A series of full-Heusler alloys, $\text{Fe}_2\text{V}_{1-x}\text{W}_x\text{Al}$, $0 \leq x \leq 0.2$, was prepared, characterized and relevant physical properties to account for the thermoelectric performance were studied in a wide temperature range. Additionally, off-stoichiometric samples with similar compositions have been included, and a 10 % improvement of the thermoelectric figure of merit was obtained. The V/W substitution causes i) a change of the main carrier type, from holes to electrons as evidenced from Seebeck and Hall measurements and ii) a substantial reduction of the lattice thermal conductivity due to a creation of lattice disorder by means of a distinct different mass and metallic radius upon the V/W substitution. Moreover $ZT$ values above 0.2 have been obtained. A microscopic understanding of the experimental data observed is revealed from ab-initio calculations of the electronic and phononic structure.

Keywords: thermoelectricity, Heusler systems, DFT calculations

PACS numbers: abc

I. INTRODUCTION

Half-Heusler XYZ and full-Heusler systems, $X_2YZ$ have attracted growing interest in many functional materials related fields, like in spintronics, optoelectronic, superconductivity, shape memory or thermoelectricity. For the latter, a variety of promising properties like the mechanical and chemical stability and for several members of XYZ systems a thermoelectric performance with good prospects have been found. Here, X and Y are in general transition metal elements and Z is a main group element like aluminium. While XYZ systems consist of 3 $fcc$ sublattices, $X_2YZ$ systems are composed of four $fcc$ sublattices. Since Heusler systems are prone for anti-side occupations, the cubic crystal structures might change with respect to its space groups and $fcc$ based crystals might transform to $bcc$ type materials. A recent review summarises many of the above indicated aspects.

Full-Heusler compounds are known for its closeness to an insulating state, i.e., the proximity of the Fermi energy to a gap in the electronic density of states (eDOS). Specifically, the Fermi energy $E_F$ of $\text{Fe}_2\text{VAI}$ is located very slightly below a pseudo-gap in the eDOS. Consequently, holes are the main charge carriers and positive Seebeck and Hall values can be obtained experimentally. Small changes of the electron concentration by electron or hole doping is expected to shift either $E_F$ towards the conduction band or more deep into the valence band, resulting in electron or hole dominated transport, as one of the pre-requisites of thermoelectric materials.

$\text{Fe}_2\text{VAI}$ offers the possibility to exchange elements on all lattice sites, i.e., on the Fe-site (8c) on the V site (4a) and the Al site (4b) of the $\text{Cu}_2\text{MnAl}$ structure type. Appropriate substitutions may generate two beneficial features: i) an intended modification and tuning of the eDOS and ii) disorder in the crystal lattice, expected to distinctly decrease the lattice thermal conductivity of the material.

The aim of the present work is to demonstrate such an advantageous tunability of $\text{Fe}_2\text{VAI}$ by substituting Y by W and, in addition, by making this substitution off-stoichiometric, i.e., changing $\text{Fe}_{50}(\text{V},\text{W})_{25}\text{Al}_{25}$ towards $\text{Fe}_{50}(\text{V},\text{W})_{24}\text{Al}_{26}$. In this study, experimentally derived results obtained on samples up to 20 % exchange of V by W are presented and analyzed and these findings are compared and confronted with first principles DFT calculations, allowing to draw some microscopic picture of this series of alloys.

A variety of studies regarding substitutions, dopings, or off-stoichiometric sample preparation has already been carried out previously and reported in literature.\(^{[32]}\) Most successful studies with respect to the thermoelectric performance, expressed by the dimensionless figure of merit $ZT = S^2/(\rho\lambda)$, where $T$ is the absolute temperature, $S$ is the Seebeck effect, $\rho$ the electrical resistivity and $\lambda$ is the thermal conductivity, have been undertaken by substituting Si/Ge and V/W. $ZT$ values of up to about 0.2 have been obtained. Here, we are going one step further, by additionally preparing such substituted materials in an off-stoichiometric manner; we have observed an improvement of $ZT$ by about 10 %.

II. EXPERIMENTAL

$\text{Fe}_2\text{V}_{1-x}\text{W}_x\text{Al}$ alloys and off-stoichiometric variants (about 3.5 gram each) were prepared by high frequency melting of high purity starting materials on a water-
cooled copper hearth under argon atmosphere. To ensure homogeneity of the samples, the melting process was repeated several times. Subsequently, all alloys were sealed in quartz tubes and annealed at 900°C for one week.

X-ray powder diffraction data at room temperature from as-cast and annealed alloys were taken on a Siemens D5000 diffractometer employing CuKα1 radiation (10 < 2θ < 100°). Refinement of the crystal structures was performed with the program PowderCell.

Measurements of the various physical properties were carried out with a series of standard techniques. A commercially available set-up (ULVAC, ZEM3) was used to study the electrical resistivity and the Seebeck coefficient above room temperature.

