

Effect of magnetic entropy in the thermoelectric properties of Fe-doped Fe₂VAl full-Heusler alloy

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The effect of spin entropy on the transport of heat/charge carriers in the Fe-doped full-Heusler alloy Fe_{2+x}VAl_{1-x} with $x = 0 - 0.1$ has been studied through low-temperature magnetic and thermoelectric measurements. Magnetization (M) measurements confirm itinerant-electron weak-ferromagnetic behavior. A systematic increase of the magnetic transition temperature T_C (from 40 K to 223 K) and of the saturation magnetization (from 0.13 to 0.41 μ_B/Fe) with increasing Fe doping (from $x = 0$ to 0.1) is observed. Applying a magnetic field causes significant suppression of the Seebeck coefficient (S) and the entropy term (S/T) with a negative magnetoresistance near T_C for all weak-ferromagnetic samples, demonstrating a clear effect of spin fluctuations. Analyzing $M(T)$ and $S(T)$, we rule out sizeable magnon drag contributions. A large spin fluctuations-induced enhancement in the thermoelectric power factor PF of about 18% is achieved for $x = 0.1$ near T_C when compared to measurements in a magnetic field of 7 T. The actual improvement in PF is even much higher, as the S shows a significant enhancement (about 34%) compared to the estimated diffusion term of $S(T)$ at T_C . The number of point defects also increases with Fe doping, causing a significant reduction of the lattice thermal conductivity. This study demonstrates the role of spin fluctuations in enhancing the thermopower/ thermoelectric performance of Fe-doped Fe₂VAl and opens a vista for the strategy's applicability for various thermoelectric materials.

Introduction

Among all renewable energy sources, thermoelectric (TE) generators have special advantages, such as silently converting waste heat into electricity and vice versa without producing harmful byproducts [1-3]. The challenging task is developing a robust, low-cost and efficient TE material near room temperature [2]. The efficiency of thermoelectric materials is determined by the dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where T , S , σ and κ are absolute temperature, Seebeck coefficient, electrical and thermal conductivity, respectively. The numerator, $S^2\sigma$, is called the power factor (PF), and represents another important figure to describe the performance of TE materials, in addition to ZT . Here, S is sensitive to the electronic band structure near the Fermi level (E_F). The convergence of two or more closely lying energy levels near E_F [3-6], resonant doping [6-9] and the interaction of charge carriers with magnetic moments [10-12] are commonly employed, effective ways to enhance the Seebeck coefficient without significantly deteriorating σ , and hence enhancing the power factor $S^2\sigma$.

Optimization of the electron and phonon transport properties of a magnetic semiconductor is a hot topic in the field of thermoelectrics due to the additional contribution of spins for achieving high thermoelectric performance [12-14]. Fe₂VAl has been attracting huge attention in the last couple of decades as a promising and cost-effective thermoelectric material with exceptional power factors and very robust mechanical properties [15-18]. The interest in this material has recently been further enhanced, achieving a record-high ZT (~ 6) at 380 K when prepared as a W-doped thin film [19].

Pristine Fe₂VAl, a non-magnetic semimetal with a narrow pseudo-gap of -0.01 eV [20], crystallizes in the Cu₂MnAl-type, L2₁, crystal structure. However, the formation of small numbers of antisite defects can easily affect its magnetic and thermoelectric properties [21]. The electronic structure of Fe₂VAl exhibits a large differential density of states (DOS) at either side of the Fermi energy. The Seebeck coefficient S is highly sensitive to DOS ($N(E)$) at the Fermi level (E_F) and can be well described via the modified Mott formula [22]:

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

where $N(E_F)$ is the DOS at E_F . The sharply rising DOS on either side of the pseudo-gap of Fe₂VAl gives an opportunity to enhance S and PF . When E_F shifts to the rising edge of the DOS, S becomes very large (negative in sign) due to a large positive value of $\partial N(E)/\partial E$ at E_F . This can be achieved through doping or the formation of off-stoichiometric compositions. Recently, an exceptionally large power factor $PF_{\max} = 73 - 100 \mu\text{Wcm}^{-1}\text{K}^{-2}$ near room temperature was reported by tuning the pseudo-gap states in n -type doped Fe₂V_{1-x}(Ti,Ta)_xAl_{1-y}Si_y, attributed to a large DOS effective mass ($m_c^* > 11.1m_v^*$) [15,23]. Similar ideas of high power factors through large effective masses for n - and p -type Fe₂VAl are reported in the literature [24]. Indeed, off-stoichiometric compounds Fe_{2-x}V_{1+x}Al_{1-y}Si_y, Fe₂V_{1+x}Al_{1-x} and Fe₂VTa_xAl_{1-x} also demonstrate high PF s ($> 60 \mu\text{Wcm}^{-1}\text{K}^{-2}$) [17,25,26].

On the other hand, theoretical calculations by Guo *et al.* [27] suggest that spin fluctuations are the major cause of the enhanced effective mass observed in FeVFeAl. Tsujii *et al.* [10] reported an interesting magnetic spin fluctuation-induced enhancement in $S^2\sigma$ of Fe₂VAl by incorporating magnetic atoms. The formation of magnetic antisite defects (Fe_V, V_{Fe} or Fe_{Al}) in semi-metallic Fe₂VAl is a common phenomenon and highly sensitive to heat treatment (quenching rate and temperature) [21,26,28-30]. Contrary to a desirable large PF , it exhibits a low figure of merit ($ZT_{\max} = 0.34$ at 300 K [31]) due to its high thermal conductivity. Recently, Garmroudi *et al.* reported a quenching-induced large PF s of $76 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 300 K for undoped Fe₂VAl, which was attributed to the formation of additional spin-polarised DOS arising from magnetic Fe_V antisite defects near the conduction band edge inside the pseudo gap [21]. Moreover, these antisite defects can also help to reduce the large lattice thermal conductivity.

The bottom of the conduction band at the X-point and the top of the valence band at the Γ -point, close to the Fermi level, predominantly exhibit e_g and t_{2g} characters from V and Fe atoms, respectively [15,23,32]. Adding defects at V or Fe sites is expected to scatter the charge carriers more and deteriorate the weighted mobility [32]. Mikami *et al.* reported that W-doping at the V site in Fe₂VAl led to a decrease in the magnitude of S as well as the weighted mobility compared to Si doping at the Al site, attributed to the change in the DOS at the E_F [33]. Therefore, the Al site

is the most ideal site for doping in order to optimize the charge carrier concentration and shift E_F to the desirable position at the rising edge of $N(E)$.

The combination of thermal quenching alongside band engineering through magnetic doping techniques is believed to cause a significant change in the DOS and a considerable shift of E_F from the center of the pseudogap, which can bring some uncommon results. Thus, it would be interesting to explore the effect of Fe doping, which is expected to create many magnetic antisite defects (Fe_{Al} or Fe_{V}), on the thermoelectric performance of Fe_2VAl prepared at optimized thermal treatment conditions. With this motivation, we have investigated the low-temperature thermoelectric and magnetic properties of off-stoichiometric $\text{Fe}_{2+x}\text{VAl}_{1-x}$ and, for the first time, reported the effect of spin fluctuations enhancing the power factor near the transition temperature in these compounds.

