Electronic and magnetic properties of nearly spin-gapless semiconducting FeVTaAl and FeCrZrAl

Caden Sadler,[1,#] Samuel Smith,[2] Nhat Phat Nguyen,[1] Brandon Schmidt,[1] Parashu Kharel,[3] Paul M. Shand,[1] Pavel V. Lukashev[1,#]

[1]*Department of Physics, University of Northern Iowa, Cedar Falls, IA 50614, USA*

[2]*Cedar Falls High School, Cedar Falls, IA 50613, USA*

[3]*Department of Chemistry, Biochemistry and Physics, South Dakota State University, Brookings, SD 57007, USA*

Corresponding authors: sadlecac@uni.edu pavel.lukashev@uni.edu

Abstract

Here, we present results of a computational study of electronic, magnetic, and structural properties of FeVTaAl and FeCrZrAl, quaternary Heusler alloys that have been recently reported to exhibit spin-gapless semiconducting behavior. Our calculations indicate that these materials may crystallize in regular Heusler cubic structure, which has a significantly lower energy than the inverted Heusler cubic phase. Both FeVTaAl and FeCrZrAl exhibit ferromagnetic alignment, with an integer magnetic moment per unit cell at equilibrium lattice constant. Band structure analysis reveals that while both FeVTaAl and FeCrZrAl indeed exhibit nearly spin-gapless semiconducting electronic structure at their optimal lattice parameters, FeVTaAl is a 100% spin-polarized semimetal, while FeCrZrAl is a magnetic semiconductor. Our calculations indicate that expansion of the unit cell volume retains 100% spin-polarization of both compounds. In particular, both FeVTaAl and FeCrZrAl are 100% spin-polarized magnetic semiconductors at the largest considered lattice constant. At the same time, at smaller lattice parameters, both compounds exhibit a more complex electronic structure, somewhat resembling half-metallic properties. Thus, both of these alloys may be potentially useful for practical applications in spin-based electronics, but their electronic structure is very sensitive to the external pressure. We hope that these results will stimulate experimental efforts to synthesize these materials.

I. Introduction

Generation of highly spin-polarized current is one of the main building blocks of spin-based electronics (spintronics). Among various types of materials and systems studied, half-

metallic Heusler compounds attracted particular attention, since, in principle, they can provide 100% spin-polarization at room temperature. Here, spin-polarization P is defined as $P = \left|\frac{N_\uparrow(E_F)-N_\downarrow(E_F)}{N_\uparrow(E_F)+N_\downarrow(E_F)}\right|$, where $N_{\uparrow\downarrow}(E_F)$ is the spin-dependent density of states (DOS) at the Fermi level, E_F.[1] As immediately follows from the definition of spin-polarization, it can reach its maximum possible value of 100% in systems that behave as electric conductors for one spin channels, and insulators / semiconductors for the opposite spin. Such materials are usually called half-metallic, and their existence was predicted in early 1980s by de Groot et al.[2] Since then, many half-metals were suggested and discovered.[3,4,5,6,7,8,9,10]

In addition to half-metals, a new class of compounds, namely spin-gapless semiconductors (SGS) have attracted recent attention, mostly because of their potential applications in semiconductor spintronics. Spin-gapless semiconductor is a material with semiconducting properties for one spin channel, and gapless band structure for the opposite spin. Thus, in principle SGS compounds should provide semiconducting electron transport, while exhibiting nearly 100% transport spin-polarization. The concept of spin-gapless semiconductivity was suggested by X. L. Wang in 2008.[11] Since then, several systems have been reported to exhibit SGS behavior, including various Heusler alloys such as Mn_2CoAl, FeCrTiAl, CoCrFeAl, etc.[12,13,14,15] To some extent, achieving ideal (or nearly ideal) SGS behavior in a given system may be more challenging than achieving half-metallicity, since many factors that are nearly unavoidable in real systems (atomic vacancies and other lattice imperfections) may have a detrimental impact on SGS properties of a given material.[16]