### III. ELECTRONIC STRUCTURE

VASP was applied for deriving the electronic as well as vibrational and structural properties of ordered Fe2VAl, Fe16V7WAl8 and Fe16V6W2Al8. Calculations were carried out in terms of general gradient approximation potential within the projector augmented wave approach. Details of the distinct procedures are outlined in Ref.

### IV. RESULTS AND DISCUSSION

Figure upper panel, shows an example of the x-ray diffraction pattern taken for the sample x = 0.1. The respective Rietveld refinement is shown in addition (solid line), together with the respective Bragg positions (vertical lines) and the difference between the experimental and the fit data. Since besides the positions of the expected Bragg peaks no intensity is found in the respective X-ray data, good phase purity is evident.

In order to appropriately account for the intensities of the various Bragg peaks, the standard full-Heusler structure (Cu2MnAl-type, space group no. 225) was slightly modified such that about 5% of Al is located at the V (4b) site and vice-versa, 5% of V is located at the Al (4a) site. It is well known from literature that different types of anti-side occupation occurs in Heusler systems; as a consequence, a variety of cubic structure types can be realized. Specifics of this interesting phenomenon are discussed in detail in Ref. Based on these Rietveld fits, the lattice parameters of the entire series were derived; values are summarised in lower panel, together with a sketch of the crystal structure of Fe2VAl. Obviously, there is a monotonic increase of the lattice parameter a with increasing W content, as a result of the larger atomic radius of W (193 pm) with respect to V (183 pm).

Results of the first-principles electronic structure calculations carried out for Fe2V1−xWxAl are summarised in Fig. 2.

For stoichiometric Fe2VAl, a pseudo-gap in the electronic density of states $N(E)$ is found, in full accordance with earlier full potential calculations of Weiner. The Fermi energy $E_F$ is located right at the edge of the valence band. An estimation of the gap width reveals values well below 1 eV. Below and above the gap, there is a strong energy dependence of occupied and unoccupied states (see our previous study on (Fe, Ni)VAl).

The non-isoelectronic substitution of V by W provides extra electrons to the system; as a consequence, the Fermi level should rise. Indeed, this can be observed from the present DFT calculations carried out for for substituted samples in terms of supercells, i.e., the chemical composition Fe2V0.875W0.125Al would correspond to Fe16V7WAl8 and Fe2V0.75W0.25Al is equivalent to Fe16V6W2Al8. Both samples are near to real compositions of the present study. In both cases, $E_F$-
FIG. 2: (Color online) Energy dependent partial and total electronic density of states $N(E)$ near to the Fermi energy $E_F$. Upper panel: $\text{Fe}_{16}V_{1-x}W_x\text{Al}$ (corresponding to $\text{Fe}_{2}V_{0.875}W_{0.125}\text{Al}$). Lower Panel: $\text{Fe}_{16}V_xW_{1-x}\text{Al}$ (corresponding to $\text{Fe}_{2}V_{0.75}W_{0.25}\text{Al}$)

moves towards the edge of the conduction band, while the the pseudo-gap structure is maintained. The colour codes indicate that predominantly Fe contributes to the electronic densities in the vicinity of the pseudo-gap, while the bunch of W-states is about 1 eV above $E_F$. The overall eDOS structure keeps pretty much the same, but the densities almost double from $x=0.00$ to $x=0.25$, i.e., $N(E) \approx 1.5 \text{states/eV} \ (x=0.125)$, and $N(E) \approx 3 \text{states/eV} \ (x=0.25)$. Moreover, the slopes of $N(E)$ slightly flatten with increasing $x$. This might distinctly influence the absolute thermopower values. The shift of the Fermi energy from the valence band edge in case of $\text{Fe}_{2}V_{0.75}\text{Al}$ to the conduction band edge for finite W content should go along with a change of the majority charge carriers, from $p$-type to $n$-type electronic transport. This, in fact, is obvious from the present experimental data (see below).

A. Hall data

In order to qualitatively check the results of electronic structure calculations and to obtain information about the mobility of the charge carriers, Hall measurements were carried out and analyzed in terms of a single band model.

Shown in Fig. 3 is the charge carrier density (left axis) together with the mobility (right axis) for various concentrations of $\text{Fe}_{2}V_{1-x}W_x\text{Al}$, taken at $T = 300 \text{ K}$. Obviously, there is a distinct change of the sign of charge carriers, from a positive signature as observed for FeWAl to the conduction band edge towards the conduction band edge. Moreover, the change of the charge carrier density by about one order of magnitude is quantitatively in agreement with the electronic density of states near right at the Fermi energy, changing also roughly by one order of magnitude, when proceeding from $x=0$ to $x=0.2$. The mobility $\mu = 1/(en\rho)$ of this series as evaluated from the charge carrier density and the electrical resistivity (see below) shows a clear trend towards enhanced values upon the V/W substitution.

B. Electrical resistivity

Shown in Fig. 4 is the temperature dependent electrical resistivity $\rho$ for various concentrations of W in...
$\text{Fe}_2\text{V}_{1-x}\text{W}_x\text{Al}$. Obviously, $\rho(T)$ of this series neither follows a simple metallic behaviour nor is characterized by a typical semiconducting one. Rather, a subtle overlay of both scenarios is quite likely; hence the temperature dependent resistivity of the present samples consists of metallic like and semiconducting like contributions together with faint, sample dependent maxima in $\rho(T)$.