2. Experimental section

Synthesis method: Fe-doped Fe_2VAl samples were prepared using arc-melting, spark plasma sintering, and annealing processes. Firstly, we have prepared the nominal Fe_2VAl through arc-melting of the stoichiometric composition of constituent elements Fe (99.98%), V (99.9%) and Al (99.999%). For homogeneity, the ingot was flipped and remelted 3 times. After this, it was wrapped in a Ta-foil and homogenized at 1653 K for 20 min using induction heating under an Ar atmosphere. The resulting ingot was hand crushed in fine powder ($<300\text{ }\mu\text{m}$) and then ball milled in a WC-coated jar using 5 mm diameter balls at 280 rpm for 5h. The milled powder was then consolidated by the spark-plasma sintering (SPS, SPS-1080 System, SPS Syntex INC) at 1273 K for 10 min under an axial pressure of 50 MPa in Ar gas atmosphere. The obtained pellet was cut into the bar shape, wrapped in Ta foil, and kept inside the Nb tube for homogeneous heating. It was annealed at 1648 K for 10 min under Ar gas flow and left to cool down to 300 K by just switching off the furnace. The sample prepared with this process is named as $\beta\text{-Fe}_2\text{VAl}$. The details of induction furnace annealing, ball milling, and SPS are discussed in the supplementary file (see Synthesis details section).

However, the high T synthesis route is known to be advantageous for its thermoelectric performance [21]. Unfortunately, the arc-melted ingots of $\text{Fe}_{2+x}\text{VAl}_{1-x}$ samples with $x > 0$ reacted with Ta foil and partially melted during annealing at high T (1653 K). It is unclear why this melting occurred. The possible reason could be the presence of inhomogeneity in the ingots of Fe-rich samples, which react with Ta during high- T annealing (see the Synthesis details section of the supplementary file). Therefore, we skipped the high T annealing step of ingot in the abovementioned method, directly crushed it into fine powder and ball milled, followed by the SPS steps. A bar-shaped piece of SPS pellet was annealed at low T of 1603 K for 10 min under the same conditions followed for $\beta\text{-Fe}_2\text{VAl}$. A series of samples, $\text{Fe}_{2+x}\text{VAl}_{1-x}$ with $x = 0 - 0.1$, was prepared through this process and named as $\alpha\text{-Fe}_{2+x}\text{VAl}_{1-x}$. The resulting annealed pellets can be used directly for further thermoelectric characterizations.

Characterization and measurements:

For structural analysis, X-ray diffraction was collected in powder form at room temperature in a 2 theta (2θ) range $20^\circ\text{--}90^\circ$ with a scan step of 0.02° and speed of 2° per min in the RINT TTR-3 diffractometer (Rigaku Co., Akishima, Tokyo, Japan) with Cu K_α radiation. Low-temperature

thermoelectric measurements were carried out by the thermal transport option (TTO) in the physical property measurement system, PPMS by Quantum Design. The direction of an applied magnetic field, temperature gradient, and electric current were kept parallel to the length of the bar-shaped sample ($\sim 10 \times 2 \times 2$ mm³). Magnetization measurements on a small piece (~ 25 mg) of samples were performed by using MPMS (magnetic property measurement system), a superconducting quantum interference device magnetometer from Quantum Design. Hall effect was investigated in PPMS. Field-dependent Hall resistivity was scanned from -5 to 5 T at various temperatures, and its linear fit gives the Hall coefficient.

3. Results and discussion:

3.1 X-ray diffraction analysis

For structural analysis, the XRD patterns are collected in powder form for all Fe-doped Fe₂VAI samples before annealing i.e. just after SPS (see Fig S1a) and after annealing (Fig. 1a). All peaks are well matched with a reference card (ICSD#1-073-8878) of face-centered cubic Fe₂VAI with the space group of $Fm\bar{3}m$. In the XRD patterns, the (111) peak at 26.78° is vanishingly small for all doped samples, which can be attributed to site exchange between V and Al (B2 disorder). In addition, the intensity of the (200) peak at 31.02° also decreases with increasing Fe doping (inset of Fig. 1a), which is possible when Fe exchanges its site with V or Al. Figure 1b is the enlarged view of the most intense peak, (220), showing a systematic peak position shift towards lower 2θ with Fe-doping.

The Rietveld refinement of powder XRD data confirmed the formation of single-phase Fe₂VAI (Fig. 1c). The crystallographic unit cell of Fe₂VAI with L2₁-type structure is shown in the inset of Fig. 1c, sketched by VESTA [34], using CIF file obtained after Rietveld refinement. Fe, V, and Al occupy the 8c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2), and 4a (0, 0, 0) Wyckoff sites (positions), respectively [30]. The site occupation of Al and V is varied in the Rietveld analysis, and it is found that in order to completely suppress the (111) peak, at least 25% of V and Al have to exchange their sites in the L2₁-type structure of Fe₂VAI (see Fig. S2a and Table S1). This reveals that in all samples, at least 20-25% of V and Al exchange their sites with each other. Further, using lab source XRD data, it is very difficult to consider the site exchange of all constituent atoms Fe, V, and Al in the structural Rietveld analysis. So, in the Rietveld refinement for all Fe_{2+x}VAI_{1-x}, the occupation of 4a site of Al is shared with Fe as per x by keeping that of 8c site of Fe fixed. The parameters obtained after Rietveld refinement for all Fe_{2+x}VAI_{1-x} are tabulated in Table S2.

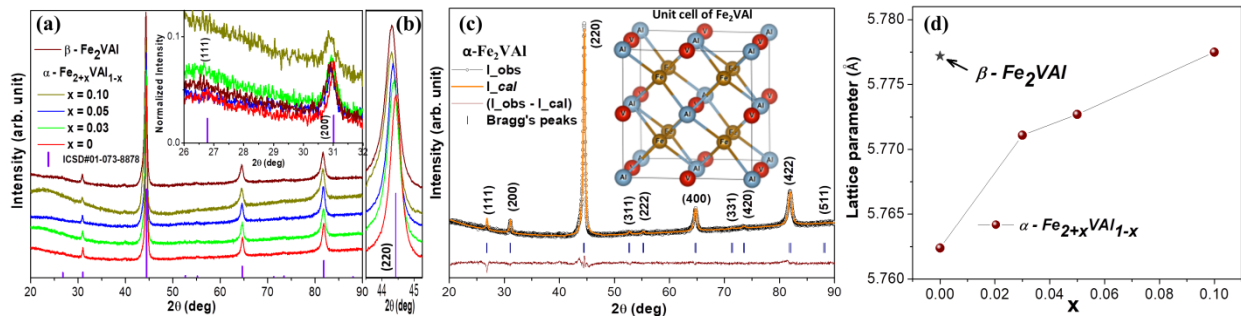


Figure 1 (a) XRD pattern of all Fe-doped Fe₂VAI and inset shows the enlarged view of (111) and (200) peaks. (b) Enlarged view of the most intense peak at 44.43°. (c) Rietveld refinement of α -Fe₂VAI and (d) obtained lattice parameters from refinements for all Fe-doped Fe₂VAI.