In this work, we employ density functional calculations to study two quaternary Heusler alloys, FeVTaAl and FeCrZrAl that have been recently reported to exhibit SGS properties.[14] Our band structure analysis indicates that while both FeVTaAl and FeCrZrAl indeed exhibit nearly SGS electronic structure at their optimal lattice parameters, more precisely FeVTaAl is a 100% spin-polarized semimetal, while FeCrZrAl is a magnetic semiconductor. At different than optimal lattice constants, these compounds exhibit a somewhat complex behavior. In particular, at the largest considered unit cell volumes, both materials are magnetic semiconductors, while at the smallest considered lattice constants, both alloys somewhat resemble a half-metallic structure. We hope that these results will stimulate experimental efforts to synthesize these materials.

II. Computational methods

In this work, we use density functional calculations implemented in the Vienna *ab initio* simulation package (VASP).[17] In particular, we use the projector augmented-wave method (PAW)[18] and generalized-gradient approximation (GGA) method proposed by Perdew, Burke, and Ernzerhof,[19] as well as the integration method by Methfessel and Paxton with a 5×10^{-2} eV width of smearing.[20] The energy convergence criterion of 10^{-3} meV and a *k*-mesh of 8×8×8 are implemented for the electronic and magnetic structure calculations. The MedeA® software environment[21] is used for visualizing the crystal structures (not shown in the text) and for calculating and plotting electronic band structures. The reported calculations were performed using the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) (formerly known as Extreme Science and Engineering Discovery Environment (XSEDE)) resources located at the Pittsburgh Supercomputing Center (PSC)[22], the resources of the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory (BNL), as well as the high-performance computing cluster located at the University of Northern Iowa (UNI).

III. Results

FeVTaAl and FeCrZrAl belong to a class of regular cubic Heusler alloys, with the following Wyckoff atomic coordinates: Fe (0,0,0), V/Cr (1/2,1/2,1/2), Ta/Zr (3/4,3/4,3/4), Al (1/4,1/4,1/4). The other possible crystal structures (such as inverted cubic phase) have much higher energies, which was reported earlier,[14] and which was also verified by ourselves (the data not shown here for brevity reasons). The calculated lattice parameters are 6.093 Å for FeVTaAl, and 6.189 Å for FeCrZrAl, in good agreement with the results reported by Gao et al.[14] Figures 1(a) and 2(a) show calculated total energy (black line and circles) and magnetization (blue line and squares) values of FeVTaAl and FeCrZrAl, correspondingly, as a function of lattice constant (for the results reported in this work, the volume of the unit cell was kept cubic). Figures 1(b) and 2(b) show calculated element resolved magnetic moments of FeVTaAl and FeCrZrAl, correspondingly (the magnetic moment of Al is negligible and is not shown). As one can see from the Figures 1(b) and 2(b), both FeVTaAl and FeCrZrAl are ferromagnetic in the entire range of the considered lattice parameters. In addition, both materials have essentially integer magnetization at the equilibrium lattice constant and under expansion of the unit cell. At the smaller than equilibrium lattice

constants, the magnetization somewhat deviates from its integer value. The integer value of magnetization may serve as an indication of a 100% spin-polarized compound. Indeed, in such compounds, the valence band of one of the spin channels is fully occupied, therefore the number of valence states of this spin is an integer. The total valence charge is also an integer; therefore 100% spin-polarized materials exhibit integer total magnetic moment per formula unit.[23]