Such a behaviour can be accounted for in terms of a temperature dependent charge carrier concentration in the context of electron-phonon and electron-static imperfection interactions. A model with a simplified electronic density of states, which we have developed previously (for details see e.g., Ref.\textsuperscript{18}), was successfully applied to various skutterudites, clathrates and half-Heusler systems, and recently also to the Heusler series $\text{Fe}_{2-x}\text{Ni}_x\text{VAl}$\textsuperscript{18}. Least squares fits of the model described above to the experimental data have been carried out; results are shown as solid lines in Fig. 4. Over a very broad range of temperatures, the fits reveal convincing agreements and a bunch of material related parameters, characterizing these thermoelectric materials.

Comparing $\rho(T)$ of various concentrations, several trends are obvious. The almost semi-conducting like resistivity of starting $\text{Fe}_2\text{VAl}$ crosses over to a feature with a smooth maximum in $\rho(T)$ at $T_{\text{max}}^\rho$. The latter increases with increasing W concentration. Forming a maximum in $\rho(T)$ is due to the thermal excitation of electrons across the gap in the eDOS of the system. Qualitatively this means that that the gap of the series grows with growing W content. In fact, the least squares fits reveal an increase of the gap, from about 45 meV for $\text{Fe}_2\text{VAl}$ to 205 meV for the sample with $x = 0.2$. The resulting $\rho(T)$ curve itself is a subtle balance of the growing charge carrier density as the temperature increases with respect to an increasing electron-phonon interaction with increasing temperature. Moreover, the increasing charge carrier concentration with increasing W content competes with the tendency of the lattice to become more disordered which would enlarge the residual resistivity owing to the V/W substitution.

Following the evolution of the electronic density of states, the substantially reduced eDOS at $E_F$ slightly below the pseudo-gap causes an almost simple semi-conducting behaviour; the temperature dependence, however, does not coincide with a simple exponential dependence. The increase of the W content causes a change from hole to electron-type charge carriers, together with a density increase. This causes, overall, a decrease of the absolute resistivity values and a slight shift of the maxima towards higher temperatures. Obviously, since the sample with the largest W concentration exhibits the smallest electrical resistivity in the entire temperature range, the increase in disorder scattering is supposed to be overcompensated by an increase of the charge carrier concentration due to the V/W substitution.

\textbf{C. Thermopower}

As already indicated from both the Hall effect as well as from the electronic structure calculations, the V/W substitution is responsible for a change of the charge carrier type, from hole dominated ($\text{Fe}_2\text{VAl}$) to electron dominated transport. As a consequence, thermopower changes sign, from positive ($\text{Fe}_2\text{VAl}$) to negative (W-substituted samples). This becomes obvious, too, from

\textbf{FIG. 4: (Color online) Temperature dependent electrical resistivity $\rho$ of $\text{Fe}_{2-x}\text{Ni}_x\text{VAl}$ for various concentrations $x$. The solid lines are least squares fits (see the text).}

\textbf{FIG. 5: (Color online) Temperature dependent thermopower $S$ for various concentrations $x$ of $\text{Fe}_2\text{V}_{1-x}\text{W}_x\text{Al}$.}
Mott’s theory of thermopower,
\[ S(T) = AT \frac{1}{N(E)} \frac{\partial N(E)}{\partial E} |_{E=E_F} \]

which indicates that the sign and the absolute thermopower values are determined by the logarithmic derivative of the density of states with respect to energy at the Fermi energy. In Eqn. 1, \( A \) is a constant. Taking into account Eqn. 1 in the context of the eDOS of the present materials (compare Fig. 2) would provoke larger \( S(T) \) values for \( x = 0.1 \) than for \( x = 0.2 \), since \( N(E_F) \) is larger in the latter and \( \partial N(E)/\partial E|_{E=E_F} \) is smaller.

The simple overall behaviour of \( S(T) \) as inferred from Eqn. 1 however, becomes modified from the fact that the observed thermopower not only consists of contributions from a single charge carrier type. Rather, because of the relatively narrow gap in \( N(E) \) next to the Fermi energy, both electrons and holes are becoming actively involved, i.e.,
\[ S = \frac{\sigma_h S_h + \sigma_e S_e}{\sigma_h + \sigma_e}. \]

Here, \( \sigma_{h,e} \) and \( S_{h,e} \) are the electrical conductivities and the Seebeck coefficients of holes and electrons, respectively. Eqn. 2 indicates that the measured thermopower data of narrow gap semiconductors might exhibit quite complicate temperature dependencies, where the almost linear temperature dependence as inferred from Eqn. 1 can become dramatically modified from the temperature dependent change of the charge carrier density \( n \) as well as from the temperature dependent electron - phonon interaction, distinctly influencing the electrical conductivity of a certain system. Various measurements carried out on doped/substituted Fe\(_2\)VAl samples demonstrate a behaviour which is similar to the one of Fig. 5 including changes from positive to negative values (compare e.g. Refs. 8-21).