The obtained lattice parameters, a , from Rietveld analysis for all $\alpha\text{-Fe}_{2+x}\text{VAl}_{1-x}$ samples show a systematic increase with increasing x (Fig. 1d). This is consistent with other reports of Fe doping on the Al site [35]. It should be noted that the formation energy of a defect of Fe_V (1.882 eV/defect) is lower than that of Fe_Al (2.422 eV/defect), and even lower for V_Al (0.944 eV/defect) [36]. However, the difference in atomic radii for Fe (140 pm) and V (135 pm) is quite small [37], and doping Fe at the V site leads to a very trivial increase of the lattice parameter [25,35]. From the calculated formation energies, it is very likely that doped Fe atoms preferentially occupy the $4b$ site of V and form Fe_V defects, while the ejected V atoms occupy the $4a$ site of Al to form V_Al defects. Thus, the formation of V_Al alongside $\text{Fe}_\text{V}/\text{Fe}_\text{Al}$ antisite defects leads to a systematic increase in the lattice parameter, which is also consistent with the extensive B2-type disorder reflected in the significant lowering of the normalized (200)/(111) intensities (Fig. 1a). A similar unintentional ejection of V atoms in $\text{Fe}_2\text{VAl}_{1-x}\text{Ta}_x$, where doped Ta atoms went to the V site and the ejected V occupied the Al site as antisite defects, previously resulted in a high PF of $65 \mu\text{Wcm}^{-1}\text{K}^{-2}$ for $x = 0.05$ at 340 K [26]. Lastly, in the case of $\beta\text{-Fe}_2\text{VAl}$, the (111) peak almost disappeared and the intensity of (200) is slightly lower than $\alpha\text{-Fe}_2\text{VAl}$, reflecting significant site exchange among Fe, V, and Al. As a result, the obtained a for $\beta\text{-Fe}_2\text{VAl}$ annealed at high T is much larger than that of the low- T annealed one, attributed to the formation of large numbers of antisite defects (Fig. 1d). It aligns with similar lattice constant enhancements through small off-stoichiometric effect in the Fe_2VAl [25,35,38]. The formation of such antisite defects should play a crucial role in enhancing the magnetic and thermoelectric properties of the Fe_2VAl -based system, as discussed later.

3.2 Thermoelectric properties

The temperature-dependent electrical resistivity (ρ) for all samples, measured at zero-field, is shown in Fig. 2a. All $\alpha\text{-Fe}_{2+x}\text{VAl}_{1-x}$ exhibit a semiconducting behavior near 300 K and switch to a metallic behavior at low T with a local maximum, which shifts toward higher T with increasing x , consistent with earlier reports on off-stoichiometric Fe_2VAl [20,38-40]. This downturn in ρ is attributed to magnetic ordering at low temperatures. As the number of valence electrons of Fe (8) is higher than that of V (5) or Al (3), the Fe doping acts as electron doping and hence increases the overall carrier density (n). This leads to a systematic decrease of ρ with increasing Fe doping at low temperatures. Additionally, the resulting antisite defects (Fe_V , V_Fe and Fe_Al) also carry magnetic moments, which interact with conduction electrons, thus reducing the carrier mobility (μ). The overall reduction of ρ suggests, however, that the increase in carrier density dominates over the decrease in carrier mobility. The temperature dependence of ρ is complex above the low T downturn, attributed to the combined effect of magnetic phase transition and thermal excitation of charge carriers across the pseudo gap. The high- T semiconductor-like behavior, $d\rho/dT < 0$, stems from the intrinsic activation of minority charge carriers across the pseudo gap. Thus, an Arrhenius equation fitting of high T resistivity data is performed (Fig. S3), which gives an activation energy E_g of 98, 97, 91, and 82 meV for $x = 0, 0.03, 0.05$ and 0.1 , respectively (inset of Fig. 2a). These values agree well with those reported for pristine Fe_2VAl [23,40]. The band gap obtained systematically decreases with increasing Fe-doping, coinciding with increasing metallic contributions. However, annealing at higher T leads to the formation of even more antisite defects and hence, higher n [21]. On the other hand, SEM analysis confirms that the high T synthesis

process yields lower thickness/density of grain boundaries (see Fig. S4). Thus, high T processing could reduce the inter-grains barrier, and create delocalized states in the pseudo gap [21], leading to an enhanced carrier's mobility. Thus, the overall ρ for β -Fe₂VAI drops even more than for the other α -Fe_{2+x}VAI_{1-x} samples.

Figure 2b shows the temperature dependence of S for all Fe_{2+x}VAI_{1-x} samples. All samples exhibit negative thermopower in the entire studied temperature range, reflecting electrons as the majority carriers. As S inversely varies with n [41], a systematic decrease in the magnitude of S is consistent with the behavior of electrical resistivity with increasing x in α -Fe_{2+x}VAI_{1-x}. A maximum in $|S|$ of $x = 0$ is located near 250 K, attributed to the bipolar effect. This broad maximum in S is shifted towards high T with increasing x , attributed to the shifting of E_F deep inside the conduction band. Interestingly, β -Fe₂VAI shows lower $|S|$ with no bipolar maxima than α -Fe₂VAI, agreeing with higher n for the sample annealed at high T . In contrast, $|S|$ of α -Fe_{2.1}VAI_{0.9} is lower in the entire temperature range than that of high- T annealed β -Fe₂VAI. This can be explained by the Anderson transition, in that the delta-like defect states formed in the pseudo gap region by high T quenching of Fe₂VAI [21]. It can resist bipolar transition below a critical concentration level of defects. Hence, a large S can be achieved for β -Fe₂VAI even with a very large n , and a high thermoelectric power factor (PF , S^2/ρ) can be realized (Fig. 2c). This mechanism is further explored later through Hall data. In α -Fe_{2+x}VAI_{1-x}, the highest PF is obtained for Fe₂VAI, whereas Fe-doped samples display lower PF than undoped-one due to their higher n . The PF for β -Fe₂VAI is 39 $\mu\text{Wcm}^{-1}\text{K}^{-2}$ at 325 K, which is comparable to that of the state-of-the-art n-type Bi₂Te₃ (30-45 $\mu\text{Wcm}^{-1}\text{K}^{-2}$) [42].

