

Effect of off-stoichiometry on the transport properties of the Heusler-type Fe_2VAl compound

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We report on the effect of off-stoichiometry on the temperature dependence of electrical resistivity, the Seebeck coefficient, and the Hall coefficient in the Heusler-type Fe_2VAl compound. While the stoichiometric Fe_2VAl exhibits a semiconductorlike resistivity behavior, a small deviation of the Al content from stoichiometry causes a significant decrease in the low-temperature resistivity and a large enhancement in the Seebeck coefficient. Substantial enhancements for the Seebeck coefficient are in reasonable accord with changes in the Hall coefficient and can be explained on the basis of the electronic structure, where the Fermi level shifts slightly from the center of a pseudogap due to off stoichiometry.

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The Heusler-type intermetallic compound Fe_2VAl has attracted strong attention because of the occurrence of the semiconductorlike temperature dependence of electrical resistivity over a wide temperature range up to 1200 K and above.^{1,2} Surprisingly, however, photoemission measurements clearly manifested the presence of a sharp Fermi cut-off in its valence-band spectra, which was taken as an evidence for the possession of a metallic band structure. Moreover, Fe_2VAl is found to be in a marginally magnetic state and to exhibit an anomalous enhancement in the electronic specific-heat coefficient at low temperatures, reminiscent of a $3d$ heavy-fermion system coupled with spin fluctuations. Recent band-structure calculations³⁻⁸ consistently predicted that Fe_2VAl should be a compensated semimetal having a deep pseudogap centered right at the Fermi level. The observed unusual transport properties have been interpreted as arising from spin fluctuations^{3,4} or from excitonic correlations.⁵ Indeed, a large electronic mass enhancement has been deduced by analyzing the low-temperature specific-heat data on the basis of the band calculations.^{9,10} A nuclear magnetic resonance (NMR) study of Fe_2VAl revealed a pseudogap with a residual density of states (DOS) at the Fermi level,¹¹ while Hall-effect measurements demonstrated that a majority carrier is holes with the density of about $5 \times 10^{20} \text{ cm}^{-3}$ at 300 K.¹² More recently, the existence of a pseudogap of 0.1–0.2 eV in width has been experimentally confirmed by optical conductivity measurements,¹³ which is apparently consistent with the photoemission results mentioned above.

The unusual transport properties of Fe_2VAl so far reported have been found for nearly stoichiometric compounds and discussed in terms of the band calculations for an ideal Heusler-type compound. However, as mentioned above, the presence of excess holes has been experimentally derived from Hall-effect measurements¹² for stoichiometrically prepared Fe_2VAl samples. We believe that the possession of excess holes is most likely due to either nonstoichiometry or compensating vacancies inevitably introduced in the measured samples. In other words, a small deviation from stoichiometry could cause a large change in the transport prop-

erties of Fe_2VAl . Therefore we consider it to be of crucial importance to study the effect of off-stoichiometry on all the transport properties of Fe_2VAl , including thermoelectric power, taking into account the possession of a deep pseudogap with a rather sharp band edge near the Fermi level.

Mahan and Sofo¹⁴ proposed that the existence of a sharp singularity in the DOS only a few tens of meV from the Fermi level would be a key element in developing a highly efficient thermoelectric material. Thus one can expect the thermoelectric power of Fe_2VAl to be well enhanced by doping or off-stoichiometry, because the DOS rises sharply in both sides of the pseudogap. The purpose of this study is to measure systematically the temperature dependence of electrical resistivity, the Seebeck coefficient, and the Hall coefficient in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys, where the Al content y is varied only in the vicinity of the stoichiometric value of 25.0 at.%. We report a significant decrease in the low-temperature resistivity and a large enhancement in the Seebeck coefficient due to off-stoichiometry and we further discuss both Seebeck and Hall coefficient data on the basis of the electronic structure obtained from the band calculations.