The Seebeck coefficient of narrow gap semiconductors exhibit very frequently extrema in its temperature dependence. According to Ref. 22, the gap in the eDOS \( E_g \) near to \( E_F \) is related to the maximum value of the thermopower at that temperature \( T_{max}^S \) according to
\[ E_g = 2e|S_{max}|T_{max}^S. \]

Here, \( e \) is the electron charge \( S_{max} \) the thermopower at the maximum in the \( S(T) \) curve at a temperature \( T_{max}^S \). This extremum is a consequence of a bipolar conduction mechanism, involving thermal excitations of holes and electrons across the band gap. The sign change of \( S(T) \) of starting material Fe\(_2\)VAl at elevated temperatures is thus a result of the promotion of electrons across the gap in the eDOS near the Fermi energy \( E_F \).

Applying Eqn. 2 to experimental data of Fig. 5 allows to derive a rough estimation for \( x = 0.1 \), revealing \( E_g \approx 45 \) meV.

### D. Phonon dispersion and thermal conductivity

Measurements of the temperature dependent thermal conductivity \( \lambda \) of Fe\(_2\)VAl based alloys reported so far, demonstrated that the lattice thermal conductivity dominates the overall measured quantity. Hence, the knowledge of the phonon system in such materials is of importance to understand the respective behaviour. We have carried out DFT calculations in order to obtain reliable dispersion and phonon density of state data of these materials. Vibrational properties of Fe\(_2\)V\(_{1-x}\)W\(_x\)Al were derived in the harmonic approximation employing the direct force-constant-method as implemented in the program package fPHON 23-24. For deriving the force constants density functional perturbation theory calculations as implemented in VASP were performed. Atomic positions were optimized until the residual forces were less than \( 2 \times 10^{-5} \) eV/Å. For anharmonic contributions a quasi-harmonic approach was applied 25-26. For this approach bulk moduli are needed which amount to 207 GPa for Fe\(_2\)VAl and 218 GPa for Fe\(_2\)V\(_{0.875}\)W\(_{0.125}\)Al and 226 GPa for Fe\(_2\)V\(_{0.75}\)W\(_{0.25}\)Al.

In order to obtain reliable phonon data for the W substituted systems, \( 2 \times 2 \times 2 \) supercells have been constructed such that Fe\(_2\)W\(_7\)Al corresponds to Fe\(_2\)V\(_{0.875}\)W\(_{0.125}\)Al and Fe\(_{16}\)W\(_6\)Al corresponds to Fe\(_2\)V\(_{0.75}\)W\(_{0.25}\)Al. Results are presented for the respective DFT volumes in Fig. 6.

The acoustic branches in Fe\(_2\)VAl form the quite shallow part up to 6 THz, followed by optical branches. Above a gap of about 2 THz, almost dispersion-less Al branches are located. Relevant parameters with respect to thermal conductivity are the sound velocities (2 transversal \( (v_{1,2}) \) and one longitudinal contribution \( (v_l) \)) as well as the Grüneisen parameter. These data are collected in Table 4 for Fe\(_2\)VAl.

Substituting V/W reveals various changes of the overall phonon dispersion (Fig. 3(b,c)). i) The acoustic phonon branches are less steep in comparison to the starting material. As a consequence, the average sound velocity reduces from 5263 to 4908 and finally to 4632 m/s for \( x = 0.1, 0.25 \), respectively (compare Table 4). As the thermal conductivity is a function of the sound velocity, a decrease in this sequence can be expected without considering any further scattering processes. Interestingly, the acoustic branches get very flat in the range of about 4 THz, driven mostly from W vibrations. ii) The optical branches are lowered upon the increasing W content, too. A gap opens in the case \( x = 0.25 \) between the acoustic and optical branches and the Al bands lower slightly in both substituted systems. Due to the usage of supercells, containing much more atoms, the number of optical branches increases as a consequence. The lower lying optical bands result from Einstein-like vibrations, which might constitute additional scattering of the heat carrying phonons; hence, the thermal conductivity of the W substituted alloys is expected to further decrease. iii) The Grüneisen parameter \( \Gamma \) is increasing as well for an
increasing W content. Since the lattice thermal conductivity \( \lambda_{ph} \) depends on \( \Gamma \), i.e., \( \lambda_{ph} \propto 1/\Gamma^2 \), an additional decrease of thermal conductivity is expected. Note that \( \Gamma \) accounts for the anharmonicity of lattice effects.

These three scenarios obtained from the DFT calculations infer that the modifications of the phonons intrinsically lead to a reduction of the lattice thermal conductivity. Besides, enhanced scattering of the heat carrying phonons on increased static disorder in the lattice due to the random distribution of V and W on the (4a) sites of the Cu2MnAl-type structure is expected. Primarily mass and sized differences between V and W matter.