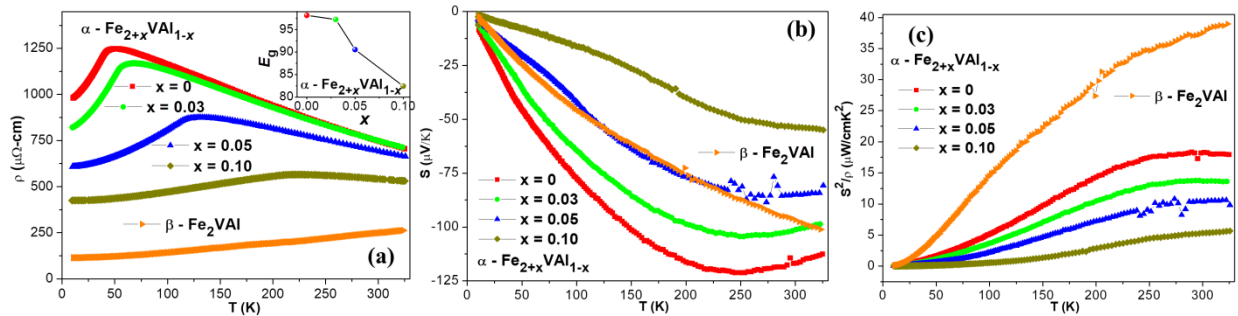


Figure 2 Temperature dependence of (a) electrical resistivity ρ , (b) Seebeck coefficient S , and (c) power factor S^2/ρ at $H = 0$ T for all Fe-doped Fe₂VAI samples. The inset of (a) shows the activation energy obtained from the Arrhenius equation fitting of ρ data for α -Fe_{2+x}VAI_{1-x}.

As thermopower is well defined as entropy per charge carrier and antisite defects in Fe₂VAI are magnetic in nature, magnetic field-dependent thermoelectric data are required to explore further the effect of magnetic defects on its thermoelectric properties. First, the magnetization data are analyzed, followed by the field-dependent TE data.

3.3 Magnetization study

The field-dependent magnetization of α -Fe_{2.1}VAI_{0.9}, measured at different temperatures, is shown in Fig. 3a; for other samples, see Fig. S5a-d in the Supplementary files. All α -Fe_{2+x}VAI_{1-x} samples exhibit saturation at low temperatures, indicating the evolution of ferromagnetic ordering. The saturation magnetization p_s for $x = 0.1$ (α -Fe_{2.1}VAI_{0.9}) is 0.41 μ_B/Fe at 2 K (Fig. 3a). The

temperature-dependent magnetization M is collected at $H = 0.1$ T and shown in Fig. 3b along with its 1st temperature derivative ($\partial M/\partial T$) for $x = 0.1$ to estimate the transition temperature. For others, see Fig. S5e-h. The $\partial M/\partial T$ curve exhibits a sharp peak, corresponding to the Curie temperature (T_C) of 223 K. Figure 3c depicts the temperature dependence of M and H/M (inverse magnetic susceptibility) for $x = 0.1$ measured at $H = 1$ T. The inverse magnetic susceptibility exhibits Curie-Weiss behavior, $H/M = (T - \theta)/C$, where θ is the Weiss temperature and C is the Curie constant. A linear fitting of the H/M curve gives $C = 5.186$ emu-K/mol-Oe and $\theta = 226.7$ K, which is well aligned with $T_C = 223$ K. The effective magnetic moment (p_{eff}) is calculated using C through $p_{\text{eff}} = (3k_B C/N)^{1/2}$ where k_B and N are Boltzmann constant and the number of magnetic ions, respectively. The obtained p_{eff} is $4.44 \mu_B/\text{Fe}$ for $x = 0.1$, close to the theoretical value of Fe^{2+} ($4.9 \mu_B$) [10]. The observation of a positive θ and reasonable p_{eff} assured that ferromagnetism is the bulk effect, i.e., all Fe sites contribute to the low T ferromagnetic behavior. This ruled out the possibility of the formation of ferromagnetic nanoclusters. The ratio p/p_s (8.67 for $x = 0.1$) is compared with other ferromagnetic materials employing the Rhodes-Wohlfarth plot [10,17,43] (Fig. S6), confirming weak itinerant ferromagnetism.

Similarly, saturation magnetization (p_s) and Curie temperature (T_C) are obtained for all samples, revealing a systematic increase with increasing x (Figs. 3d and S5). The rapid increase in M below T_C for all samples suggests a ferromagnetic transition. The saturation magnetization (p_s), ranging from 0.132 to $0.41 \mu_B/\text{Fe}$ for $x = 0$ to 0.1 , are much smaller than p_{eff} values obtained from the Curie-Weiss fits. The Rhodes-Wohlfarth plot of the obtained values of p/p_s for $x = 0, 0.05, 0.1$ and 0.125 is consistent with the weak ferromagnetic behavior of all doped samples (see Figs. S5-6 and Table S3). The effect of thermal fluctuations of the local spin-density i.e. spin fluctuations, is expected to be noticeably high in weak ferromagnets [10,27,28].

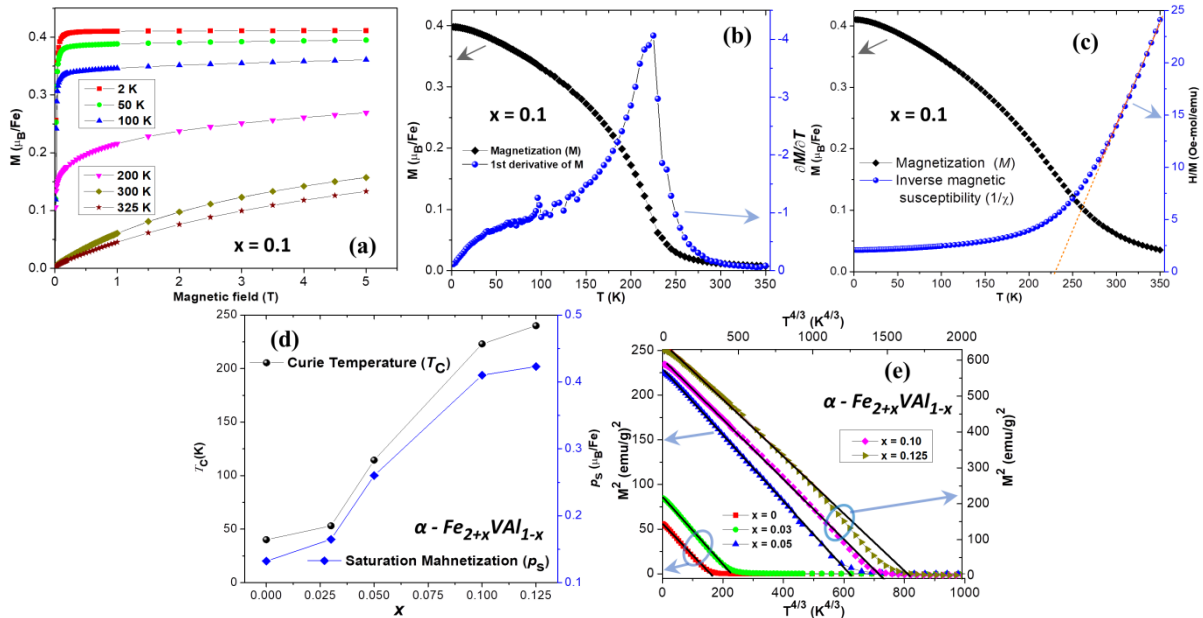


Figure 3 (a) Field dependence of magnetization at various temperatures, the temperature dependence of (b) magnetization M at $H = 0.1$ T and its first derivative with respect to the temperature measured and (c) M at $H = 1$ T and the inverse magnetic susceptibility (H/M) for $x = 0.1$ ($\alpha\text{-Fe}_{2.1}\text{VAl}_{0.9}$). (d) Transition temperature T_C , determined

by the $\partial M/\partial T$ curve peak and saturation magnetization p_s at 2 K, and (e) M^2 versus $T^{4/3}$ plots for all α -Fe_{2+x}VAI_{1-x} samples.

