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# Low-temperature electrical transport in Heusler-type $\text{Fe}_2\text{V}(\text{AlSi})$ alloys

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## Abstract

The temperature variation of the electrical resistivity  $\rho$  and the Seebeck coefficient  $S$  of Heusler-type  $\text{Fe}_2\text{VAl}_{1-x}\text{Si}_x$  ( $0 \leq x \leq 1$ ) alloys has been investigated. We have shown that the transport parameters are very sensitive to doping. For the  $x = 0$  sample, high values of  $\rho$  and negative temperature coefficient of resistivity (TCR) have been observed. As the Si concentration increases,  $\rho$  decreases and the TCR changes its sign, while  $S$  shows significant changes in magnitude as well as sign when Al is replaced with Si. These changes appear to be reminiscent of a metal to semiconductor transition. It has been shown that the conventional transport theories proposed for intermetallic alloys or semiconductors cannot explain the transport behaviour in the whole temperature range of the present study. Low-temperature resistivity data of  $x = 0$ – $0.02$  samples could be described with a gapless semiconductor model. The strong composition dependence of  $S$  and  $\rho$  is attributed to the sharp variations in electronic density of states at the Fermi energy. It is also shown that by optimum doping one can achieve very large values of power factor ( $P$ ). The estimated power factor at room temperature is observed to be highest ( $2.23 \times 10^{-3} \text{ W mK}^{-2}$ ) for  $x = 0.06$  and comparable to that of conventional thermoelectric material. At lower temperatures  $P$  is found to be even higher than that of conventional thermoelectric material.

## 1. Introduction

Recently there has been considerable interest in the materials with complex band structure that exhibit peculiar magnetic and electrical transport properties [1]. Phenomena such as heavy fermion behaviour, a Kondo insulating state and unconventional superconductivity

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are frequently found in these materials [2, 3]. It has been argued that the hybridization is responsible for these observations. This may further lead to the formation of narrow electronic gaps or pseudogaps at the Fermi level, contribute to unusual physical properties. Another class of materials exhibiting intriguing interplay between the electronic structure and magnetic properties is the so-called Heusler alloys. Heusler compounds of the form  $X_2YZ$ , where X and Y are elements with partly occupied *d-electron* orbital and Z is an sp electron metal, are formed as cubic ( $L2_1$ ) metals. From the band structure calculations on the intermetallic Heusler compounds, a half-metallic structure was first reported. In these materials, the bands for minority spin electrons show a gap at the Fermi level, whereas the Fermi level intersects the majority spin electron band, or vice versa. On the basis of an extended study, it has been suggested that the onset of ferromagnetism in these compounds and alloys is associated with a semiconductor to metal transition. The  $Fe_2VAl$  alloy system is identified as a Heusler system with unusual electronic properties [4, 5]. As far as fundamental physics is concerned, contrasting experimental results have appeared in the literature on this system. For instance, its high electrical resistivity ( $\rho \sim 10^3 \mu\Omega \text{ cm}$ ) and negative temperature coefficient of resistivity (TCR) distinguish it from conventional intermetallic compounds. The resistivity values are quite sensitive to the substitution elements, which is reminiscent of doped semiconductors [4–6]. But unlike intermetallic semiconductor, nuclear magnetic resonance and photoemission experiments on  $Fe_2VAl$  suggest a reasonable density of states (DOS) at the Fermi level  $E_F$  [6, 7], while Hall-effect measurements suggest that the majority carriers are holes with a density of about  $5 \times 10^{20} \text{ cm}^{-3}$  at 300 K [8]. The optical conductivity studies provided evidence for a pseudogap in the density of states of  $Fe_2VAl$  [9], a view supported by various band structure calculations [1, 10, 11]. These theoretical calculations further consistently predicted that  $Fe_2VAl$  is a compensated semimetal having a deep pseudogap of 0.1–0.2 eV at the Fermi level [7–12]. Other possible mechanisms such as heavy-Fermion [13] and spin-fluctuations [7, 8] have also been suggested in order to explain the anomalous electronic behaviour in this system. A non-magnetic behaviour down to 4.2 K is reported in spite of having 50% of Fe in the alloy [12]. However, recently it has been suggested that the presence of superparamagnetic clusters gives rise to the large values of magnetoresistance [1, 14–17]. The off-stoichiometric  $Fe_2VAl$  also showed an anomalously large Seebeck coefficient ( $S$ ), indicating its potential for a new thermoelectric material. Unfortunately the large Seebeck coefficient encountered in these alloys cannot be useful in practice, as the power factor is reduced drastically due to high electrical resistivity. One of the current challenges is therefore to reduce the relatively high electrical resistivity ( $\rho$ ) and thermal conductivity ( $\kappa$ ) values but retaining the high values of  $S$ , in order to obtain the higher values of figure of merit ( $Z = S/\rho\kappa$ ). It has been shown that, in some half-Heusler alloys, by optimal doping one can reduce the resistivity and even increase the  $S$ -values to further enhance the power factor.

