Electronic and thermoelectric properties of Fe$_2$VAl: The role of defects and disorder

Daniel I. Blic and Philippe Ghosez

Physique Théorique des Matériaux, Université de Liège (B5), B-4000 Liège, Belgium

Using first-principles calculations, we show that Fe$_2$VAl is an indirect band gap semiconductor. Our calculations reveal that its, sometimes assigned, semimetallic character is not an intrinsic property but originates from the antisite defects and site disorder, which introduce localized ingap and resonant states changing the electronic properties close to band gap. These states negatively affect the thermopower $S$ and power factor $PF=S^2\sigma$, decreasing the good thermoelectric performance of intrinsic Fe$_2$VAl.

Energy-related issues are becoming more and more crucial. Devices based on thermoelectric (TE) materials are very appealing in this context, and they are one of the main thrusts in energy research on the global scale. They can be used for cooling or heating and for energy generation from recovered waste heat. The efficiency of a TE material depends on the dimensionless TE figure of merit, $ZT=(S^2\sigma T)/\kappa_{th}$, where $S$ is the electrical conductivity, $\sigma$ is the thermopower, $T$ is the absolute temperature, and $\kappa_{th}$ is total thermal conductivity which has electronic and lattice contributions. Improving the TE efficiency is not obvious because the different parameters entering $ZT$ are linked and compete with each others. Moreover, $ZT$ has to be maximized in the regime at which the TE device will be operated and other aspects must also be considered, such as the cost of materials, their toxicity and availability. For many applications, large scale installations will be essential for harnessing the full potential of thermoelectricity and the use of less efficient but cheap compounds might offer a valuable solution.

In this respect, Fe$_2$VAl has electronic properties potentially interesting for TE applications (ZT~0.13 at 300K for Fe$_2$VAl$_{0.9}$Ge$_{0.1}$ [1] and ZT~0.15 at 300K for Fe$_2$VAl$_{0.9}$Si$_{0.07}$Sb$_{0.03}$ [2]). Fe$_2$VAl has a L2$_1$ Heusler structure. It is more than a decade since Nishino et al. have reported its unusual properties, but the ground state of the intrinsic system is still unclear [2]. Fe$_2$VAl shows a semiconducting or semimetallic behaviour with a pseudogap of $\sim0.1$-0.27 eV [4, 5]. Fe$_2$VAl is nonmagnetic (no long range FM order) but possesses magnetic anti-site defects and superparamagnetic clusters [6, 7]. It has a large specific heat at low T and first it was suggested to be a possible candidate for a 3d heavy-fermion system [3, 8]. Later, field-dependent specific heat measurements showed that the large specific heat was not an intrinsic behaviour and it was assigned to magnetic defects [9]. Fe$_2$VAl has also a negative resistivity slope at high T [8]. It has a dominant p-type transport character, with a high hole concentration of $n_h=4.8\times10^{20}$ cm$^{-3}$ [10] and shows a very large residual resistivity [2]. All these properties suggest that defects and disorder play an important role in this material.

Previous electronic structure calculations on Fe$_2$VAl were based on density functional theory (DFT) using usual exchange-correlations functionals such as the generalized gradient and local density approximations (GGA, LDA) and predicted Fe$_2$VAl to be a compensated semimetal with a deep pseudogap of $\sim0.1$-0.2 eV [11-13]. The presence of pseudogap with a finite density of states at the Fermi level is supported by optical reflectivity [5] and NMR [4] experiments, but the compensated character of carriers is in contradiction with Hall measurements [10] which found excess of holes. Usual DFT functionals are known to underestimate semiconductor band gaps and usually fail to describe strongly correlated systems. Hybrid functionals often allow to circumvent these problems and so constitute a promising alternative to better characterize Fe$_2$VAl.