To further confirm the contribution of spin-fluctuations of the weak ferromagnetic samples, the temperature dependence of $M(T)$ was collected at $H = 0.1$ T and fitted with various models [28,40]. Figure 3e shows the linear fitting of M^2 versus $T^{4/3}$ curves for validating the model of $M = M_0[1 - (T/T_C)^{4/3}]^2$, where M_0 is the zero-temperature magnetization. Other models, the mean-field model $M = M_0[1 - (T/T_C)^2]^2$ along with Bloch law (spin-wave model) $M = M_0[1 - BT^{3/2}]$ are demonstrated in Fig. S5m-n. We find that M^2 versus $T^{4/3}$ plots give a linear fit below T_C , whereas others show a nonlinear behavior below T_C . This confirms that the majority part of the magnetic excitations is due to spin fluctuation, whereas the contribution of the magnon (spin-wave) is of minor importance in weak ferromagnetic α -Fe_{2+x}VAI_{1-x}.

Figure S7a-b depicts the field and temperature-dependent magnetization of β -Fe₂VAI. Its magnetic behavior looks somewhat different from that of α -Fe_{2+x}VAI_{1-x}; a spontaneous magnetization at $H = 0$ T is not seen even at $T = 2$ K (Fig. S7a) and no anomaly is seen in the temperature dependence of the electrical resistivity (Fig. 2a), although a rapid increase in magnetization occurs at low temperature (Fig. S7b). Hence, the magnetic state of this sample is most likely a superparamagnetic state without any long-range ordering. It is contrasting with the case of α -Fe_{2+x}VAI_{1-x}, which showed a clear bulk weak-ferromagnetic behavior as discussed above. The superparamagnetic-like nature in high- T synthesized Fe₂VAI reflects the non-uniform distribution of magnetic moments. A similar rising M with increasing H was observed in Fe₂VAI quenched at 1323 K [21]. The M - H curve at 2 K is analyzed as the sum of superparamagnetic and paramagnetic contributions, revealing the formation of magnetic nanoclusters of a diameter of ~ 3 nm with an average magnetic moment of $12.57 \mu_B$ (see Fig. S7a). If we consider the magnetic moment of Fe_{Al} is $2.7 \mu_B$ [21], nearly five Fe_{Al} are present in a single cluster and the number may be high for Fe_V or V_{Fe}. Thus, the synthesis process has proven to have a significant impact on the magnetic properties of Fe₂VAI.

3.4 Magnetic field-dependent thermoelectric properties

Magnetic field-dependent TE transport measurements were performed at 7 T for all samples in the temperature range of 10-325 K (see Figs. 4 and S8). The temperature dependence of ρ , S , $-S/T$, and the power factor S^2/ρ for α -Fe_{2.1}VAI_{0.9} is shown in Fig. 4a-c. A linear fitting of the low-temperature Seebeck coefficient in the absence of an external magnetic field, S_{0T} , gives the diffusion thermopower, $S_{\text{diff}} = S_0 + S_1T$, where S_0 is set to 0 at $T = 0$ K, extrapolated till 325 K and represented by the black solid line in Fig. 4b. The obtained $S_1 = (\pi k_B)^2/3eE_F$ gives the E_F of 0.15 eV where E_F is the difference between E_F and the bottom conduction band, suggesting E_F lies deep inside the conduction band. The obtained difference $S_{0T} - S_{\text{diff}}$ is quite large near T_C , revealing an enhancement of up to 34% in S_{0T} at T_C when compared to S_{diff} (Fig. 4b). This difference reduces when applying the magnetic field but cannot be suppressed completely. The peak in the temperature-dependent $-S/T$ (entropy term) is noticeably dropped and exhibits a broad hump at T_C for $H = 7$ T (Fig. 4b, inset). This suggests that under an external field, spin fluctuations are significantly suppressed. As a result, the power factor at $H = 0$ T is higher than that of $H = 7$ T by up to 18% near T_C for α -Fe_{2.1}VAI_{0.9} (Fig. 4c, inset). A remarkable suppression in the $|S/T|$ and $|S|$, and a clear negative magnetoresistance of -6% at T_C (223 K) under $H = 7$ T is stemming from a

reduction of spin entropy of the system, which points to the benefit of spin fluctuations for enhancing the thermoelectric performance [10,18,44] and well aligned with the similar observation in magnetization data.

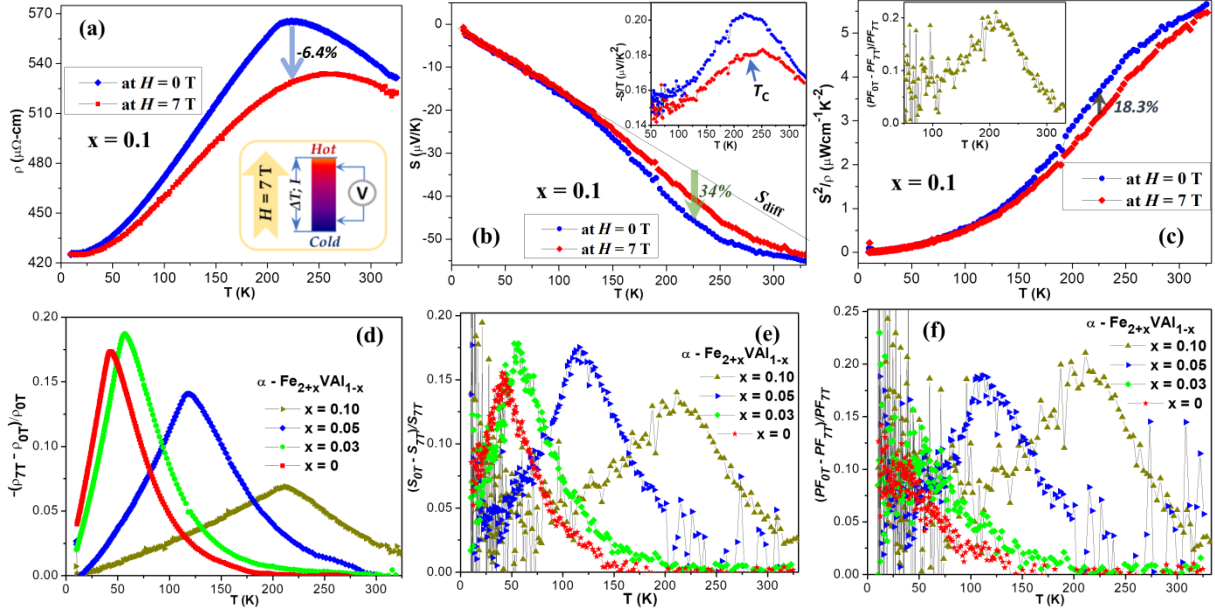


Figure 4 Temperature dependence of (a) electrical resistivity ρ , (b) Seebeck coefficient S and $-S/T$ (in inset), and (c) power factor and $|PF_{0T} - PF_{7T}|/PF_{7T}$ (in inset) for $x = 0.1$ (α -Fe_{2.1}VAl_{0.9}) at $H = 0$ T and 7 T. The inset of (a) shows a typical schematic of thermoelectric measurements in the magnetic field. Here, the diffusion thermopower S_{diff} was extracted from a linear fit of low-temperature S_{0T} data, $S_{\text{diff}} = S_0 + S_1T$, where S_0 is set to 0 at $T = 0$ K. The obtained S_{diff} is extended to 325 K and shown as the solid black line in (b). The difference of $H = 0$ T and 7 T data with respect to the values at 0 T/7 T of (d) electrical resistivity $(\rho_{0T} - \rho_{7T})/\rho_{0T}$, (e) Seebeck coefficient $|S_{0T} - S_{7T}|/S_{7T}$ and (f) power factor $|PF_{0T} - PF_{7T}|/PF_{7T}$ as a function of T for all α -Fe_{2+x}VAl_{1-x}.