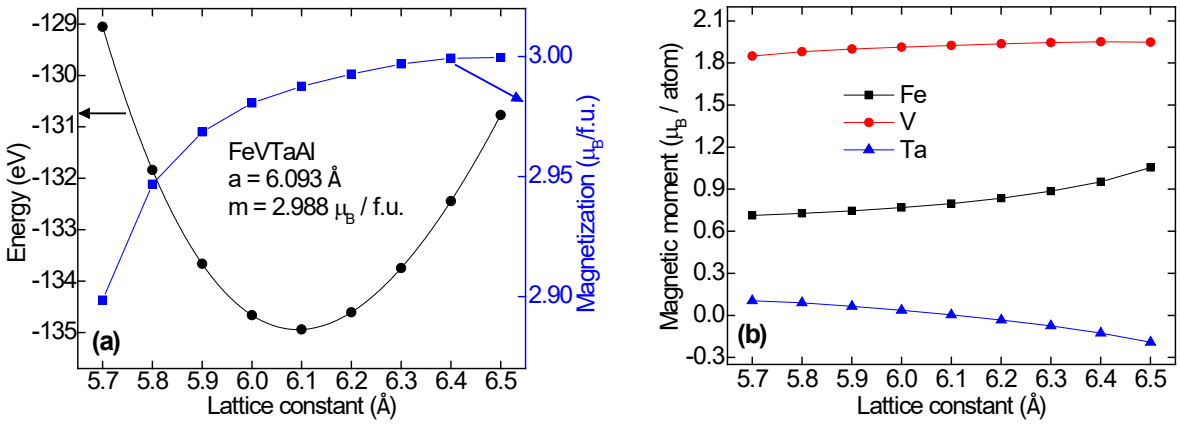

Figure 1: Calculated total energy (black line and circles) and magnetic moment (blue line and squares) (a), as well as element resolved magnetitic moments of FeVTaAl (b) as a function of lattice constant. The element resolved magnetic moments are colored / labeled as indicated in the figure, i.e. Fe – black line and squares, V – red line and circles, Ta – blue line and triangles.

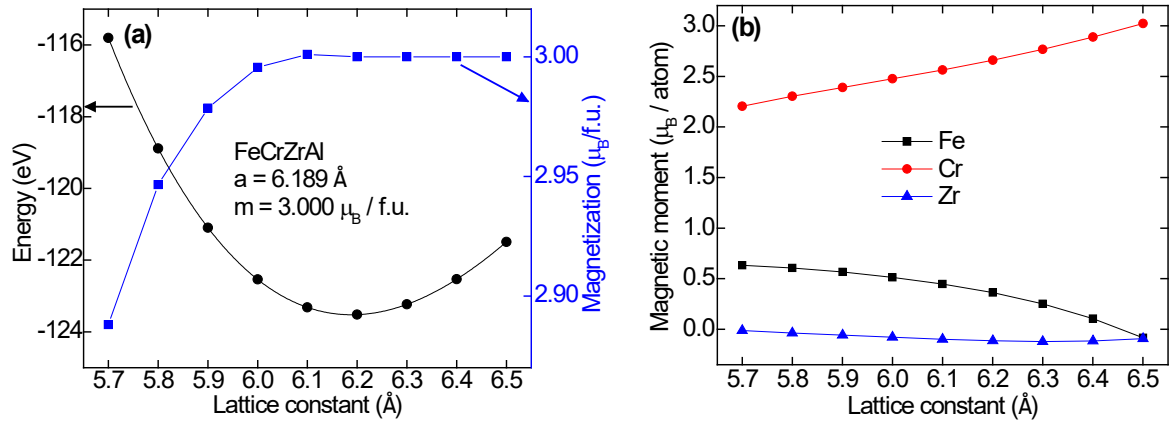

Figure 2: Calculated total energy (black line and circles) and magnetic moment (blue line and squares) (a), as well as element-resolved magnetitic moments of FeCrZrAl (b) as a function of lattice constant. The element resolved magnetic moments are colored / labeled as indicated in the figure, i.e. Fe – black line and squares, Cr – red line and circles, Zr – blue line and triangles.