In order to further understand the electronic properties, various elements have been doped in this ternary system [18–21]. Recently, Jemima *et al* have reported a metal to insulator transition (MIT) in Si-doped  $Fe_2VAl$ , though the actual ground state of the undoped alloy is still not clear [18]. On the other hand Si-substituted alloys exhibit large Seebeck coefficient and lower resistivity values at elevated temperatures [19, 20], making them potential candidates for thermoelectric applications. However, a particular mechanism encompassing the peculiarities of their electronic structure and their unusual transport properties within a unifying scheme still remains elusive. The puzzle includes the basic fundamental question whether the purported transport anomalies should be mainly attributed to the characteristic electronic band structure or structural/chemical disorder. Although a large number of systematic investigations on ternary systems are available, such investigations on Si-substituted  $Fe_2VAl$  are still lacking, and they will be useful for further understanding of the electronic ground state of these

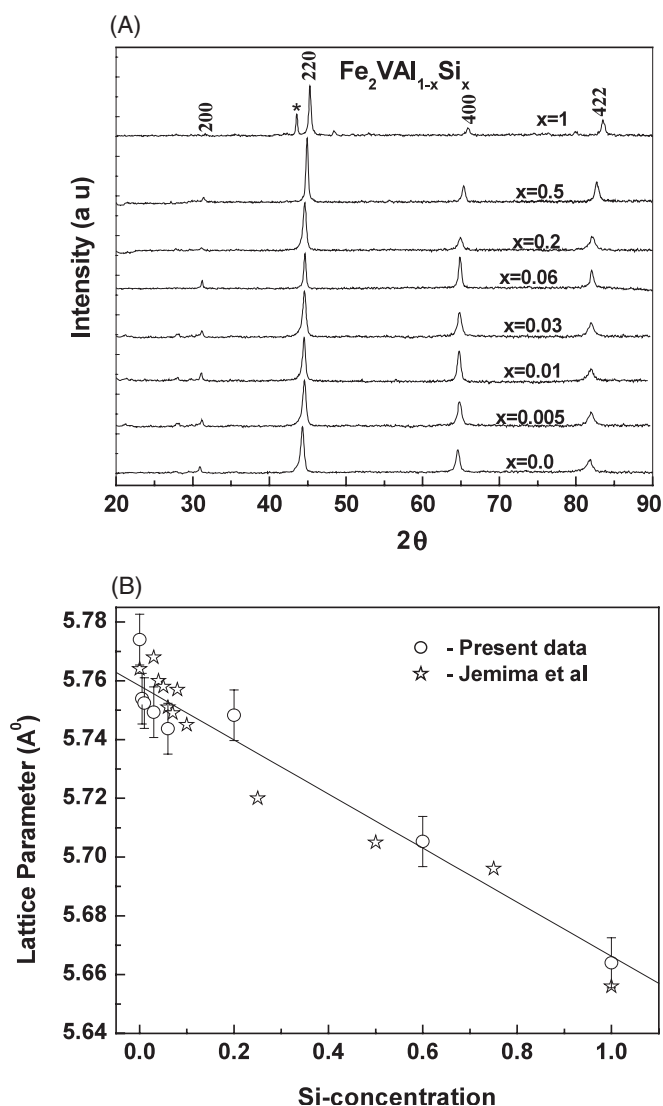
materials. While low-temperature resistivity and high-temperature Seebeck coefficient studies have been reported on similar systems [18, 19], a detailed transport measurement over the same temperature range is still missing. Hence further investigations are needed to understand the scattering processes involved in causing such unusual behaviour mentioned above. In the present work, we report the temperature dependence of the electrical resistivity ( $\rho$ ) and Seebeck coefficient ( $S$ ) of the Fe<sub>2</sub>VAl<sub>1-x</sub>Si<sub>x</sub> alloys with  $x = 0-1$ . The present investigation also attempts to understand the scattering processes involved in the transport mechanism. Further, we investigate whether the optimum transport parameters observed in this system can provide us with some power factor values comparable to the conventional commercial thermoelectric materials.