Furthermore, Fe doping enables shifting the transition temperature T_C towards higher T as well as increasing the strength of the spin fluctuations. Bringing T_C near room temperature would be highly beneficial for TE applications, but due to the simultaneous increase of overall n upon Fe doping, the magnitude of S decreases as well and hence reduces the power factor. Similar spin fluctuation effects of the field-dependent TE data are observed for other α -Fe_{2+x}VAl_{1-x}, too (Figs. S8a-o). The relative suppression of ρ and S under a magnetic field is depicted in Figs. 4d and 4e, respectively, where $-(\rho_{7T} - \rho_{0T})/\rho_{0T}$ and $|S_{0T} - S_{7T}|/S_{7T}$ are plotted against T for all samples. At T_C , a noticeable negative magnetoresistance $-(\rho_{7T} - \rho_{0T})/\rho_{0T}$ of 17%, 18%, 14% and 6% for $x = 0, 0.03, 0.05$ and 0.1 , respectively, is observed. The $x = 0.1$ sample, with the highest defect density, shows a much smaller magnetoresistance compared to compositions with smaller Fe concentrations, due to its poor carrier mobility. The peak of the enhancement ratio $|S_{0T} - S_{7T}|/S_{7T}$ located at T_C is 16%, 18%, 18%, and 13% for $x = 0, 0.03, 0.05$ and 0.1 , respectively. Additionally, all samples show a remarkable suppression in the entropy (S/T) at $H = 7$ T near T_C (Figs. S8j-l, inset of 4b). A reasonably large enhancement in $|S_{0T} - S_{7T}|/S_{7T}$ can be seen even in a wide temperature range above T_C . This suggests that the enhancement of S near T_C is not due to a magnon drag effect, which is expected to be observed only in the ferromagnetically ordered state [45,46]. A complete suppression of the spin fluctuations-induced enhancement in S at $H = 7$ T is observed only for low-doped samples, $x = 0$ and 0.03 , whereas it survives in the case of $x = 0.05$ and 0.1 (Figs. 4b and

S8d-f). The maximum enhancement in the $|PF_{0T} - PF_{7T}|/PF_{7T}$ ratio is 18% for $x = 0.1$ and 19 % for $x = 0.05$, whereas low-doped samples show a relative enhancement of $\sim 10\%$ at T_C (Fig. 4f). This demonstrates that spin fluctuations lead to a large enhancement of the thermoelectric power factor of $\sim 18\%$ for $x = 0.05/0.1$ at $T = T_C$. As S doesn't get completely suppressed at 7 T and the difference $|S_{0T} - S_{diff}|$ is nearly 34 % at T_C for $x = 0.1$, the actual enhancement in power factor due to spin fluctuations is most likely even higher.

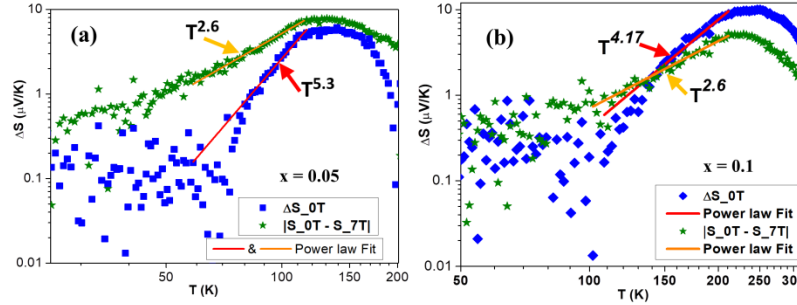


Figure 5 The temperature dependence of $\Delta S_{0T} = |S_{0T} - S_{diff}|$ and $|S_{0T} - S_{7T}|$ for (a) $x = 0.05$ ($\alpha\text{-Fe}_{2.05}\text{VAl}_{0.95}$) and (b) $x = 0.1$ ($\alpha\text{-Fe}_{2.1}\text{VAl}_{0.9}$). Solid lines show fitting results with a power law.

We further analyze the Seebeck coefficient below T_C to see if magnon drag contributions can be detected. The temperature dependence of $|S_{0T} - S_{diff}|$ (ΔS_{0T}) could predict the dominant phenomena. It is predicted that the magnon drag term varies with $T^{3/2}$ and is indeed confirmed experimentally [48]. Figure 5a-b depicts the temperature dependence of ΔS_{0T} along with $|S_{0T} - S_{7T}|$ for $\alpha\text{-Fe}_{2.1}\text{VAl}_{0.9}$ and $\alpha\text{-Fe}_{2.05}\text{VAl}_{0.95}$. Nevertheless, extracting S_{diff} is difficult for the $x \leq 0.03$ samples with T_C at low T regions. A power law fitting reveals that ΔS varies with $T^{4.17}$ and $T^{5.3}$ in the $0.5T_C < T < T_C$ temperature range for $x = 0.1$ and 0.05 , respectively. These type of power laws are close to what would be theoretically expected in the case of spin fluctuations (T^4 [10,47]) and are far away from those exponents expected for magnon-drag-driven thermopower ($T^{3/2}$ [48]). Additionally, both samples exhibit a $T^{2.6}$ power law of $|S_{0T} - S_{7T}|(T)$. This also demonstrates that spin fluctuations are the major cause for enhancement in S near T_C and rules out the possibility of a dominant magnon drag contribution.