In this letter we report the electronic and transport properties of Fe$_2$VAl using both the usual GGA functional of Perdew, Burke, and Ernzerhof (PBE [14]) and the recently developed B1-WC hybrid functional [15], which mixes the GGA of Wu and Cohen [16] with 16% of exact exchange. Whereas PBE reproduces the semimetallic character found in previous calculations, we predict Fe$_2$VAl to be a narrow gap semiconductor within B1-WC. Going beyond previous studies, we also investigate the role of single antisite defects and disorder on the transport properties. Our calculations strongly support that Fe$_2$VAl is intrinsically a semiconductor and that its semimetallic character originates from antisite defects and disorder, which introduce localized ingap and resonant states in the vicinity of the band gap. We show that such states negatively affect the power factor $PF=S^2\sigma$.

The calculations [17] were performed using the augmented plane wave and local orbital (APW+lo) method as implemented in WIEN2k [18]. We use the experimental lattice constant of 5.76 Å for a better comparison with previous calculations. The spin-orbit interactions and scalar relativistic effects were included. For the antisite defects and disordered configuration we considered supercells (SCs) with rhombohedral symmetry having 32 formula units (f.u) of Fe$_2$VAl which were derived from a 2x2x2 fcc cell with 4 atoms/cell along [1,1,1] direction [17]. The transport calculations were performed using Boltzmann transport formalism within the constant relaxation time approximation using BoltzTraP [19].

First, we consider the electronic properties. Our calculations describe Fe$_2$VAl to be nonmagnetic within both PBE and B1-WC. Although, it is described as a
semimetal within PBE (Fig. 1b), as consistently obtained in previous calculations, it is predicted to be a semiconductor with an indirect band gap $E_g=0.34$ eV (Fig. 1), within B1-WC. This is not specific to B1-WC: other hybrid functionals, such as B3PW91, similarly predict a semiconducting character, although the exact value of the gap depends on the percentage of exact exchange included in the functional. In comparison to PBE, B1-WC opens an indirect band gap by shifting up in energy the lowest conduction band (CB) states with mixed V and Fe $e_g$ character with respect to the top valence band states with Fe $t_{2g}$ character. The states close to CB minimum (X point in Brillouin zone) have a highly dispersive V $e_g$ character, a very desired feature for good TE performance. We notice also that the charge of Al resulting from Bader analysis is equal to $1.68e$. This highlights that Al p states hybridize with V and Fe d states and that Al does not donate all its 3 electrons to the Fe-V complex.

Let us now focus on the transport properties, using the constant relaxation time approximation. Within this approximation, $S$ is independent of the relaxation time $\tau$, whereas $\sigma$ and the power factor $PF=S^2 \sigma$ depend linearly on $\tau$. Mainly due to Al deficiency, Fe$_2$VAI naturally forms as a hole-doped system with a carrier concentration $n_h=4.8x10^{20}$ cm$^{-3}$. The value of $\tau$ was estimated at this carrier concentration by fitting the electrical resistivity $\rho$ at 300 K to the experimental value of 0.75 m$\Omega$cm [1] [21]. This yielded a hole relaxation time $\tau_h^{PBE}=0.9x10^{-14}$ s within PBE and $\tau_h^{B1-WC}=1.4x10^{-14}$ s within B1-WC. The electronic specific heat was also estimated for this hole-doped system. We obtained a value of 1.00 mJ/molK$^2$ within B1-WC, in better agreement with the experimental estimate of $1.5\pm0.3$ mJ/molK$^2$ [9] than the PBE value of 0.76 mJ/molK$^2$.

Electron doping of Fe$_2$VAI can be achieved from atomic substitution at Al site. We so estimated $\tau_e$ for electron doped Fe$_2$VAI$_{1-x}$M$_x$ (M=Si, Ge) systems by fitting $\rho$ at 300K to the experimental value of 0.65 m$\Omega$cm corresponding to a doping $x=0.03$ [1] [21]. Assuming that each atom M brings one additional electron, this corresponds to an electron concentration $n_e\sim6.0x10^{20}$ cm$^{-3}$, which adds to the initial $n_h$, assumed to be unchanged. Taking this into account, we get the electron relaxation times $\tau_e^{PBE}=1.5x10^{-14}$ s and $\tau_e^{B1-WC}=3.4x10^{-14}$ s. These values are slightly larger than those of the naturally formed hole-doped system, in qualitative agreement with the observation that the residual resistivity of Fe$_2$VAI decreases with doping at Al site [1] [21].