Ingots of $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys ($23.8 \leq y \leq 26.3$), including the stoichiometric Fe_2VAl ($y = 25.0$), were prepared by repeating arc-melting of appropriate mixtures of 99.99% pure Fe and Al and 99.9% pure V in an argon atmosphere. The chemical composition was determined within the accuracy of $\pm 0.2\%$ by inductively coupled argon plasma atomic-emission spectroscopy. As a matter of fact, the composition thus determined agreed with the nominal one for all samples studied and, therefore, we can safely discuss the composition dependence of various transport properties with the accuracy of $\pm 0.1\%$ in the present work. The ingots were homogenized at 1273 K for 48 h in vacuum. Samples were cut from the ingot with a SiC blade saw to the size of $1 \times 1 \times 15 \text{ mm}^3$ for resistivity measurements, $0.5 \times 0.5 \times 5 \text{ mm}^3$ for thermoelectric measurements, and $0.5 \times 1 \times 7 \text{ mm}^3$ for Hall-effect measurements. Each sample was sealed in an evacuated quartz capsule and was annealed at 1273 K for 1 h and then at 673 K for 4 h followed by furnace cooling. According to x-ray

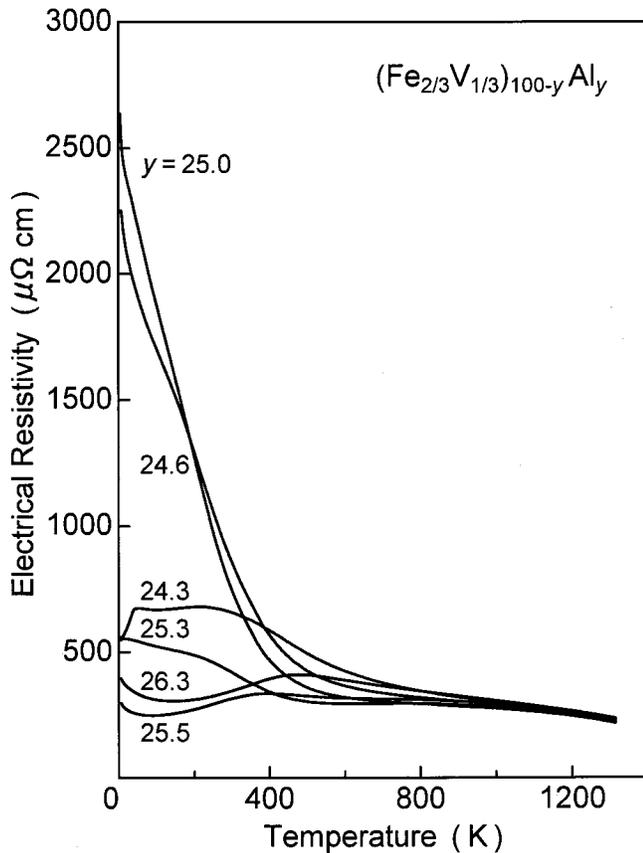


FIG. 1. Temperature dependence of electrical resistivity in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ with $24.3 \leq y \leq 26.3$. Note that the stoichiometric Fe_2VA ($y = 25.0$) exhibits a semiconductorlike behavior.

diffraction analysis, all samples were identified as a single-phase Heusler-type ($L2_1$) structure.

The electrical resistivity was measured by a standard dc four-terminal method with a current of 100 mA over the temperature range 4.2–1273 K and with a rising rate of 0.05 K/s: the measurements at high temperatures were carried out in a vacuum of 4×10^{-4} Pa. Figure 1 shows the temperature dependence of the electrical resistivity in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys. As was reported in Ref. 1, the stoichiometric Fe_2VAI ($y = 25.0$) exhibits a semiconductorlike behavior with the resistivity of about $2600 \mu\Omega \text{ cm}$ at 4.2 K. The $\ln \rho$ versus $1/T$ plots (ρ , resistivity; T , temperature) for the data on $y = 25.0$ becomes almost linear in the temperature interval 400–800 K, and an energy gap of approximately 0.1 eV is deduced from its slope. A similar thermal excitation behavior has been observed by NMR experiments,¹¹ which yield an energy gap of about 0.2 eV. We consider the thermal excitation to originate from the presence of a pseudogap at the Fermi level in Fe_2VAI , as predicted by the band calculations^{3–8} and experimentally confirmed by optical conductivity measurements.¹³

As soon as the Al content deviates from 25.0 at.%, the semiconductorlike resistivity behavior disappears rapidly, as shown in Fig. 1. It can be seen that an increase in the Al content beyond 25.0 at.% is more effective in reducing the resistivity. In particular, the resistivity for $y = 25.5$ is reduced