**FIG. 6:** (Color online) Calculated \( \bar{\nu} \) dependent phonon dispersion at DFT equilibrium volumes weighted according to local atomic contributions (Fe – red, V – green, Al – blue, W – black, mixed colours indicate mixed contributions). upper panel: Fe2VAl, middle panel: Fe2V0.875W0.125Al lower panel: Fe2V0.75W0.25Al.

The average velocities of sound \( \bar{\nu} \) and the Debye temperatures were obtained according to Ref. 27. As discussed previously, the DFT values of Fe2VAl are larger than those directly derived from measurements of the sound velocity, but roughly agree with heat capacity studies. The concentration dependent variation of data, however, are very reasonable. Due to the V/W substitution, the strength of the material increases, as expressed by the bulk modulus \( B_0 \), while the increase of mass upon the increase of the W content reduces the sound velocities and thus the Debye temperatures, too, by about 10 % for the 20 % exchange of V/W.

The temperature dependent thermal conductivity \( \lambda \) of Fe2V\( x \rightarrow x \) W-Al is plotted in Fig. 7 for various concentrations \( x \). It is well known from literature that \( \lambda(T) \) of Fe2VAl is, at least in certain temperature ranges, roughly 40 to 50 times larger than that of archetypal Bi2Te3. It is, in the most simplest picture, a consequence of the very large sound velocity (more than 5200 m/s) and the relative simple type of crystal structure. As already discussed in the previous paragraph, the V/W substitution causes an intrinsic decrease of \( \lambda_l(T) \) together with improved scattering on point defects from the disorder at the (4a) sites. In fact, these mechanisms substantially influence \( \lambda(T) \) as can be seen from the large overall drop of \( \lambda(T) \) in the experimental data.

In a standard procedure, as described in many details, e.g., in our recent work on Fe2-xNi4VA13, the thermal conductivity can be analyzed and proper conclusions can be drawn. The lattice thermal conductivity follows simply from \( \lambda_{ph} = \lambda - \lambda_e \), where the subscript \( e \) refers to the

| TABLE I: Calculated velocities of sound \( \nu \) at 300K for DFT equilibrium. Values given for the three acoustic modes (l: longitudinal, t1,t2: transversal) and mode average \( \bar{\nu} \), the Debye temperature \( \theta_D \) and the Bulk modulus \( B_0 \) |
|---------------------------------|-----------------|-----------------|-----------------|
| \( \nu_l \) [m/s] | \( \nu_t \) [m/s] | \( \bar{\nu} \) [m/s] | \( \theta_D \) [K] | \( B_0 \) [GPa] |
| Fe2VAl | Fe2V0.875W0.125Al | Fe2V0.75W0.25Al |
| 4568 | 4247 | 4013 | 696 | 644 | 606 |
electronic thermal conductivity. The latter is derived employing the Wiedeman Franz law. Obviously, $\lambda_e$ is small; its contribution is just a few percent to the overall measured effect. The analysis of the remaining part, $\lambda - \lambda_e$, is carried out in the context of Callaway's theory, where phonons are considered in terms of the Debye model, and scattering processes are accounted for by a total relaxation time, $1/\tau_c = \sum 1/\tau_i$. The individual scattering processes are considered independent from each another and are characterized by distinct temperature and frequency dependencies.\[25\]

The Callaway model can be expressed as\[29\]

$$\lambda_{ph} = \frac{k_B}{2\pi^2 v_s} \left( \frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \frac{x^4 \exp(x)}{\tau_c (\exp(x) - 1)^2} dx.$$  \[4\]

$x = \hbar \omega/(k_B T)$, $k_B$ is the Boltzmann constant and $\omega$ the phonon frequency; $\hbar = h/(2\pi)$. $\tau_c$ for the relevant phonon scattering processes is given by

$$1/\tau_c = v_s/L + A \omega^4 + B \omega^2 T \exp(-\theta_D/T) + E \omega$$  \[5\]

where the terms of the rhs of Eqn. 5 refer to scattering on grain boundaries with average size $L$, on point defects, Umklapp-processes and electrons, respectively. $A$, $B$ and $E$ are material dependent constants. Least squares fits according to Eqns. 4 and 5 have been performed and results are shown in Fig. 7 as solid and dashed lines. Adding a $T^3$ term to account for radiation losses inherent to the steady state heat flow technique, reveals a fairly well agreement between experiment and theory. In all cases, the sound velocity and the Debye temperature was changed linearly from $x = 0 \rightarrow x = 0.20$ as inferred from the DFT results.

The parameters derived from these least squares fits allow to trace, among others, the evolution of the point defect scattering parameter $A$ as a function of the W concentration (compare Fig. 8 left axis). It demonstrates that W constitutes a significant scattering center, as this parameter grows substantially, by more than one order of magnitude. This is about twice as large as observed in a similar study concerning the Fe/Ni substitution in (Fe,Ni)$_2$VA\[33\] and can be attributed to much larger mass/volume differences between V and W compared to Fe and Ni. Because of this significant enhancement of scattering on point defects as well as intrinsic parameters like the sound velocity, the thermal conductivity drops, to below a quarter of the value of Fe$_2$VAI at $T = 300$ K for the system with 20% V exchange by W (compare Fig. 8 right axis).