3.5 Hall effect study

Furthermore, Hall measurements are performed for $\alpha\text{-Fe}_{2.1}\text{VAl}_{0.9}$ (Fig. 6). The Hall resistivity is generally expressed as $\rho_{xy} = R_0 H + 4\pi R_s M$, where R_0 is the normal Hall coefficient and R_s is the anomalous Hall coefficient due to anomalous Hall effect (AHE), M is the magnetization, respectively. Figure 6a depicts the measured field-dependent ρ_{xy} . A clear nonlinear behavior below 300 K is due to AHE. The fitting of ρ_{xy} data using magnetization M from Fig. 3a gives R_0 and R_s , at all temperatures. The fittings are represented by solid lines in Fig. 6a-b. Separated contributions of normal and anomalous Hall in measured ρ_{xy} at 2 K are shown in Fig. 6b. The obtained anomalous part of ρ_{xy} is greater than $10 \mu\Omega\text{-cm}$ at 2 K, which is unusually large and comparable to that of $\text{Fe}_2\text{V}_{0.9}\text{Cr}_{0.1}\text{Al}_{0.9}\text{Si}_{0.1}$ at 10 K [10]. Observation of the large AHE and enhancement in S near T_C reflect strong interaction of charge carriers with magnetic moments of Fe atoms, which can affect the DOS effective mass. The carrier density (n) and mobility (μ) are calculated using the obtained R_0 , shown in Figs. 6c and S9a. The derived anomalous Hall coefficient is depicted in Fig. S9b. The sign of R_0 is positive below 300 K, and above, it turns into negative, reflecting the

contribution of both electrons and holes, presumably due to the semimetallic nature of the studied system. A systematic decrease in n with decreasing temperature can be seen in Fig. 6c, whereas the carrier mobility monotonously increases with decreasing T (Fig. S9a). This competing behavior of n and μ explains the temperature dependence of ρ . The initial semiconducting rise in ρ with decreasing T is due to the decrease in n . Below T_C , the increase in μ due to magnetic ordering dominates over n , leading to a metallic downturn in ρ at low T . The power law fitting of the carrier mobility ($\mu \propto T^{-p}$) is depicted in Fig. S9a. The low-temperature region shows good fit $p = 0.5$, which corresponds to alloy scattering in non-degenerate limits, whereas near/above 300 K, it looks like it varies with $p > 1.5$, which may correspond to acoustic phonon scattering ($p = 3/2$), ferromagnetic spin fluctuation ($p = 5/3$), or normal Fermi liquid ($p = 2$).

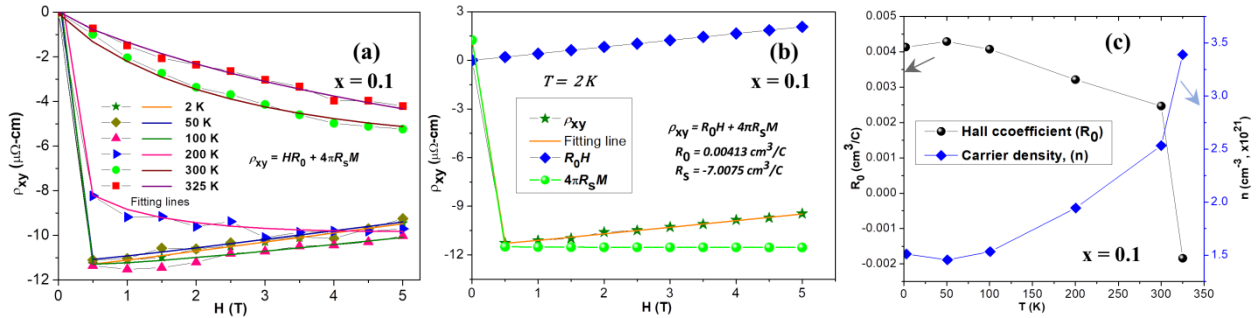


Figure 6 (a) Magnetic field dependence of Hall resistivity ρ_{xy} , (b) separate normal R_0H and anomalous $4\pi R_sM$ components of Hall resistivity at 2 K, (c) calculated Hall coefficient R_0 and carrier density n for $x = 0.1$ ($\alpha\text{-Fe}_{2.1}\text{VAl}_{0.9}$). The solid lines in (a,b) represent the fit using $\rho_{xy} = R_0H + 4\pi R_sM$.

Interestingly, the field-dependent Hall resistivity at 300 K for $\alpha\text{-Fe}_2\text{VAl}$ shows a clear non-linearity at low fields, attributed to bipolar contribution (Fig. S9c). On the other hand, the Hall measurements on $\beta\text{-Fe}_2\text{VAl}$ show linear ρ_{xy} versus H curves at various T down to 10 K and give the negative Hall coefficient (R_0), confirming electrons as majority charge carriers (Fig. S9d-e). The obtained n for $\beta\text{-Fe}_2\text{VAl}$ is $3.84 \times 10^{21} \text{ cm}^{-3}$ at 300 K, which is smaller than $4.4 \times 10^{21} \text{ cm}^{-3}$ of Fe_2VAl quenched at 1653 K [21]. Its μ monotonously decreases with increasing T and exhibits $\mu = 6.53 \text{ cm}^2/\text{V-s}$ at 300 K (Fig. S9f), slightly lower than in Ref. [21], attributed to differences in synthesis routes. Interestingly, superparamagnetic M - H data at 2 K imply the formation of magnetic nanocluster in the paramagnetic matrix (Fig. S7a-b) and the absence of long-range ferromagnetic order in the system. Consequently, the temperature dependences of S and $-S/T$ also do not show any difference between $H = 0\text{ T}$ and 7 T data (Fig. S7c-d).

Overall, $\beta\text{-Fe}_2\text{VAl}$ exhibits higher n as well as S than $\alpha\text{-Fe}_{2.1}\text{VAl}_{0.9}$ at 300 K, which signifies a higher density of states effective mass. As Hall and S data of $\beta\text{-Fe}_2\text{VAl}$ do not show bipolar effect till 300 K, we use the single parabolic band model assuming acoustic phonon scattering ($\lambda = 0$) as dominant scattering to calculate the conduction band DOS effective mass (m_2) [49]. The obtained m_2 is $12.42m_e$ using experimental S , σ and n at 300 K. It gives the ratio of conduction to valence band effective mass $m_2/m_1 = 2.64$ if we consider $m_1 = 4.7m_e$ [32]. It well matches with 2.6 of Fe_2VAl [32] calculated with $\lambda = 0$. Similarly, there are several reports with different m_2 [15,23,24]. Here, the interaction of charge carriers with ionized impurity or magnetic moments of defects/dopants is not considered in the calculations [50,51]. Thus, the reported large m_2 by

assuming $\lambda = 0$ may not be accurate. However, the high- T annealed superparamagnetic sample has no signs of spin fluctuations, anomalous Hall effects, or bipolar effects. It reflects that its simultaneous large S and n are attributed to Anderson localization [21]. Nevertheless, due to the difference in curing time at high T and cooling rate during quenching, the obtained PF is lower than that of Ref. [21].