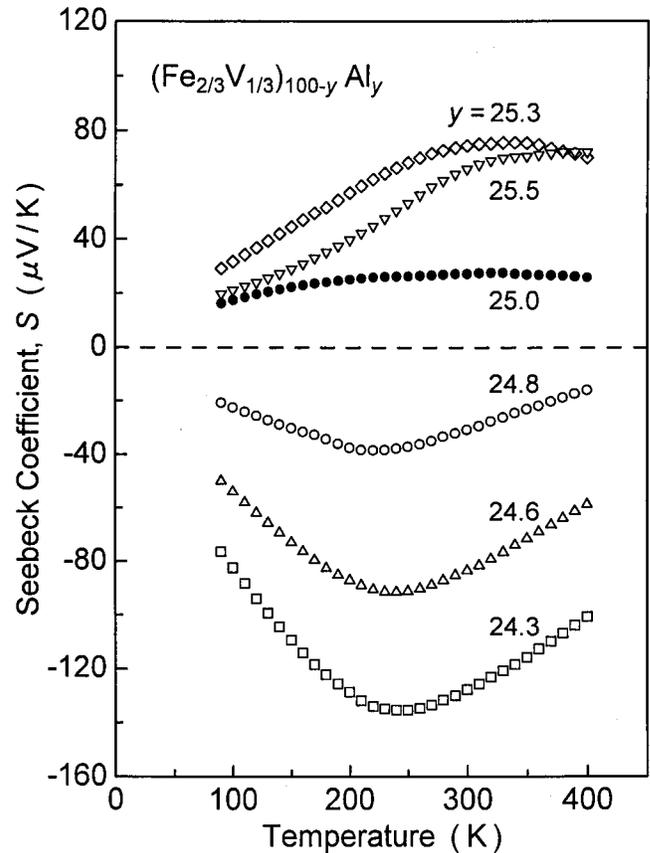


FIG. 2. Temperature dependence of Seebeck coefficient S in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ with $24.3 \leq y \leq 25.5$. A sign of S is positive for $y \geq 25.0$ but is negative for $y < 25.0$.

to only $300 \mu\Omega \text{ cm}$ at 4.2 K, which is almost an order of magnitude lower than that for $y = 25.0$, and a positive slope in its temperature dependence appears in the region below 400 K. Similarly, the lowering of the Al content below 25.0 at.% also leads to a rapid decrease in the low-temperature resistivity, to $600 \mu\Omega \text{ cm}$, and the resistivity curve for $y = 24.3$ shows an angular change around 50 K due to the ferromagnetic ordering. In spite of a significant decrease in the low-temperature resistivity, all the resistivity curves almost coincide with each other at high temperatures above 900 K. A substantial reduction in the resistivity at room temperature due to off-stoichiometry certainly acts in favor of the development of thermoelectric materials.

The Seebeck coefficient was measured with a commercially available apparatus (MMR Technologies, SB-100) in the temperature range 90–400 K. In Fig. 2 the Seebeck coefficient S for a series of $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys is shown as a function of temperature. The value of S for the stoichiometric Fe_2VAI ($y = 25.0$) is positive and centered around $20\text{--}30 \mu\text{V/K}$ over the whole temperature range examined. A relatively small value of S most likely reflects the fact that the numbers of carriers of electron and hole pockets are nearly compensated. A positive sign of S indicates that a majority carrier must be holes, being consistent with Hall-effect measurements reported earlier.¹² When the Al content is increased above 25.0 at.%, the Seebeck coefficient in-

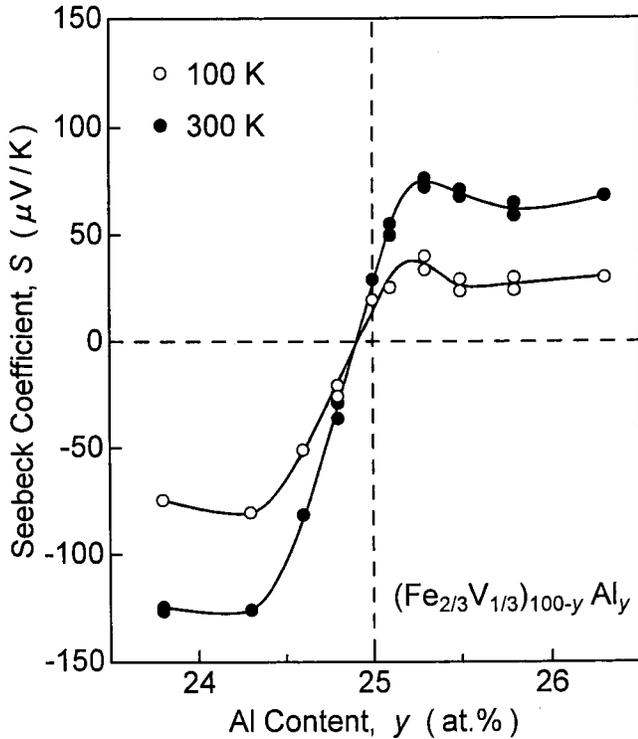


FIG. 3. Seebeck coefficient S at 100 and 300 K as a function of Al content y in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$.