## 2. Experimental details

Alloy ingots of Fe<sub>2</sub>VAl<sub>1-x</sub>Si<sub>x</sub> ( $0 \leq x \leq 1$ ) were prepared with high-purity elemental constituents using an arc-melting furnace under argon atmosphere. The ingots were annealed in evacuated quartz tubes at 1200 K for 48 h to improve the homogeneity of the alloys. Properties of both as-cast and annealed samples have been investigated for some compositions. The samples were structurally characterized by powder x-ray diffraction (XRD) with Cu K $\alpha$  radiation. The nominal composition assigned to each sample was regarded as accurate, because the weight loss was found to be less than 0.3–0.5%. However, the bulk composition was analysed using an energy dispersive x-ray (EDX) analysis in a scanning electron microscope (SEM). The analytical values are quite consistent with the nominal compositions reported in this study. Since the ingots are mechanically hard, they were then cut into suitable shapes for the physical property measurements with a spark-erosion apparatus. The samples for electrical resistivity were prepared by cutting the ingots in the form of small rectangular bars 2 mm  $\times$  2 mm  $\times$  6 mm by spark erosion. The resistivity of samples was measured using a standard dc four-terminal method with a current of 20–100 mA. The Seebeck coefficient ( $S$ ) was measured using a homemade apparatus over the temperature range from 12 to 300 K. The sample was sandwiched between two copper blocks using a spring-loaded plunger-type sample holder. A calibrated platinum resistance thermometer was used to measure the absolute temperature of the sample. A small heater of constantan wire (180  $\Omega$ ) wound non-inductively on one end of the sample holder is used to create the required temperature gradient. The temperature difference between two copper blocks was measured using a calibrated Au 0.07% Fe–chromel differential thermocouple, while the temperature of the bottom copper block was directly measured with a calibrated platinum sensor coupled to a Lakeshore (Model 850) temperature controller. The thermo emf,  $\Delta E$ , developed across the specimen with reference to copper and the emf of the differential thermocouple (giving  $\Delta T$ ) were measured using a Keithley nanovoltmeter (Model 192). The absolute temperature of the sample was estimated as  $T_{\text{ave}} = T_{\text{coldblock}} + \frac{\nabla T}{2}$ , where  $\nabla T$  is the temperature difference between the upper and lower copper blocks. The absolute  $S$  value of the sample was calculated after correcting for the  $S$  value of copper ( $S_{\text{sample-cu}} = S_{\text{cu}} - S_{\text{sample}}$ ). Details of the sample holder and the cryostat to measure ' $S$ ' at low temperatures (12–300 K) are given elsewhere [20].

## 3. Results and discussion

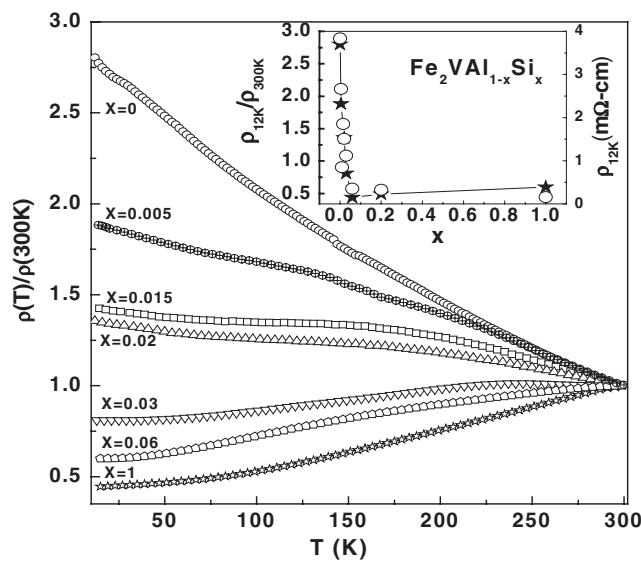
As-cast ingots and those annealed at 1200 K for 48 h of Fe<sub>2</sub>VAl alloy do not show any significant differences in x-ray diffraction patterns [20, 21]. Therefore, in the present investigation, we have presented the results on as-prepared samples. The presence of strong reflections at (200),



**Figure 1.** (A) XRD patterns of as-prepared  $\text{Fe}_2\text{VAI}_{1-x}\text{Si}_x$  alloys. (B) Variation of lattice parameter as a function of Si concentration.

(220), (400) and (422) in the XRD patterns confirms the existence of the  $\text{DO}_3$  structure. The overall XRD pattern essentially remains unaltered on replacement of Al by Si (see figure 1(A)). This observation is consistent with the earlier reports on Si-doped  $\text{Fe}_2\text{VAI}$  alloys [18]. The variation of the lattice parameter extracted from these patterns as a function of Si substitution is shown in figure 1(B). The lattice parameter is found to decrease linearly with Si content and this can be attributed to the fact that the ionic radius of Al is larger than that of Si.

Electrical transport studies on off-stoichiometric  $\text{Fe}_2\text{VAI}$  alloys suggest that these properties are sensitive to the electron concentration [18–20]. The observed large electrical resistivity value at low temperatures for the case of  $x = 0$ , is in agreement with published results [4–8, 18]. Anomalies observed in the temperature variation of resistivity,  $\rho(T)$ , are



**Figure 2.** Normalized electrical resistivity as a function of temperature for  $\text{Fe}_2\text{VAl}_{1-x}\text{Si}_x$ . Inset: variation of change in resistance and absolute resistivity as a function of Si content. Open and filled symbol scales are represented by left and right axes respectively.