Figure 3 shows calculated density of states of FeVTaAl (a) and FeCrZrAl (b) at their corresponding optimal lattice constants. As seen from this figure, both compounds exhibit nearly

spin-gapless semiconducting electronic structure. At the same time, the DOS profile around Fermi energy of these materials is distinctly different. In particular, while both spin-up and spin-down channels have energy gap around Fermi level, the gapless DOS feature of FeVTaAl is produced by top of the spin-up valence states "touching" the bottom of the spin-down conduction states. At the same time, for FeCrZrAl, the spin-up states appear to exhibit gapless profile at the Fermi energy, while the spin-down states have an energy gap of around 1 eV. The described DOS profile of FeVTAl is referred in literature as type-II SGS, while the DOS profile of FeCrZrAl is called type-I SGS.[11,13,14,24]

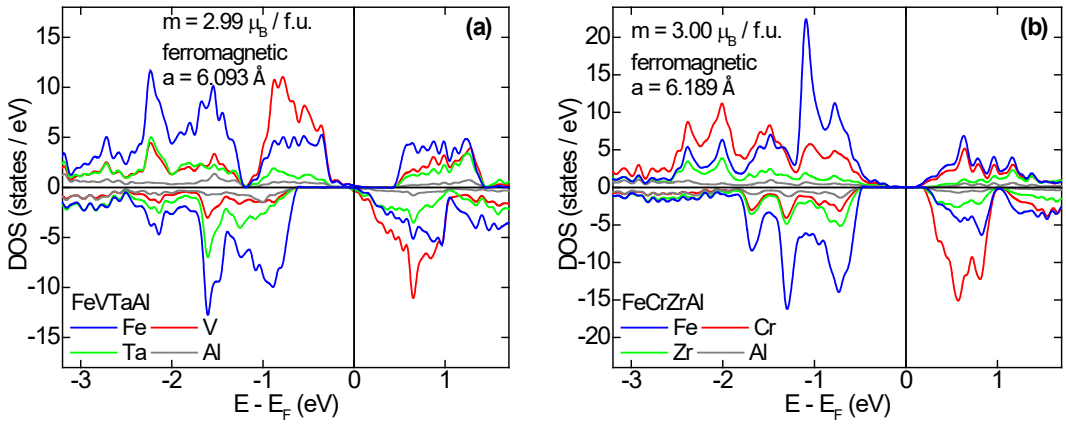

Figure 3: Calculated total and element resolved density of states of FeVTaAl (a) and FeCrZrAl (b) at the equilibrium lattice constants. The vertical line corresponds to the Fermi level. Positive / negative DOS represents spin-up / spin-down states, correspondingly. Element resolved density of states are colored as indicated in the figure: blue – Fe, red – V/Cr, green – Ta / Zr, gray – Al.

Figure 4 shows calculated total density of states of FeVTaAl (a) and FeCrZrAl (b) at different lattice parameters (indicated in the figure). One of the features seen in the figure is that reduction of the unit cell volume has a detrimental effect on spin-gapless semiconducting behavior of both compounds, consistent with the conclusions drawn from Figures 1(a) and 2(a) (deviation of magnetization from its integer value at smaller lattice constants). It appears from Figure 4 that for both FeVTaAl and FeCrZrAl the detrimental effect on SGS behavior at smaller lattice constants is mainly caused by a shift of the Fermi level towards higher energies relative to the spin-down states. At the same time, for FeVTaAl, the Fermi level appears to be shifted toward the lower energy spin-up states at smaller lattice constants. More detailed analysis of the effect of external pressure on electronic structure of these compounds is somewhat difficult with the DOS profiles

only, in particular since they are calculated with a non-zero smearing of 0.1 eV. With that in mind, we next analyze the electronic band structure of these materials.