increases with increasing temperature and reaches $S = 75 \mu\text{V/K}$ at 300 K for $y=25.3$. When the Al content is lowered below 25.0 at.%, the sign of S becomes negative and the absolute value increases remarkably with decreasing y : $S = -125 \mu\text{V/K}$ at 300 K for $y=24.3$. In Al-poor samples, the absolute value of S increases gradually as the temperature increases, forming a broad maximum at around 240 K, and then turns to decrease. The decrease in $|S|$ above about 240 K is probably due to an increasing number of thermally excited carriers across the pseudogap, being consistent with the NMR relaxation behavior.¹¹

In order to make clear the effect of off-stoichiometry, the Seebeck coefficient S , measured typically at 100 and 300 K, is shown in Fig. 3 as a function of the Al content y in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys. The most spectacular feature is that an increase in y causes a rapid change from a large negative to a positive value of S . In particular, the value of S varies most significantly in the vicinity of the stoichiometric composition and passes through $S=0$ at $y=24.9$. It is clear that electrons serve as a majority carrier for Al-poor samples with $y < 24.9$ while holes for Al-rich samples with $y > 25.0$. A similar change in the Seebeck coefficient with composition has been reported by Ferrier and Herrell¹⁵ for the amorphous Mg-Bi alloy system, where the pseudogap grows as a metal-insulator transition is approached.

We expect a change in the sign of the Seebeck coefficient most likely to occur concomitantly with the y dependence of the Hall coefficient. For a valuable counterpoint to Fig. 3, the Hall coefficient measured at 100 and 300 K is shown in Fig. 4 as a function of the Al content y in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$ alloys. It was found that the Hall resistivity increased almost

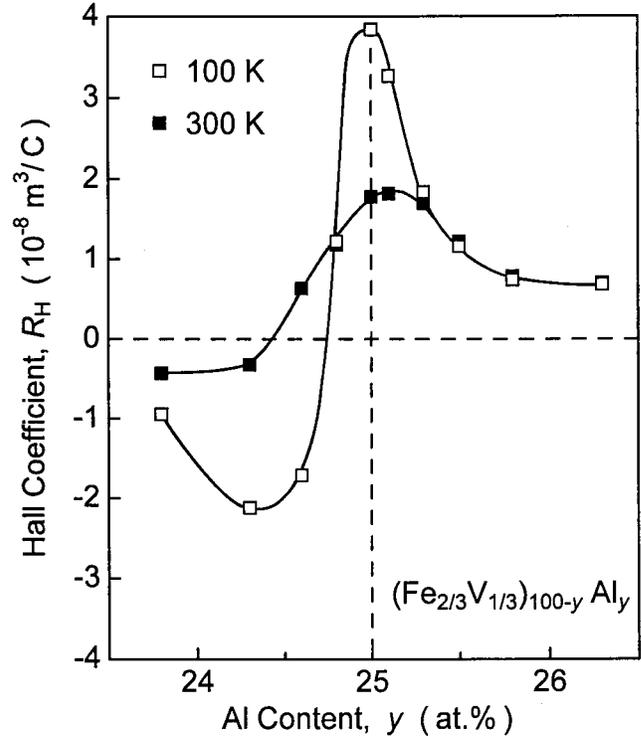


FIG. 4. Hall coefficient R_H at 100 and 300 K as a function of Al content y in $(\text{Fe}_{2/3}\text{V}_{1/3})_{100-y}\text{Al}_y$.

linearly with increasing magnetic fields up to 5 T and that we could determine the Hall coefficient R_H by taking its slope at high fields. The magnitude of R_H for the present samples is found to be of the order of $10^{-8} \text{ m}^3/\text{C}$, which is 10^2 – 10^3 times larger than that found in conventional metals and is nearly equal to that of elemental semimetals like Sb. As reported earlier,¹² the value of R_H for the stoichiometric Fe_2VAl ($y=25.0$) is positive and increases remarkably as the temperature decreases. This demonstrates that the hole-type carriers dominate in good agreement with the possession of a positive sign of the Seebeck coefficient for $y = 25.0$. Both the Hall and Seebeck coefficient data strongly support that Fe_2VAl is a low-carrier density semimetal having slightly excess holes relative to electrons. As is clearly seen from Fig. 4, a change in R_H at 100 K is extremely large as the Al content passes through stoichiometry. In particular, when the Al content is lower than 25.0 at.%, the value of R_H becomes negative and rapidly decreases with decreasing y , indicating that the electron-type carriers dominate the transport properties of Al-poor samples. In contrast, when the Al content exceeds 25.0 at.%, the value of R_H becomes positive, taking its maximum near the stoichiometric composition. Therefore, the y dependence of the Hall coefficient agrees well with that of the Seebeck coefficient shown in Fig. 3.