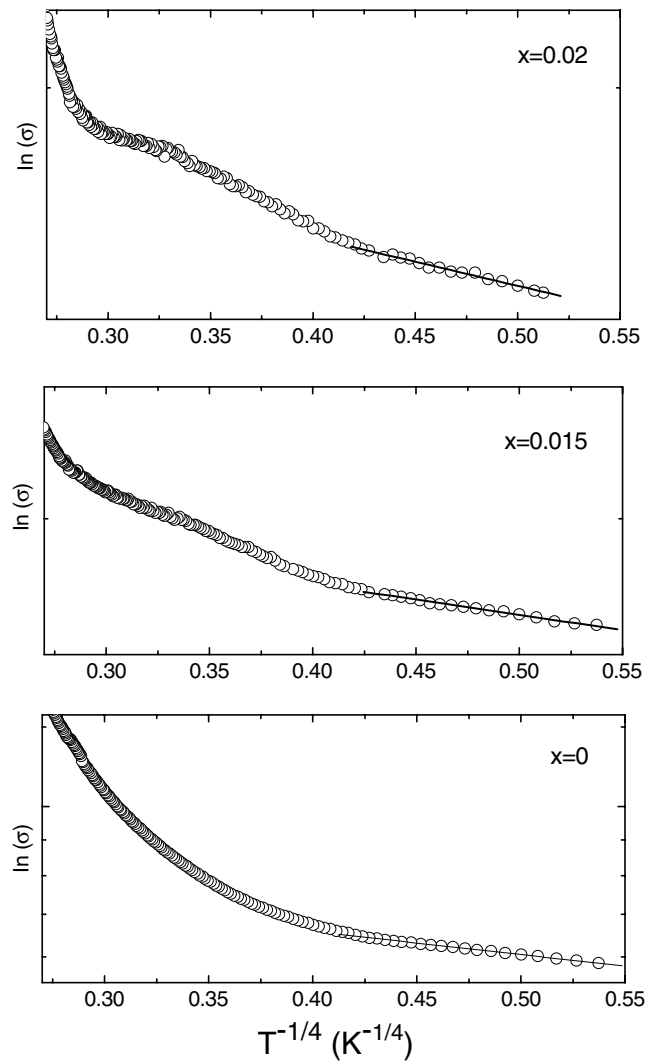
barely discernible if they are plotted together on the same scale. This is because the absolute values of resistivity change rapidly with Si concentration. Therefore, normalized resistivity  $\rho(T)/\rho(300\text{ K})$  as a function of temperature is plotted for all the samples in figure 2. The  $\text{Fe}_2\text{VAl}$  ( $x = 0$ ) exhibits a negative TCR with a room-temperature resistivity value of ( $\rho_{300\text{ K}}$ )  $\sim 2\text{ m}\Omega\text{ cm}$ . As shown in the figure, a minute amount of Si substitution for Al causes a sharp decrease in electrical resistivity and the sign of the TCR changes from negative value to positive, while intermediate compositions develop a minimum and maximum in the  $\rho(T)$  curve. Finally, the  $\text{Fe}_2\text{VSi}$  sample shows positive TCR with higher values of  $\rho$  compared to that of pure metals or intermetallic alloys. The net change in resistance with temperature for a particular sample can be estimated by the resistance ratio  $\text{RR} = \{\rho(12\text{ K})/\rho(300\text{ K})\}$ , which is plotted as a function of Si content (see inset of figure 2) along with the absolute values of resistivity. The changes are reminiscent of a semiconductor to metal transition. But identification of the metal to semiconductor transition (MST), particularly in the vicinity of a transition, is difficult. Earlier workers have adopted various schemes to decide reliably whether a particular composition lies in the metallic or semiconducting region, by studying the temperature dependence of electrical conductivity. Generally samples are termed as metallic as long as the extrapolated conductivity at absolute zero,  $\sigma(0)$ , is positive. However, this extrapolation method runs into difficulty when the system is close to the MIT. On the other hand, in a logarithmic derivative method, one considers a parameter defined as  $w(T) = d \ln(\sigma)/d \ln(T)$ , which is far more sensitive than the conductivity itself [22]. It was suggested that with this method one can identify whether a particular composition lies in the insulating or metallic side of the MIT by evaluating  $w$  as  $T \rightarrow 0\text{ K}$ . Such an analysis on low-Si-content samples results in a finite value of  $w$  as  $T \rightarrow 0\text{ K}$ , indicating a weakly insulating character, while for  $x = 1$ ,  $w$  turned out to be zero, indicating metallic behaviour. It would be helpful to perform this kind of analysis on the conductivity data taken down to the millikelvin range. In the present case we have extracted the low-temperature data by fitting  $\sigma(T)$  data to a suitable functional form and subsequently the

above analysis has been performed. We obtained reasonable results considering the crudeness of data extraction.

On the other hand, observed large residual resistivity values in the range 3833–152  $\mu\Omega$  cm could be due to the electronic or structural disorder. But when samples were annealed at 1200 K for 48 h, the resistivity values further increased, while for rapidly solidified ribbons the resistivity values were found to be lower compared to as-cast samples. This is contrary to the expectations for the normal intermetallic alloys, where on annealing the structural disorder is reduced and in turn the resistivity is reduced. Therefore, it may be concluded that the source of high resistivity values is not the structural disorder like in disordered materials. Alternatively, such high resistivity values could be due to localization effects. In disordered systems the quantum interference effects such as weak localization and electron–electron interactions can give rise to the higher values of  $\rho$  and negative TCR [23]. Our attempts to fit the data to the quantum interference effect theories did not, however, yield good fits. This is also consistent with the magnetoresistance results [4, 5], where it was argued that the weak localization effects may not be the primary mechanism causing negative TCR. Since the conventional theories proposed for metals and disordered alloys failed to explain the  $\sigma(T)$  behaviour, alternative mechanisms to explain the non-metallic character have to be explored. However, the  $\sigma(T)$  data could not be fitted to the classical law of strong localization. On the other hand, in Mott–Anderson insulators, conduction at lower temperatures is expected to proceed via electron hopping between exponentially localized states. In the mechanism of variable range hopping (VRH) proposed by Mott [24], electrons may preferentially hop to localized sites which are close in energy, but not necessarily close spatially. The conduction law of VRH is given by the following equation:

$$\sigma(T) = \sigma_0 \exp - \left( \frac{T_0}{T} \right)^p \quad (1)$$

with  $p = 1/4$ . The activation temperature  $T_0$  varies as  $1/\xi^3$  where the localization length ( $\xi$ ) diverges at the MIT. The widely studied VRH conduction mechanism has been observed at low temperatures in many disordered insulators including highly doped semiconductors, and semiconductor–metal or insulator–metal alloys. We have plotted  $\ln \sigma(T)$  versus  $T^{-p}$  with  $p = 1, 1/2$  and  $1/4$ . As shown in figure 3, the VRH law with  $p = 1/4$  fits well to  $\sigma(T)$  in the limited temperature range 12–40 K for  $x = 0, 0.015$  and  $0.02$ . From these fits we extracted the activation temperature  $T_0$ , which is in the range of 1–10 mK. Following the usual interpretation of the activation law, one can estimate  $\xi$  from  $T_0 \approx 18/\xi^3 k_B n(E_F)$ , provided the nature of electronic density of states,  $n(E_F)$ , at the Fermi level is known. A rough estimate of  $n(E_F)$  can be obtained from specific heat measurements. However, such data are not available on these samples to determine  $\xi$ . The energy gap of a few meV obtained from the present analysis for low-Si-containing alloys appears to be unphysical. Therefore, we rule out the possibility of the presence of a gap in this system. Further, we also observed that, above 50 K, a VRH description is too strong to explain the data. Instead a simple power law,  $\sigma(T) = A + BT^n$ , seems to be an adequate approximation at higher temperatures. A power law fit to the data in the temperature range  $200 \text{ K} < T < 300 \text{ K}$  resulted in a value of  $n = 3/2$ . In figure 4,  $\sigma(T)$  is plotted as a function of  $T^{3/2}$ , which shows a linear behaviour for low-Si-containing alloys. As the Si concentration increases, the deviation from  $T^{3/2}$  dependence is observed to be more significant. A close observation of figure 2 indicates that as the Si concentration increases the TCR goes from negative to positive along with the co-existence of negative and positive TCR at the intermediate compositions. These observations indicate the gradual diminishing of the non-metallic nature as the Si concentration increased. It is known that such a  $\sigma(T)$  dependence is typical of doped semiconductors in temperature ranges corresponding



**Figure 3.**  $\ln \sigma(T)$  versus  $T^{-1/4}$  for samples  $x = 0, 0.015$  and  $0.02$ .

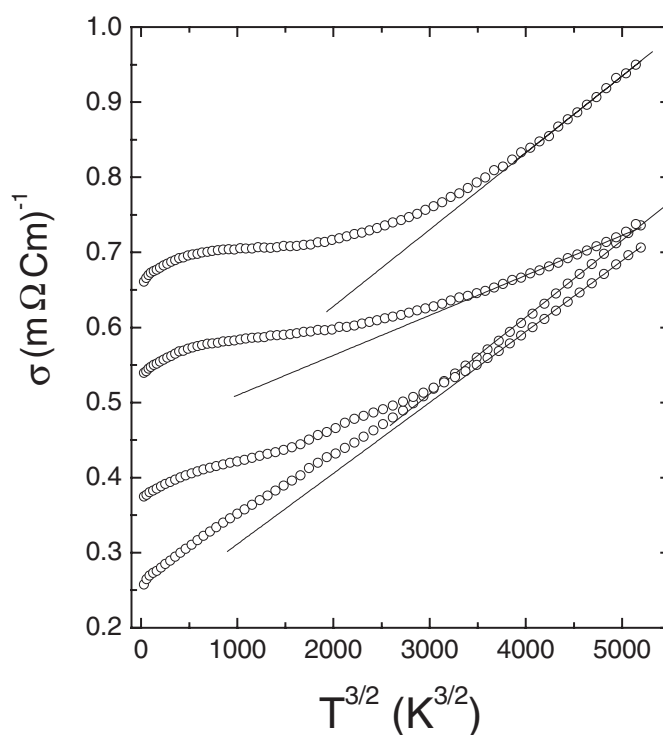
to the intrinsic conductivity, in which the concentration of charge carriers is described by the expression

$$n_{e,h} = 2(m_e m_h)^{3/4} \left( \frac{k_B T}{2\pi \hbar^2} \right)^{3/2} \exp\left(-\frac{E_g}{2k_B T}\right) \quad (2)$$

where all symbols have their usual meaning. Since no data on the temperature dependence of the mobility are available, we assume the mobility to be constant in the conductivity expression  $\sigma(T) = (n_e e \mu_e + n_h e \mu_h)$ , in the zero band gap approximation. On this basis, our results can be regarded as an experimental proof of the fact that the intrinsic conductivity of the Fe<sub>2</sub>VAl sample at higher temperatures follows the  $T^{3/2}$  law. This is consistent with the results of infrared reflectance data and the theoretical predictions of a narrow energy gap.

