of the early transition metal elements, such as Ti and V, would have a less important contribution to the pseudogap formation at the Fermi level, and therefore tentatively employed Ti substitution for V in the present sample, Fe\textsubscript{2−\textit{x}}Ir\textsubscript{\textit{x}}V\textsubscript{0.9−\textit{y}}Ti\textsubscript{0.1+\textit{y}}Al. Although the effect of Ti substitute for V on electronic structure has not been well understood yet, we leave this point unsolved and will investigate it in detail in near future.

We should also make a comment on the potential of Fe\textsubscript{2}VAl as a thermolectric material. We propose in our previous paper that, the practical thermolectric materials should possess a large magnitude of Seebeck coefficient $|S|$ exceeding 200 µV/K to realize ZT > 1, provided that the lattice thermal conductivity $\kappa_\text{lat}$ is effectively reduced to become comparable with the electronic thermal conductivity $\kappa_\text{el}$. To the best of my knowledge, Fe\textsubscript{2}VAl based alloys do not possess such a large Seebeck coefficient. It is honestly argued, therefore, that in order to utilize Fe\textsubscript{2}VAl as a thermolectric material, we have to find the elements which lead not only to the reduction of lattice thermal conductivity but also to a drastic increase of absolute value of Seebeck coefficient. Further analysis both from theoretical calculation and experiments should be strongly required for producing the practical thermolectric materials in the Fe-V-Al-X alloys.

Before closing discussions, we make comments on the previously reported results of the element substitution of Fe\textsubscript{2}VAl. Recently Sugiuira and Nishino\cite{Sugiuira} reported that 3% substitution of Ir for Fe effectively increases the magnitude of Seebeck coefficient of Fe\textsubscript{1.98}V\textsubscript{0.02}Al up to $-176$ µV/K. This fact sounds contradictory to the present calculation and the present experimental result of Fe\textsubscript{2−\textit{x}}Ir\textsubscript{\textit{x}}V\textsubscript{0.9−\textit{y}}Ti\textsubscript{0.1+\textit{y}}Al.

Although we cannot ignore the effect of Ti substitution for V in our samples, we propose the following scenario to account for the two different Ir-substitution effects on the Seebeck coefficient of Fe\textsubscript{2}VAl. It should be mentioned that the increase of Seebeck coefficient due to the Ir substitution is observed only for the \textit{n}-type samples,\cite{Sugiuira} while all the present Fe\textsubscript{2−\textit{x}}Ir\textsubscript{\textit{x}}V\textsubscript{0.9−\textit{y}}Ti\textsubscript{0.1+\textit{y}}Al samples are classified into the \textit{p}-type possessing a positive sign of Seebeck coefficient. This fact suggests that the impurity state of substituted Ir would be located at slightly lower energy than that predicted by our calculation, and therefore that the \textit{n}-type materials, which possess a higher Fermi energy than that of \textit{p}-type materials, were not greatly affected by the small amount of the Ir substitution for Fe while the significant reduction of the Seebeck coefficient was observed for the present \textit{p}-type samples. The variation of valence band just below the Fermi level was observed by means of photoemission spectroscopy,\cite{Sugiuira} and this experimental fact lends a great support to our proposing scenario. Since the present calculation has an ambiguity in energy as it was explained in Results, we need to evaluate the energy eigenvalue of cluster orbitals with a better precision in future work.
5. Conclusion

By making combinational use of the first principles cluster calculation and the band calculation, we identified that Ru or Rh substitution for Fe and Zr, Nb and Mo substitution for V would be useful for decreasing the lattice thermal conductivity without greatly affecting the electron transport properties. The Fe$_2$V$_{1-x}$Zr$_x$Al$_{0.9-x}$Si$_{0.1+x}$ (x = 0, 0.02, 0.04, 0.06, and 0.1) alloys selected as a result of cluster calculation indeed possess a rather weak Zr substitution effect on Seebeck coefficient, while its lattice thermal conductivity is effectively reduced. The Seebeck coefficient of Fe$_2$Ir$_x$V$_{0.9-x}$Ti$_{0.1+x}$Al (x = 0, 0.02, 0.04, 0.06, and 0.1) alloys, on the other hand, decreased with increasing Ir concentration presumably due to the impurity states in association with the Ir 5d electrons persisting in the pseudogap. We conclude, therefore, that the proper understanding of the electronic structure near the Fermi level is strongly required to optimize the thermoelectric properties for obtaining the best performance of thermoelectric materials.

REFERENCES