Let us discuss further the y dependence of the Seebeck and Hall coefficients in terms of the electronic structure obtained from the band calculations for Fe_2VAl . The band structure near the Fermi level is roughly illustrated in Fig. 5: the Fermi level E_F is denoted by the horizontal solid line. The Fermi surface consists of small hole pockets centered at

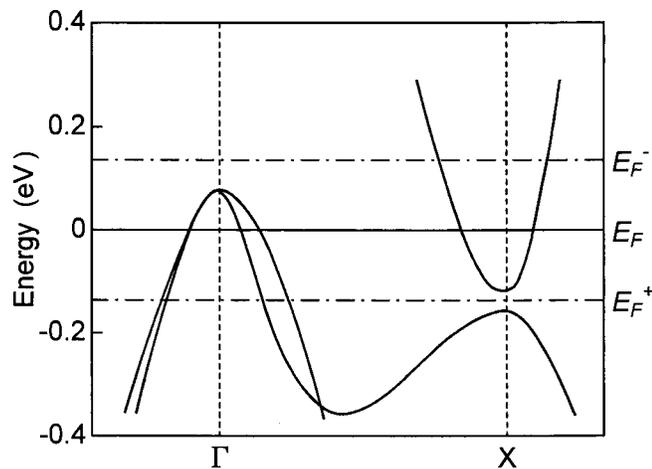


FIG. 5. Schematic illustration of the band structure near the Fermi level, reproduced from the band calculations for Fe_2VAI (Ref. 3). The Fermi level is denoted as E_F (solid line) for the stoichiometric Fe_2VAI , and E_F^+ and E_F^- (dash-dotted lines) for Al-rich and Al-poor samples, respectively.

point Γ and a small electron pocket at point X .^{3,4} The hole pocket arises from the Fe $3d$ -dominant bands while the electron pocket arises mainly from the V $3d$ bands. Both electron and hole pockets are very small, thereby giving rise to a very small number of carriers, as evidenced by NMR relaxation¹¹ and Hall-effect measurements.¹²

Since the DOS within the pseudogap is very small, a small change in the electron concentration would result in an appreciable shift of the Fermi level from the central region in the pseudogap. We believe that there is an almost rigid-band-like shift of the Fermi level as the Al content varies only

within ± 1.5 at. % from 25.0 at. %. In this picture, a decrease in the Al content below $y=25.0$ leads to an increase in the total density of valence electrons because of an accompanying increase in the Fe and V contents, whereas an increase in the Al content above $y=25.0$ leads to a decrease in the total density of valence electrons or a downward shift of E_F^+ , as shown in Fig. 5. Thus an increase in the hole density is expected to occur in Al-rich samples, being consistent with the possession of a positive sign of the Seebeck coefficient. Similarly, Al-poor samples give rise to an upward shift of E_F^- , and an increase in the electron density must be responsible for a negative sign of the Seebeck coefficient.

The thermoelectric performance is often characterized by the figure of merit, $Z=S^2\sigma/\kappa$, where σ and κ are the electrical and thermal conductivity, respectively. We have shown that off-stoichiometric samples of Fe_2VAI exhibit a large enhancement in both S and σ , although the value of κ is not yet known. In particular, a large magnitude of the Seebeck coefficient has been obtained by varying the Al content only slightly from stoichiometry, i.e., $S=-125\ \mu\text{V/K}$ for the Al-poor sample with $y=24.3$ at 300 K, and $S=75\ \mu\text{V/K}$ for the Al-rich sample with $y=25.3$. We conclude that a substantial shift of E_F from the center of the pseudogap due to off-stoichiometry can account for a large enhancement in the Seebeck coefficient with both positive and negative signs and for a significant reduction in the low-temperature resistivity. In this respect, the pseudogap system Fe_2VAI deserves further studies as an intriguing candidate for low- and intermediate-temperature thermoelectric applications.

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