With the increase in Si concentration, the resistivity and RR (see inset of figure 2) decrease further and attain metallic character, though the resistivity values are higher than those observed





**Figure 4.** Electrical conductivity as a function of  $T^{3/2}$  for  $\text{Fe}_2\text{VAl}_{1-x}\text{Si}_x$ ,  $x = 0, 0.005, 0.015$  and  $0.02$  (bottom to top). The solid lines represent fits to the data.

in metals. It is interesting to point out here that the values of  $\rho_{300\text{ K}}$  for present as-cast alloys are higher than those observed by Nishino *et al* and Jemima *et al* (see in figure 6). These deviations could be due to the microstructural differences in the samples or intrinsic disorder. The origin of the crossover (negative to positive TCR) and the sensitivity of the electrical conductivity with impurity appear to be related to the band structure modification. The remarkable changes in  $\rho_{300\text{ K}}$  with Si concentration suggest a possible existence of a sharp singularity in the density of states (DOS). Band structure calculations also predicted that  $\text{Fe}_2\text{VAl}$  is a compensated semimetal having a deep pseudogap at the Fermi level. Such properties certainly acts in favour of the development of thermoelectric materials.

The temperature dependence of the Seebeck coefficient,  $S(T)$ , is more sensitive than  $\sigma(T)$  to the variation in the energy spectrum,  $\sigma(E)$ , near  $E_F$ . Therefore  $S(T)$  provides complementary information about the electronic band structure near the Fermi level. Some of the samples of the present series exhibit large values of  $S$  when compared to those of metallic materials. The temperature dependences of  $S$  for the alloys  $\text{Fe}_2\text{VAl}_{1-x}\text{Si}_x$  with  $x = 0-1$  are depicted in figure 5. For  $x = 0$ ,  $S$  is observed to be positive over the entire temperature range of the present study. As the temperature increases,  $S$  increases and passes through a maximum at about 180 K, while for  $x = 1$ ,  $S$  is negative, decreases with temperature and shows a broad minimum in the intermediate temperature range. In these compositions the maximum value of  $S$  was observed to be  $+50\ \mu\text{V K}^{-1}$  ( $x = 0$ ), increases to a very large negative value of  $-220\ \mu\text{V K}^{-1}$  ( $x = 0.06$ ) and eventually reverts to  $-28\ \mu\text{V K}^{-1}$  ( $x = 1$ ). Contrary to our expectations, a small variation in the chemical composition (few at.% of Si, for Al) resulted in a remarkable change in the magnitude ( $>220\ \mu\text{V K}^{-1}$ ) as well as in the sign

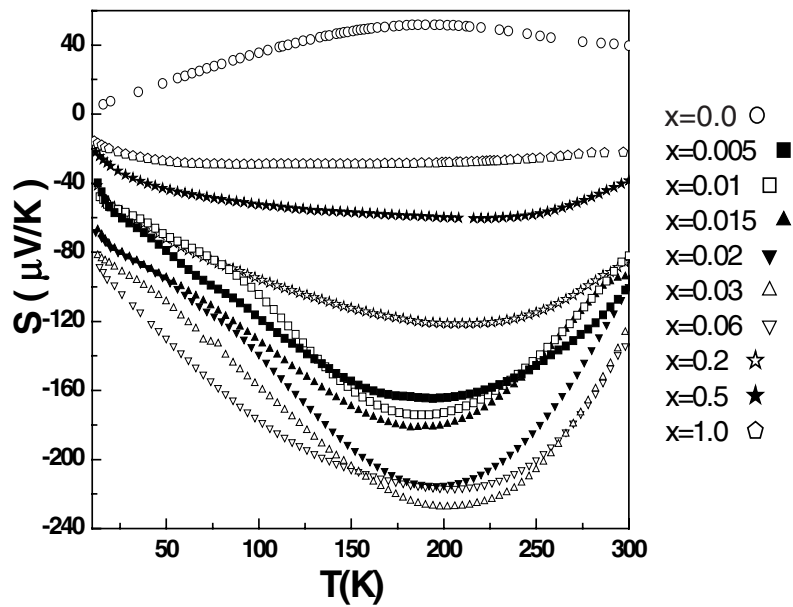
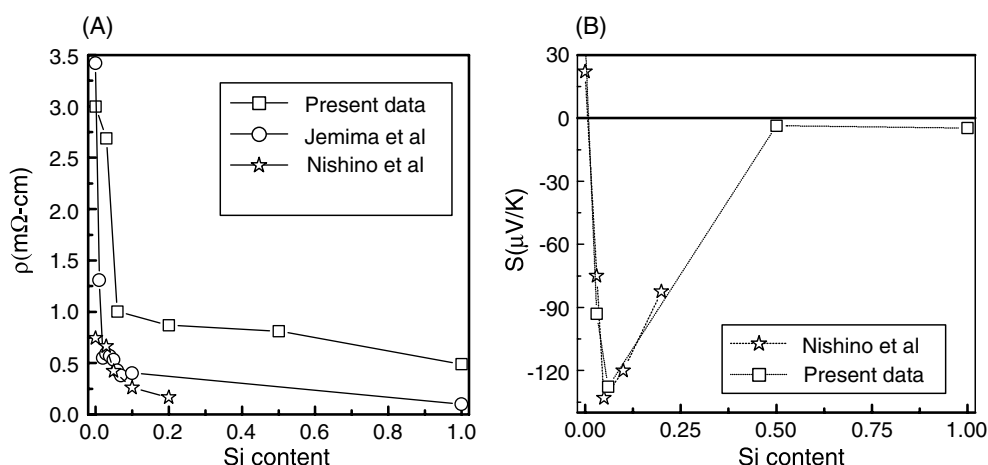