The efficiency of point defect scattering is a result of contributions from mass fluctuations and volume differences of atoms on certain sublattices of the crystal structure. In general, it can be expressed by a disorder parameter $\Gamma$ as $\Gamma = \Gamma_m + \Gamma_s$, where the subscripts $M$ and $S$ refer to mass and strain field, respectively.\[31\]

Following the procedure as outlined in Refs.\[32\] reveals a substantial contribution from mass differences between V and W, almost 2 orders of magnitude larger than the respective contribution due to size differences (Fig. 9). The parameter $\Gamma_{expt}$ is derived from the experimental thermal conductivity data, as described in detail by Yang et al.\[32\] The gap between $\Gamma_{expt}$ and $\Gamma$ is closed by an empirical factor (in general between 10 and 100)\[31\] accounting for an appropriate pre-factor of the strain field contribution.

![FIG. 7: (Color online) Temperature dependent thermal conductivity $\lambda$ for various concentrations $x$ of Fe$_2$V$_{1-x}$W$_x$Al. The solid and dashed lines are least squares fits as explained in the text.](image1)

![FIG. 8: (Color online) Concentration dependent point defect scattering parameter $A$ of Fe$_2$V$_{1-x}$Ni$_x$Al (compare Eqn. 5) (left axis) and lattice thermal conductivity $\lambda_{ph}$ taken at room temperature.](image2)
FIG. 9: (Color online) Concentration dependent disorder parameter of \( \text{Fe}_2\text{Ni}_x\text{VAl} \) derived experimentally (\( \Gamma_{\exp} \)) and theoretically (\( \Gamma \)); the latter consists of an mass (\( \Gamma_m \)) and volume related contribution (\( \Gamma_s \)).

\[
\begin{align*}
\text{W concentration } x & \quad 0.00 \quad 0.05 \quad 0.10 \quad 0.15 \quad 0.20 \\
\text{disorder parameter } \Gamma & \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^1 \quad 10^2 \\
\Gamma_{\exp} & \quad \Gamma & \quad \Gamma_m & \quad \Gamma_s
\end{align*}
\]

E. Thermoelectric performance

The relatively large Seebeck values and moderate electrical resistivities observed in \( \text{Fe}_2\text{V}_{1-x}\text{W}_x\text{Al} \) samples cause that the power factors \( p_f \) of the four sample studied are ranging between 1.6 and 2.55 mW/(m·K²). These values are large and compare with those of non-optimized \( \text{Bi}_2\text{Te}_3 \) systems. The figure of merit, \( ZT \), keeps modest because of the still large thermal conductivities but reaches \( ZT \approx 0.20 \) for \( x = 0.1 \). While \( \text{Bi}_2\text{Te}_3 \) based materials have thermal conductivities, ranging between 1 and 1.5 W/cmK, the room temperature value found for \( \text{Fe}_2\text{V}_{0.8}\text{W}_{0.2}\text{Al} \) is of the order of 4 W/cmK. The reduction of \( \lambda(300) \) to about 25 % of its initial value in \( \text{Fe}_2\text{VAl} \) is besides intrinsic changes of the phonon system a result of point defect scattering enhanced by the V by W exchange.

\[
\begin{align*}
\text{Fe}_2\text{V}_{1-x}\text{W}_x\text{Al} & \quad 0.00 \quad 0.05 \quad 0.10 \quad 0.15 \quad 0.20 \\
\text{disorder parameter } \Gamma & \quad 10^{-1} \quad 10^{-2} \quad 10^{-3} \quad 10^1 \quad 10^2 \\
\Gamma_{\exp} & \quad \Gamma & \quad \Gamma_m & \quad \Gamma_s
\end{align*}
\]

F. Off-stoichiometric W-based Heusler systems

Besides substitution and doping of a certain starting material, e.g., \( \text{Fe}_2\text{VAl} \), off-stoichiometric preparation, i.e., \( \text{Fe}_2\text{V}_{1.5}\text{Al}_{1.5} \) was already employed and distinct changes in the electronic and thermal transport were obtained. Here, we combine the substitution of V by W with off-stoichiometric preparation. As an example, \( \text{Fe}_{2/3}\text{V}_{0.9}\text{W}_{0.1}\text{Al}_{0.24} \) is chosen. Experimental results are shown in Figs. 10 and 11. Remarkably, the overall electrical resistivity, \( \rho \), is small, only about half of of the respective stoichiometric compound, while the charge carrier density \( n = 4 \cdot 10^{21} \text{ cm}^{-3} \) is almost equal.

\[
\begin{align*}
\text{FIG. 10: (Color online) Temperature dependent thermal conduction } \lambda \text{ for various concentrations } x \text{ of } \text{Fe}_2\text{V}_{1-x}\text{W}_x\text{Al}. \text{ The solid and dashed lines are least squares fits as explained in the text.}
\end{align*}
\]