On the other hand, all $\alpha\text{-Fe}_{2+x}\text{VAl}_{1-x}$ ($x = 0 - 0.1$) samples possess an apparent bipolar effect near 300 K (Figs. 2 and S8a-f). The two-parabolic band model assuming ionized impurity scattering yields acceptable band parameters [50]. Therefore, the $S(T)$ and $\rho(T)$ data are fitted using two-parabolic band modeling (Fig. S10), and the obtained band parameters are tabulated in Table S4 (see Supplementary file for details). The obtained ratio m_2/m_1 for $x = 0$ and 0.03 are 2.84 and 3.43, respectively. The m_2/m_1 for $x = 0$ ($\alpha\text{-Fe}_2\text{VAl}$) nearly matches with $\beta\text{-Fe}_2\text{VAl}$, whereas $x = 0.03$ clearly shows enhancement. In the present model, we have fitted the 7 T data by excluding the effect of spin fluctuations. Using first-principles calculations, Guo *et al.* [27] estimated that the large mass enhancement in Fe_2VAl is mainly due to spin excitations (spin fluctuations). As the effect of spin fluctuations on S increases with increasing x , the ratio m_2/m_1 for $x = 0.03$ could be more enhanced than for $x = 0$. Additionally, the two-parabolic band modeling gives two main conclusions: $x = 0$ is a semimetal, and band overlapping is increased for $x = 0.03$. This result contradicts some reports claiming that Fe_2VAl is a narrow-gap semiconductor [23,29,32], but well aligned with a small pseudogap semimetal [20,25,52]. As the electronic band structure of Fe_2VAl is highly affected by small compositional changes or forming intrinsic antisite defects, it can be considered as a very small band gap semiconductor that can turn into semimetal by adding a small number of magnetic defects [29].

In this context, the positive activation energy estimated from Arrhenius fitting of high-temperature ρ data (section 3.2) can be interpreted as due to the activation of charge carriers across the pseudo gap at the X-point. As a large number of defects are present in the studied system, it is quite possible that some defect states formed in the pseudo gap, participating in hopping-conduction across the gap. With this, we can say that the initial rise of ρ in low T is due to metallic conduction through overlapping bands at the Γ -point, and after T_C , conduction across the pseudo gap started at the X-point, leading to a semiconducting behavior.

3.6 Thermal transport

The field-dependent thermal conductivity for all samples is also measured to see the effect of spin fluctuations on the thermoelectric figure of merit. Although the magnetic field can affect its electronic thermal conductivity ($\kappa_e \propto 1/\rho$), it is not reflected in total thermal conductivity (κ_{tot}) due to the dominant lattice contribution (κ_L) (Figs. S8 and S11). In Fig. S11a, a noticeable drop of κ_{tot} of 19-23% at 300 K is observed for Fe-doped samples compared to undoped Fe_2VAl annealed at 1603 K ($\alpha\text{-Fe}_2\text{VAl}$). This significant drop is presumably due to Fe-doping on V/Al sites with a larger mass and atomic radius. On the other hand, $\beta\text{-Fe}_2\text{VAl}$ also exhibits a considerable reduction of 22% in κ_{tot} at 300 K as compared to $\alpha\text{-Fe}_2\text{VAl}$. The value of κ_{tot} at 325 K for high- T annealed $\beta\text{-Fe}_2\text{VAl}$ is well matched with that of Fe_2VAl quenched at 1653 K reported in ref. [21].

To better understand heat transport in the system, a detailed analysis of the thermal conductivity data using Callaway's model [53,54] is carried out (see Fig. S11a-c in the Supplementary file).

This gives several interesting results. The obtained point defects (A) and phonon-phonon (B) scattering parameters for $\alpha\text{-Fe}_{2+x}\text{VAl}_{1-x}$ show a systematic increase with increasing x , well reflected as a significant drop in κ_L (Fig. S11c, Table S5). A is more than one order of magnitude larger for $\beta\text{-Fe}_2\text{VAl}$ as compared to that of $\alpha\text{-Fe}_2\text{VAl}$, reflecting the significantly larger number of antisite defects formed due to high-temperature annealing, well corroborating the XRD results. Similarly, the grain boundary scattering term ν/D is nearly unchanged for $\alpha\text{-Fe}_{2+x}\text{VAl}_{1-x}$, whereas it is more than 6 times for $\beta\text{-Fe}_2\text{VAl}$ than $\alpha\text{-Fe}_2\text{VAl}$. However, the high-temperature quenching of Fe_2VAl with the $L2_1$ phase can lead to the formation of antiphase boundaries of two stable phases, a partly disordered B2 phase and a fully disordered A2 phase inside the $L2_1$ [30]. The analysis of M - H data of $\beta\text{-Fe}_2\text{VAl}$ also confirms the formation of superparamagnetic nanoclusters (~ 3 nm) in the paramagnetic matrix. It leads to an increase in A and ν/D , and hence decreases κ_L of Fe_2VAl quenched at higher T than the low T quenched one. Thus, due to the difference in synthesis and heat-treatment processes, $\beta\text{-Fe}_2\text{VAl}$ shows a remarkably low κ_{tot} compared to the $\alpha\text{-Fe}_2\text{VAl}$.

The temperature dependence of the calculated thermoelectric figure of merit ZT for all samples is shown in Fig. S11d. As the thermal conductivity remains quite large, the obtained ZT (0.013 - 0.094) for $\text{Fe}_{2+x}\text{VAl}_{1-x}$ is below the technical applicability. High power factor coupled with low thermal conductivity results in a maximum ZT of 0.094 at 325 K for $\beta\text{-Fe}_2\text{VAl}$, which is 2.5 times higher than that of $\alpha\text{-Fe}_2\text{VAl}$. Figure S11e depicts the temperature dependence of $(ZT_{0T} - ZT_{7T})/ZT_{7T}$ for $\alpha\text{-Fe}_{2+x}\text{VAl}_{1-x}$; it reveals that ZT at T_C is enhanced by 14%, 16%, 20%, and 22% as compared to measurements performed at $H = 7$ T for $x = 0, 0.03, 0.05$, and 0.1 , respectively. This noticeable enhancement of ZT of 22% at 223 K for $x = 0.1$ is mainly attributed to the larger Seebeck coefficient due to the spin fluctuation. The enhancement by spin fluctuations can also be very fascinating if T_C can be tuned to the appropriate temperature ranges.

Conclusions

Structural, magnetic, and thermoelectric properties of off-stoichiometric $\text{Fe}_{2+x}\text{VAl}_{1-x}$ were systematically investigated. Structural analysis confirmed that all studied samples crystallized in a single-phase cubic structure ($L2_1$ phase) with a high degree of antisite disorder. The formation of thermally activated antisite defects makes Fe_2VAl a weak ferromagnet, and its phase transition temperature (T_C) increases further with increasing Fe-doping. On the contrary, Fe_2VAl annealed at higher temperatures shows a superparamagnetic behavior down to 2 K. Transport measurements under magnetic fields reveal a strong coupling of magnetic moments and carrier transport, as reflected in a large anomalous Hall effect derived for the ferromagnetic samples. The Seebeck coefficient shows significant enhancement near T_C in ferromagnetic samples but not in the superparamagnetic sample ($x = 0$). This indicates that coherent magnetic excitations can boost the Seebeck coefficient. Careful examinations of the temperature-dependent magnetization and Seebeck coefficient strongly suggest that spin fluctuations play a dominant role and that the enhancement cannot be attributed to spin waves (magnons). Overall, spin fluctuations lead to a significant improvement of the dimensionless figure of merit ZT of $\text{Fe}_{2.1}\text{VAl}_{0.9}$ by up to 22% at T_C when compared to measurements in an external magnetic field $H = 7$ T. We anticipate that spin

fluctuations could play a favorable role in enhancing the thermoelectric performance of these types of weak-ferromagnetic systems.

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Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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