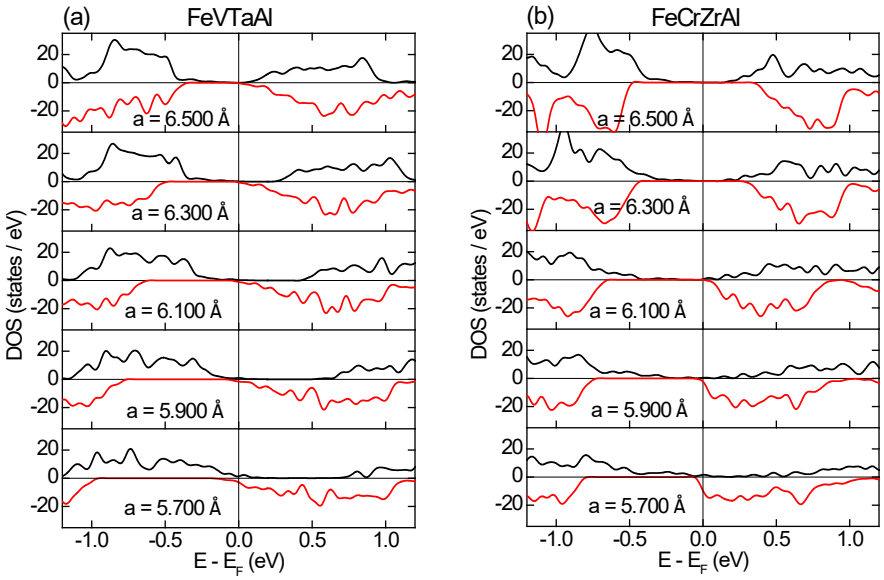

Figure 4: Calculated total density of states of FeVTaAl (a) and FeCrZrAl (b) for different values of lattice parameters (indicated in the figure) calculated at uniform pressure. The vertical line corresponds to the Fermi level. Positive (black line)/negative (red line) DOS represents spin-up / spin-down states, correspondingly.

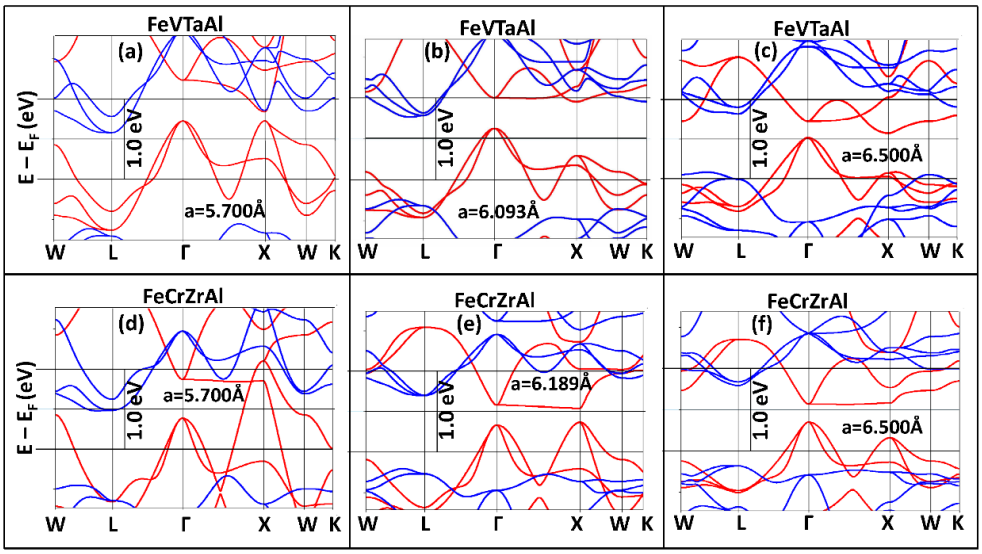

Figure 5: Band structures of FeVTaAl (a, b, c) and FeCrZrAl (d, e, f) for different values of lattice parameters (indicated in the figure) calculated at uniform pressure. The horizontal line in the middle of the plots corresponds to the Fermi level. Red / blue lines represents spin-up / spin-down bands, correspondingly.