This refers to a higher mobility of electrons in this sample. The Seebeck effect around room temperature, on the other hand, is large, about \(-135 \mu\text{V/K} \), indicating electrons as primary charge carriers. The temperature dependent thermal conductivity is similar to the equivalent stoichiometric system and the phonon contribution \( \lambda_{ph} \) at room temperature coincides within about 10 %. As a consequence, the power factor, \( p_f \), (compare Fig. 11) appears to be extraordinarily large, exceeding best behaving \( \text{Bi}_2\text{Te}_3 \) at ambient pressure. In the context of the reduced thermal conductivity observed, the figure of merit, \( ZT = 0.22 \), is one of the largest ever obtained \( ZT \) value of full Heusler systems. Here, it should be noted that while the under-stoichiometric systems (i.e., \( \text{Al}_{24} \)) are electron dominated, the over-stoichiometric systems, i.e., \( \text{Al}_{36} \) are hole dominated. This indicates that small changes of the element contents in \( \text{Fe}_2\text{VAl} \) based Heusler systems might have dramatic effects on the electronic structure and thus on electronic and thermal transport.

V. SUMMARY

The substitution of V/W in the full Heusler series \( \text{Fe}_2\text{V}_{1-x}\text{W}_x \) is responsible for a distinct change of electronic and thermal transport. This is caused by the movement of the Fermi energy from the valence band edge in \( \text{Fe}_2\text{VAl} \) across the band gap towards the conduction band, as proven from Hall and Seebeck effect measurements and confirmed by DFT calculations of the electronic structure (band dispersion and electronic density of states, eDOS). Since the Fermi energy is located at steep slopes of the eDOS, large Seebeck values are expected, and in fact are found experimentally.

Besides modifications of the electronic structure, the phonon system of the the substituted samples changes as well. This results primarily in a reduction of the var-
FIG. 11: (Color online) Temperature dependent thermal conductivity $\lambda$ for various concentrations $x$ of Fe$_{2/3}(V_{0.9}W_{0.1})_{1/3}$Al$_{0.76}$Cu$_{0.24}$. The solid and dashed lines are least squares fits as explained in the text.

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1. T. Graf, C. Felser, and S. S. Parkin, Progress in Solid State Chemistry 39, 1 (2011), ISSN 0079-6786, URL [http://www.sciencedirect.com/science/article/pii/S0079678611000021](http://www.sciencedirect.com/science/article/pii/S0079678611000021)

2. C. Felser and A. Hirohata, Springer Series in Materials Science 222 (2016).

3. Y. Nishino, S. Deguchi, and U. Mizutani, Phys. Rev. B 74, 115115 (2006), URL [http://link.aps.org/doi/10.1103/PhysRevB.74.115115](http://link.aps.org/doi/10.1103/PhysRevB.74.115115)

4. C. S. Lue, C. F. Chen, J. Y. Lin, Y. T. Yu, and Y. K. Kuo, Phys. Rev. B 75, 064204 (2007), URL [http://link.aps.org/doi/10.1103/PhysRevB.75.064204](http://link.aps.org/doi/10.1103/PhysRevB.75.064204)

5. M. Mikami and K. Kobayashi, Journal of Alloys and Compounds 466, 530 (2008), ISSN 0925-8388, URL [http://www.sciencedirect.com/science/article/pii/S0925838807022311](http://www.sciencedirect.com/science/article/pii/S0925838807022311)

6. M. Mikami, S. Tanaka, and K. Kobayashi, Journal of Alloys and Compounds 484, 444 (2009), ISSN 0925-8388, URL [http://www.sciencedirect.com/science/article/pii/S0925838809005979](http://www.sciencedirect.com/science/article/pii/S0925838809005979)

7. M. Mikami, Y. Kimemichi, K. Ozaki, Y. Terazawa, and T. Takeuchi, Journal of Applied Physics 111, 093710 (2012), URL [http://scitation.aip.org/content/aip/journal/jap/111/9/10.1063/1.4710990](http://scitation.aip.org/content/aip/journal/jap/111/9/10.1063/1.4710990)

8. K. Renard, A. Mori, Y. Yamada, S. Tanaka, H. Miyazaki, and Y. Nishino, Journal of Applied Physics 115, 033707 (2014), URL [http://scitation.aip.org/content/aip/journal/jap/115/3/10.1063/1.4861419](http://scitation.aip.org/content/aip/journal/jap/115/3/10.1063/1.4861419)

9. M. Mikami, M. Imukai, H. Miyazaki, and Y. Nishino, Journal of Electronic Materials 45, 1284 (2016), ISSN 1543-186X, URL [http://dx.doi.org/10.1007/s11664-015-3999-7](http://dx.doi.org/10.1007/s11664-015-3999-7)

10. P.-C. Wei, T.-S. Huang, S.-W. Lin, G.-Y. Guo, and Y.-Y. Chen, Journal of Applied Physics 118, 165102 (2015), URL [http://scitation.aip.org/content/aip/journal/jap/118/16/10.1063/1.4934734](http://scitation.aip.org/content/aip/journal/jap/118/16/10.1063/1.4934734)