Figure 5. Temperature dependence of the Seebeck coefficient of  $\text{Fe}_2\text{VAl}_{1-x}\text{Si}_x$ .

of  $S$ . In particular, the temperature dependence of  $S$  for all the compositions deviates from linear behaviour, exhibiting pronounced curvature (either positive or negative) at intermediate temperatures. In other words, the absolute value of  $S$  increases as the temperature increases and passes through a broad maximum. This appears to shift to higher temperatures as the Si content is increased. The temperature dependence of some of these alloys is also unlike that of metallic glasses where, except for the small electron–phonon enhancement effect observed at low temperatures,  $S \propto T$  [25]. According to the nearly free electron model,  $S$  is small, negative and linear with  $T$ . Present observations cannot be explained by the simple free electron model used for ordinary metallic alloys, where  $S(T)$  is generally dominated by electron diffusion yielding a linear temperature dependence. This observation is consistent with the temperature dependence of resistivity measurements where conventional theories proposed for metallic materials are not applicable. In figure 6 the Seebeck coefficient and resistivity values at 300 K are plotted along with the literature values for comparison [18, 19]. Both  $S$  and  $\rho$  show remarkable changes as the Si content increases. The sign change of  $S$  from positive to negative is an indication that the majority carriers are electrons in Si-containing samples; while in  $\text{Fe}_2\text{VAl}$  the majority carriers are holes since  $S$  is positive.

In most transition metals the  $S(T)$  behaviour is complicated, showing extrema, bends and changes in sign. At low temperatures many transition metals show a peak, which may be due to the phonon drag effect. Blatt *et al* [26] measured the Seebeck coefficient of Fe, Ni and their alloys and observed a broad peak in  $S$  at around 200 K for Fe and attributed it to magnon drag. In order to investigate the contribution from magnon drag in the present series of samples we have made a comparative study of  $S(T)$  on ferromagnetic  $\text{Fe}_3\text{Al}$  with the present system.  $\text{Fe}_3\text{Al}$  ( $T_C > 700$  K) showed a minimum in  $S$  at a temperature  $T = 190$  K with values of  $S = -24 \mu\text{V K}^{-1}$  [27]. Although  $\text{Fe}_2\text{VAl}$  is reported to be non-magnetic,  $\text{Fe}_2\text{VSi}$  has finite magnetic moment. Recently it has been reported that  $\text{Fe}_{2.2}\text{V}_{0.8}\text{Si}$  is ferrimagnetic with its Curie temperature between 100 and 200 K [28]. Therefore, the magnetic contribution to  $S(T)$  and  $\rho(T)$  needs to be further investigated, in order to throw light on questions such as whether



**Figure 6.** (A) Electrical resistivity and (B) Seebeck coefficient at 300 K as a function of Si concentration. Literature data are also presented in the figure, for comparison.

the magnetic order is responsible for the transport anomalies or the MIT is disorder driven. Magnetic measurements on Fe<sub>2</sub>VAl<sub>1-x</sub>Si<sub>x</sub> may throw some light on the magnetic contribution to  $S(T)$ .

A relatively small value of  $S$  (nearly 10  $\mu$ V K<sup>-1</sup>) for  $x = 0$  and 1, implies that the electron and hole pockets are nearly compensated. The hole pockets arise from the Fe 3d-dominated bands while the electron pockets arise from the V 3d-bands. As Si has higher carrier density compared to Al, a small substitution of Si for Al leads to an increase in the density of valence electrons. This is also reflected in the presently reported  $S$  and  $\rho$  values. Such an increase in charge density enables a small shift in the Fermi level ( $E_F$ ) around the pseudogap. On the other hand, the drastic changes in the resistivity and Seebeck coefficient with Si substitution indicate that the pseudogap present in these systems is quite narrow. The upturn in  $S(T)$  at higher temperatures could be ascribed to the contribution of thermally excited carriers across the pseudogap, as in the case for highly doped semiconductors. It can be understood that, with a small change in carrier concentration,  $E_F$  shifts to higher energy by suppressing the pseudogap, hence attaining a metallic behaviour. This way, by varying the density of electrons one can move the Fermi level from one side of the sharp pseudogap to the other, thereby changing the sign of the observed Seebeck coefficient. On the basis of the rigid band model, we suggest that shifting of Fermi level from the centre of the pseudogap is responsible for such a sharp decrease in the low-temperature resistivity and substantial enhancement of the Seebeck coefficient. This also results in a combination of properties that are useful for thermoelectric materials.