Figure 5 shows calculated band structures of FeVTaAl (a, b, c) and FeCrZrAl (d, e, f) at different lattice parameters (indicated in the figure). A close inspection of the band structures at the equilibrium lattice constants (Figures 5 (b) and 5 (e)) reveals some interesting features that are not clearly visible at the DOS plots (Figure 4). In particular, as one can see from Fig. 5 (b), FeVTaAl exhibits nearly perfect SGS electronic structure in equilibrium. More specifically, the gapless character is produced by alignment of the spin-up band (red line) at the Γ point with the spin-down band (blue line) at the L point. At the same time, there is a small overlap of the spin-up band at the Γ point with the Fermi level, thus, strictly speaking, FeVTaAl at equilibrium may be categorized as a 100% spin-polarized semimetal. As for FeCrZrAl, as can be seen from Fig. 5 (e), this material at equilibrium is actually a magnetic semiconductor, with a relatively small energy gap of spin-up states of ~0.2 eV. In addition to equilibrium properties, Figure 5 also reveals interesting electronic structure features of the considered two compounds under compression / expansion of the unit cell volume. In particular, as seen from Figures 5 (c) and 5 (f), at the largest considered lattice parameter of 6.500 Å, FeVTaAl and especially FeCrZrAl could be described as magnetic semiconductors, i.e. both spin channels exhibit a band gap at the Fermi level. Interestingly, the band structure of FeCrZrAl is not very sensitive to the expansion of the unit cell (compare Figures 5 (a) and 5 (f)), and overall it retains its magnetic semiconducting properties at larger lattice parameters. At the same time, the expansion of the unit cell results in a magnetic semimetal to magnetic semiconductor transition for FeVTaAl (compare Figures 5 (b) and 5 (c)). This transition is largely due to the shift of the Fermi level towards the band gap of the spin-up states. The gap itself is indirect and is reduced to around 0.1 eV upon expansion of the unit cell volume (see the top of the spin-up valence band at Γ point, and the bottom of the spin-up conduction band at X point in Fig. 5 (c)). As can be seen from the Figures 5 (a) and 5 (d), the compression of the unit cell has a somewhat more dramatic effect on the electronic structure of both FeVTaAl and FeCrZrAl than the expansion of the cell. In particular, the band gap of the spin-up states closes for FeCrZrAl, while the Fermi level moves towards the bottom of the spin-down conduction band at the L point (see Fig. 5 (d)). This results in nearly half-metallic structure of FeCrZrAl at the smallest considered lattice constant of 5.700 Å. This does not contradict the deviation of the magnetization from its integer value at the smaller lattice constants that was mentioned above. Indeed, a close inspection of Fig. 5 (d) shows that FeCrZrAl at 5.700 Å is *nearly* but not *perfectly* half-metallic, due to a small overlap of the Fermi level with the bottom of the

spin-down conduction band at the L point. As for FeVTAl under compression, comparison of Figures 5 (a) and (b) reveals that this material undergoes a transition from magnetic semimetal to something that may be described either as a half-metal or as a magnetic semimetal. In general, the distinction between these two electronic structures may be not as strict and well defined, as one can see from Fig. 5 (a)).

IV. Conclusions

Here, we presented results of a computational study of electronic, magnetic, and structural properties of FeVTaAl and FeCrZrAl, quaternary Heusler alloys that have been recently reported to exhibit spin-gapless semiconducting behavior. Our calculations indicate that these materials may crystallize in regular Heusler cubic structure. Both compounds exhibit ferromagnetic alignment, with an integer magnetic moment per unit cell at equilibrium lattice parameter. Band structure analysis reveals that while both FeVTaAl and FeCrZrAl indeed exhibit nearly spin-gapless semiconducting electronic structure at their optimal lattice parameters, FeCrZrAl is actually a magnetic semiconductor, while FeVTaAl is a 100% spin-polarized semimetal. In addition, our calculations indicate that expansion of the unit cell volume retains 100% spin-polarization of both FeVTaAl and FeCrZrAl. In particular, both alloys are 100% spin-polarized magnetic semiconductors at the largest considered lattice constant. At the same time, at smaller lattice parameters, both compounds exhibit a more complex electronic structure, resembling half-metallic properties. Thus, both of these materials may be potentially useful for practical device applications in spin-based electronics, but their properties (electronic structure, in particular) may be very sensitive to the external mechanical pressure. We hope that the presented results will stimulate experimental efforts to synthesize these materials.