11. H. Al-Yamani and B. Hamad, Journal of Electronic Materials 45, 1101 (2016), ISSN 1543-186X, URL [http://dx.doi.org/10.1007/s11664-015-4265-8](http://dx.doi.org/10.1007/s11664-015-4265-8)

12. E. Bauer, S. Berger, C. Paul, M. D. Mea, G. Hilscher, H. Michor, M. Reissner, W. Steiner, A. Grytsiv, P. Rogl, et al., Phys. Rev. B 66, 214421 (2002), URL [http://link.aps.org/doi/10.1103/PhysRevB.66.214421](http://link.aps.org/doi/10.1103/PhysRevB.66.214421)

13. G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993), URL [http://link.aps.org/doi/10.1103/PhysRevB.47.558](http://link.aps.org/doi/10.1103/PhysRevB.47.558)

14. G. Kresse and J. Furthmüller, Computational Materials Science 6, 15 (1996), ISSN 0927-0256, URL [http://www.sciencedirect.com/science/article/pii/092702569600080](http://www.sciencedirect.com/science/article/pii/092702569600080)

15. G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996), URL [http://link.aps.org/doi/10.1103/PhysRevB.54.11169](http://link.aps.org/doi/10.1103/PhysRevB.54.11169)

16. J. P. Perdew, Phys. Rev. B 33, 8822 (1986).

17. P. E. Blöchl, Phys. Rev. B 50, 17953 (1994), URL [http://link.aps.org/doi/10.1103/PhysRevB.50.17953](http://link.aps.org/doi/10.1103/PhysRevB.50.17953)

18. I. Knapp, B. Budinská, D. Milosavljevic, P. Heinrich, S. Khmelevskyi, R. Moser, R. Podlochuck, P. Preminger, and E. Bauer, Phys. Rev. B 96, 045204 (2017), URL [http://link.aps.org/doi/10.1103/PhysRevB.96.045204](http://link.aps.org/doi/10.1103/PhysRevB.96.045204)

19. M. Weinert and R. E. Watson, Phys. Rev. B 58, 9732 (1998), URL [http://link.aps.org/doi/10.1103/PhysRevB.58.9732](http://link.aps.org/doi/10.1103/PhysRevB.58.9732)

20. E. J. Skoug, C. Zhou, Y. Pei, and D. T. Morelli, Journal of Electronic Materials 43, 1922 (2014), ISSN 1543-186X, URL [http://dx.doi.org/10.1007/s11664-013-2910-7](http://dx.doi.org/10.1007/s11664-013-2910-7)

21. M. Mikami, M. Mizoshiri, K. Ozaki, H. Takazawa, A. Yamamoto, Y. Terazawa, and T. Takeuchi, Journal of Electronic Materials 43, 1922 (2014), ISSN 1543-186X, URL [http://dx.doi.org/10.1007/s11664-013-2910-7](http://dx.doi.org/10.1007/s11664-013-2910-7)

22. H. J. Goldsmid and J. W. Sharp, Journal of Electronic Materials 28, 869 (1999), ISSN 1543-186X, URL [http://dx.doi.org/10.1007/s11664-015-3999-7](http://dx.doi.org/10.1007/s11664-015-3999-7)
D. Alfè, Comp. Phys. Commun. 180, 2622 (2009).

D. Reith, PhD thesis, Vienna University (2011).

Y. Zhang, E. Skoug, J. Cain, V. Ozoliņš, D. Morelli, and C. Wolverton, Phys. Rev. B 85, 054306 (2012), URL http://link.aps.org/doi/10.1103/PhysRevB.85.054306

R. Moser, PhD thesis, Vienna University of Technology (2016).

O. L. Anderson, Journal of Physics and Chemistry of Solids 24, 909 (1963), ISSN 0022-3697, URL http://www.sciencedirect.com/science/article/pii/0022369763900672.

J. Callaway, Phys. Rev. 113, 1046 (1959), URL http://link.aps.org/doi/10.1103/PhysRev.113.1046.

Z. Zhou, C. Uher, A. Jewell, and T. Caillat, Phys. Rev. B 71, 235209 (2005), URL http://link.aps.org/doi/10.1103/PhysRevB.71.235209.

A. Pope, B. Zawilski, and T. Tritt, Cryogenics 41, 725 (2001), ISSN 0011-2275, URL http://www.sciencedirect.com/science/article/pii/S0011227501001400.

B. Abeles, Phys. Rev. 131, 1906 (1963), URL http://link.aps.org/doi/10.1103/PhysRev.131.1906.

J. Yang, G. P. Meisner, and L. Chen, Applied Physics Letters 85 (2004).

S. V. Ovsyannikov, V. V. Shechennikov, G. V. Vorontsov, A. Y. Manakov, A. Y. Likhacheva, and V. A. Kulbachinskii, Journal of Applied Physics 104, 053713 (2008), https://doi.org/10.1063/1.2973201, URL https://doi.org/10.1063/1.2973201.