In Figure 2 we report the thermopower $S$ and power factor $PF$ of electron-doped Fe$_2$VAI along the x-axis ($S=S_{xx}$, $PF=PF_{xx}$) as a function of the chemical potential $\mu$. The amplitudes of $S$ and PF corresponding to $\mu$ for which the n-type PF reaches its maximum value are indicated by arrows. This is obtained for $\mu=3.4x10^{-14}$ s and $\tau_e^{B1-WC}=3.4x10^{-14}$ s. These values are slightly larger than those of the naturally formed hole-doped system, in qualitative agreement with the observation that the residual resistivity of Fe$_2$VAI decreases with doping at Al site [1] [21].
WC which describes Fe$_2$VAl as a semiconductor, we get larger values $S \sim -137 \mu V/K$ and $PF \sim 3$ mW/mK$^2$ in close agreement with experimental data. This demonstrates that a better description of Fe$_2$VAl is obtained when properly accounting for its semiconductor nature as obtained within B1-WC.

In Figure 3 we also report the temperature dependence of $S$ and $PF$ at fixed concentrations, corresponding to $\mu$ for which the n-type $PF$ reaches its maximum value within B1-WC and PBE at 300K (see Fig 2). It can be seen that the theoretical $S$ and $PF$ do not saturate even up to 800 K within B1-WC. This shows the very good potential of Fe$_2$VAl for TE performance at high temperatures ($E_g=0.34$ eV) in comparison with other thermoelectric materials like Bi$_2$Te$_3$ (experimental $E_g=0.15$ eV). This contrasts however with the experimental observations, showing that $S$ and $PF$ are saturating around 200-250 K. We infer that this deterioration of the TE performance comes from defects and disorder, which change the electronic properties near the band gap.

In order to further prove this, we considered large SCs including 32 f.u. and performed B1-WC calculations including different types of single antisite defects and even considering a fully disordered configuration. Although the SC size corresponds to defect concentrations of $\sim 0.03$, typically one-order of magnitude larger than what is observed experimentally [9], it is sufficient to treat the defects as isolated and to highlight their influence on the electronic and transport properties.

As illustrated in Fig. 4, the $V_{Fe}$ antisite defect, arising from the permutation of one V atom with Fe, reduces the band gap of Fe$_2$VAl to $\sim 0.18$ eV, by introducing localized d states into the gap, directly associated to the V and Fe atoms forming the defect. Moreover, this defect is magnetic with a magnetic moment of $4\mu_B$/defect localized on the defect, a value which agrees well with that of $3.7\mu_B$/defect found in specific heat and NMR experiments [7, 8]. By contrast, the $V_{Al}$ antisite defect is non-magnetic and does not introduce any ingap state (Fig 4b). Finally, the Fe$_{Al}$ antisite defect introduces resonant Fe d states at the bottom (resp. top) of conduction (resp. valence) bands (Fig 4c). Again, this defect is magnetic with a magnetic moment of $4.6\mu_B$/defect. So, our B1-WC calculations reveal that some antisite defects are magnetic and that only those introduce localized ingap states and resonant states close to the gap region, significantly changing the electronic properties of Fe$_2$VAl.

In order to model further the effect of site disorder, we also considered a disordered configuration, arising from an arbitrary occupancy of the different sites within the SC and including 20 antisite defects (8 $V_{Fe}$, 6 $V_{Al}$, and 6 Fe$_{Al}$). The change in the electronic properties close to the gap region is even more obvious for this disordered configuration for which a semimetallic behaviour with a pseudogap and a magnetic moment of $53.5\mu_B$/cell is obtained (see Fig 4d). These results clearly establish that the semimetallic character seen in experiments can be explained from antisite defects and disorder.