The substitution of Si in Fe<sub>2</sub>VAl alloy resulted in the enhancement of two important parameters that are essential for the thermoelectric materials, i.e., a large value of ' $S$ ' and lower ' $\rho$ ', as the power factor of thermoelectric material is given by  $P = S^2/\rho$ . As shown in figure 6, the magnitude of ' $S$ ' increases with Si content and then gradually decreases by showing a maximum value at  $x = 0.06$ . For higher concentrations ( $x > 0.5$ ) ' $S$ ' maintains its sign to be negative, which is in good agreement with the literature values [19, 20]. On the other hand, the electrical resistivity reaches about 2 m $\Omega$  cm for Fe<sub>2</sub>VAl at room temperature but decreases rapidly with slight concentration of Si. Among the various composition,  $x = 0.06$  with maximum value of  $S = -132.7 \mu$ V K<sup>-1</sup> and  $\rho = 788 \mu$  $\Omega$  cm, showing a power

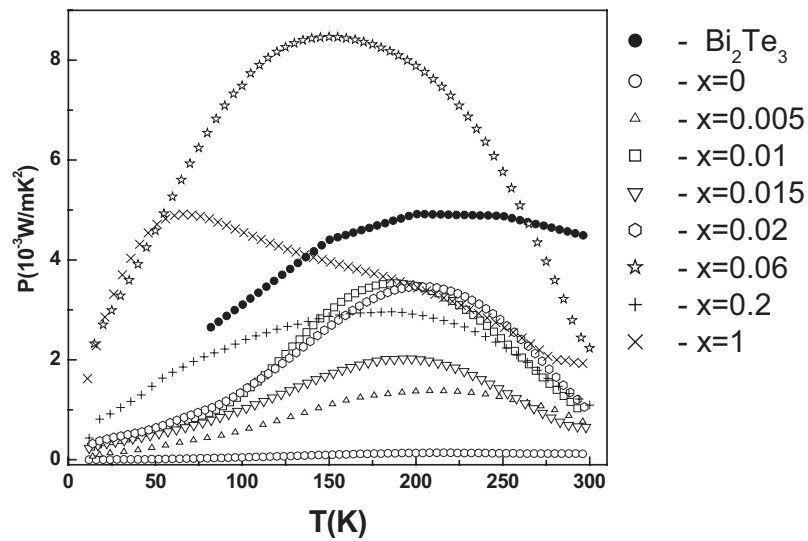


Figure 7. Power factor as a function of temperature for  $\text{Fe}_2\text{VAl}_{1-x}\text{Si}_x$  alloy and  $\text{Bi}_2\text{Te}_3$  alloy.

factor of  $2.23 \times 10^{-3} \text{ W mK}^{-2}$  at 300 K, appears to be a promising candidate for potential thermoelectric application at room temperature. As shown in figure 7, we have also plotted the temperature variation of the power factor of all the compositions along with the  $\text{Bi}_2\text{Te}_3$  alloy for comparison. At lower temperatures the power factor observed is even higher than that of conventional thermoelectric materials. This prompts us to suggest these materials as potential candidates for thermoelectric power applications in space vehicles operating at cryogenic temperatures. The large value of power factor observed in these alloys is similar to that of narrow band gap semiconductors. The similarities between the present alloy system and narrowband gap alloys also suggest that the band structure of these materials might be alike. However, further studies with optimum substitutions in  $\text{Fe}_2\text{VAl}$ -based alloys are essential in order to enhance the transport parameters that make them competent enough to replace the presently used thermoelectric materials and to understand the band structure. Extensive band structure calculations would certainly provide more guidance in the advancement and understanding in these materials.

#### 4. Conclusions

An experimental investigation of the effect of Si doping in the Heusler  $\text{Fe}_2\text{VAl}$  system is presented via electrical resistivity and Seebeck coefficient measurements as a function of temperature. We draw the following conclusions from the data presented in this work.

- (i) The substitution of Si in  $\text{Fe}_2\text{VAl}$  brings about significant changes both in magnitude as well as sign of the transport parameters, indicating a non-metal to metallic-like transition.
- (ii) The analysis of the temperature variation of conductivity and Seebeck coefficient data shows the presence of semimetal-like features. The changes observed in the transport parameters are attributed to the presence of a sharp pseudogap near the Fermi level.
- (iii) On Si substitution, enhancement of two transport parameters ( $\sigma$  and  $S$ ) has been observed. This combination of low resistivity and high Seebeck coefficient results in very high power factors for these alloys.

- (iv) A significant change in power factor has been observed with temperature. The power factor reported in the present investigation is the highest value reported in this system so far, and is much larger than that of conventional thermoelectric materials at low temperatures.

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