Acknowledgments

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Data Availability

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

References

[1] J. Velev, P. Dowben, E. Tsymbal, S. Jenkins, and A. Caruso, Surf. Sci. Rep. **63**, 400 (2008).
[2] R. de Groot, F. Mueller, P. van Engen, and K. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).
[3] I. Galanakis, P. Dederichs, N. Papanikolaou, Phys. Rev. B **66**, 174429 (2002).
[4] E. Şaşıoğlu, L. Sandratskii, and P. Bruno, Phys. Rev. B **72**, 184415, (2005).
[5] B. Balke, G. Fecher, J. Winterlik, and C. Felser, Appl. Phys. Lett. **90**, 152504 (2007).
[6] H. Kurt, K. Rode, M. Venkatesan, P. Stamenov, and J. M. D. Coey, Phys. Status Solidi B **248**, 2338 (2011).
[7] J. Winterlik, S. Chadov, A. Gupta, V. Alijani, T. Gasi, K. Filsinger, B. Balke, G. H. Fecher, C. A. Jenkins, F. Casper, J. Kübler, G. Liu, L. Gao, S. S. P. Parkin, and C. Felser, Adv. Mater. **24**, 6283 (2012).
[8] A. Nelson, P. Kharel, Y. Huh, R. Fuglsby, J. Guenther, W. Zhang, B. Staten, P. Lukashev, S. Valloppilly, and D. J. Sellmyer; J. Appl. Phys., **117**, 153906 (2015).
[9] I. Galanakis, in *Heusler Alloys*, Springer Series in Materials Science 222, C. Felser and A. Hirohata (eds.), Springer International Publishing Switzerland 2016.
[10] P. Lukashev, P. Kharel, S. Gilbert, B. Staten, N. Hurley, R. Fuglsby, Y. Huh, S. Valloppilly, W. Zhang, K. Yang, R. Skomski, and D. J. Sellmyer; Appl. Phys. Lett. **108**, 141901 (2016).
[11] X. Wang, Phys. Rev. Lett. **100**, 156404 (2008).
[12] S. Ouardi, G. H. Fecher, and C. Felser, Phys. Rev. Lett. **110**, 100401 (2013).
[13] R. Dhakal, S. Nepal, I. Galanakis, R.P. Adhikari, G.C. Kaphle, J. Alloys Compd., **882**, 160500 (2021).
[14] Q. Gao, I. Opahle, and H. Zhang, Phys. Rev. Materials **3**, 024410 (2019).
[15] P. Lukashev, S. McFadden, P. Shand, P. Kharel, J. Magn. Magn. Mater **584**, 171107 (2023).
[16] E. O'Leary, B. Dahal, P. Kharel, and P. Lukashev, J. Magn. Magn. Mater **514**, 167188 (2020).
[17] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[18] P. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[19] J. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[20] M. Methfessel and A. T. Paxton, Phys. Rev. B **40**, 3616 (1989).
[21] MedeA version 3.0; MedeA is a registered trademark of Materials Design, Inc., San Diego, USA.

[22] J. Towns, T. Cockerill, M. Dahan, I. Foster, K. Gaither, A. Grimshaw, V. Hazlewood, S. Lathrop, D. Lifka, G. D. Peterson, R. Roskies, J. R. Scott, N. Wilkins-Diehr, "XSEDE: Accelerating Scientific Discovery", Computing in Science & Engineering, vol.**16**, no. 5, pp. 62-74, Sept.-Oct. 2014.

[23] I. Tutic, J. Herran, B. Staten, P. Gray, T. Paudel, A. Sokolov, E. Tsymbal, and P. Lukashev, J. Phys.: Condens. Matter **29**, 075801 (2017).

[24] B. Schmidt, P. Shand, P. Kharel, and P. Lukashev, AIP Advances **14**, 015014 (2024).