It is now very interesting to explore the effect of the localized ingap and resonant d states on the transport properties. Mahan and Sofo have shown that a narrow energy (delta-shape) distribution of the electronic states participating in the electronic transport is needed in order to maximize ZT [22]. Therefore, such localized ingap and resonant d states are expected to increase PF in the cases where these states have a significant weight with respect to the background states [22]. However, as summarized in Fig. 5 our transport calculations including antisite defects and disorder show that the localized ingap d states do not increase PF, which takes smaller or comparable values for accessible $n_c$ doping values. For defect concentration seen in experiment, the reduction should be less apparent but these calculations establish that antisite defects will never boost the TE performance.
FIG. 5: (Color online) $\text{PF}_{xx}$ as a function of $\mu$ for the antisite defects and disordered configuration of Fe$_2$VAI within B1-WC at 300 K using $\tau_{B1-WC}$. $x$ value of 0.03 for the intrinsic Fe$_2$VAI is indicated by arrow. Note that for defects and disorder, this $x$ value is achieved at smaller $\mu$.

For $n_e$ value corresponding to the maximum PF of intrinsic Fe$_2$VAI ($x=0.03$), we show the temperature dependence of $S$ and PF in Figure 6. The antisite defects and disorder have a detrimental effect on PF, decreasing and saturating its values with $T$. For V$_{Fe}$ defect, $S$ and PF values are saturating at $\sim 350$ K, behaviour seen in experiment. It is interesting to note that our disordered configuration have a "hole-like" dominated $S$, even at $x=0.03$. This suggests that the p-type character of Fe$_2$VAI may originate also partly from site disorder, and not only from off-stoichiometry of the constituents.

In summary, our B1-WC calculations show that Fe$_2$VAI is an indirect narrow band gap semiconductor with a highly-dispersive $V_{eg}$ CB and three fold degenerate CB minimum, all features highly-compatible with good intrinsic TE performances. Our calculations including anti-site defects also demonstrate that the semimetallic character of Fe$_2$VAI seen in experiments can be explained from atomic disorder. Some anti-site defects are magnetic and introduce localized ingap and resonant states in the gap region. These defects tend to decrease the good intrinsic TE performances of Fe$_2$VAI.

Acknowledgments

We acknowledge financial support from Walloon Region through the CoGeTher, EnergyWall project.

[1] Y. Nishino, S. Deguchi, and U. Mizutani, Phys. Rev. B 74, 115115 (2006).
[2] M. Mikami, S. Tanaka, and K. Kobayashi, J. Alloys Comp. 484, 444 (2009).
[3] Y. Nishino et al., Phys. Rev. Lett. 79, 1909 (1997).
[4] C. S. Lue and J. H. Ross, Jr., Phys. Rev. B 58, 9763 (1998).
[5] H. Okamura et al., Phys. Rev. Lett. 84, 3674 (2000).
[6] M. Vasundhara, V. Srinivas, and V. V. Rao, Phys. Rev. B 78, 064401 (2008).
[7] C. S. Lue et al., J. Phys.: Condens. Matter 13, 1585 (2001).
[8] Y. Nishino, Intermetallics 8, 1233 (2000).
[9] C. S. Lue et al., Phys. Rev. B 60, R13941 (1999).
[10] M. Kato et al., J. Phys.: Condens. Matter 62, 669 (1998).
[11] R. Weht and W. E. Pickett, Phys. Rev. B 58, 6855 (1998).
[12] D. J. Singh and I. I. Mazin, Phys. Rev. B 57, 14352 (1998).
[13] G. Y. Guo, G. A. Botton, and Y. Nishino, J Phys.: Condens. Matter 10, L119 (1998).
[14] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[15] D. I. Bilc, R. Orlando, R. Shaltaf, G.-M. Rignanese, J. Inguez, and Ph. Ghosez, Phys. Rev. B 77, 165107 (2008).
[16] Z. Wu and R. E. Cohen, Phys. Rev. B 73, 235116 (2006).
[17] See EPAPS Document No. ... for technical details of the calculations.
[18] P. Blaha et al., WIEN2K, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Techn. Universitat Wien, Austria, 2001.
[19] G. K.H. Madsen and D. J. Singh, Comp. Phys. Comm. 175, 67 (2006).
[20] I. Maksimov et al., J Phys.: Condens. Matter 13, 5487 (2001).
[21] M. Vasundhara, V. Srinivas, and V. V. Rao, Phys. Rev. B 77, 224415 (2008).
[22] G. D. Mahan and J. O. Sofo, Proc. Nat. Acad. Sci. 93, 7436 (1996).