Structural, Electronic, and Magnetic Properties of CoFeVGe-based Compounds: Experiment and Theory

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Abstract

We have carried out a combined theoretical and experimental investigation of both stoichiometric and nonstoichiometric CoFeVGe alloys. In particular, we have investigated CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, $Co_{0.75}Fe_{1.25}VGe$, and $CoFe_{0.75}VGe$ bulk alloys. Our first principles calculations suggest that all four alloys show ferromagnetic order, where CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, and $Co_{0.75}Fe_{1.25}VGe$ are highly spin polarized with spin polarization values of over 80%. However, the spin polarization value of $CoFe_{0.75}VGe$ is only about 60%. We have synthesized all four samples using arc melting and high-vacuum annealing at 600 °C for 48 hours. The room temperature x-ray diffraction of these samples exhibits a cubic crystal structure with disorder. All the samples show single magnetic transitions at their Curie temperatures, where the Curie temperature and high field (3T) magnetization are 288 K and 42 emu/g; 305 K and 1.5 emu/g; 238 K and 39 emu/g; and 306 K and 35 emu/g for CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, $Co_{0.75}Fe_{1.25}VGe$, and $CoFe_{0.75}VGe$, respectively.

I. Introduction

Heusler alloys are interesting materials for research due to their various novel properties, which are useful in advancing modern technology [1]. While a wide range of interesting properties such as high perpendicular magnetic anisotropy [2], shape memory effect [3], topological magnetic order [4], and magnetocaloric effect [5] have been observed in Heusler alloys, half-metallic and spin-gapless semiconducting properties have attracted increasing attention [6]. In principle, half-metals and spin-gapless semiconductors have ability to produce fully (100%) spin polarized currents because of the nature of their electronic band structure, which is metallic for one spin channel and insulating for the opposite spin channel [7, 8]. This feature makes them useful for spin-transport-based devices [6]. For room temperature spintronic applications, these materials need to show robust half-metallicity at room temperature, which is possible in magnetic materials exhibiting high Curie temperature much above room temperature [9]. Many half-metallic Heusler alloys show Curie temperature much above room temperature and have potential for room temperature spintronic applications. In addition, the magnetic and electronic properties of these materials can be tuned as desired by adjusting the elemental composition, applying mechanical strain, etc. [10,11,12]. For example, we showed recently that half-metallicity can be induced in a half-Heusler alloy CrMnSb by chemical substitution, which results in a modification of the lattice parameter [13,14].

Heusler alloys crystallize mainly in cubic structure. The completely ordered quaternary Heusler alloys crystalize in cubic Y type (XX'YZ) structure (prototype LiMgPdSn) [1]. However, this structure is prone to various types of disorders such as $L2_1$, B2 and A2. When X and X' atoms mix in the lattice, the alloy assumes $L2_1$ type structure, whereas B2 type structure results from mixing of Y and Z atoms. The A2 disorder results from a random mixing of all atoms (X, X',Y, and Z). These disorders are typically detrimental to the magnetic and spin-electronic properties of Heusler alloys [15].

In this work, we present our combined experimental and theoretical investigations on CoFeVGe and the effect of modifying its elemental composition on the magnetic and electronic properties. Xiong et al. have shown using first principles calculation that CoFeVGe exhibits half-metallic properties in its Y structure but we have not found any experimental report in the literature yet [16]. Here, we report the results of theoretical calculations on the structural, magnetic and electronic band properties of CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, $Co_{0.75}Fe_{1.25}VGe$, and $CoFe_{0.75}VGe$ alloys, and also the results of experimental investigation of corresponding bulk alloys prepared using arc melting and annealing.

II. Methods

(i) Experimental methods

We have prepared four alloys CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, $Co_{0.75}Fe_{1.25}VGe$, and $CoFe_{0.75}VGe$ bulk ingots using arc-melting and high-vacuum annealing. First, highly pure

(99.99%) metal pieces with proper weight ratio were cut from corresponding commercially available pellets and melted on a water-cooled Cu hearth of an arc furnace in an argon environment. The arc-melted ingots were then annealed in a tubular vacuum furnace (~10^{-7} torr) at 600°C for 48 hours to further homogenize the samples. The crystal structures of the samples were analyzed using Rigaku MiniFlex600 x-ray diffractometer with Cu-Kα source (λ = 1.54 Å), and magnetic properties were measured using a Quantum Design VersaLab magnetometer.

(ii) Computational methods

All calculations are performed with the Vienna *ab initio* simulation package (VASP) [17], within the projector augmented-wave method (PAW) [18] and generalized-gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [19]. The cut-off energy of the plane-waves was set to 500 eV, and the integration method by Methfessel and Paxton with a 0.05 eV width of smearing was used [20]. The total energy and electronic structure calculations were performed with the energy convergence criteria of 10^{-6} eV. The Brillouin-zone integration was performed with a *k*-point mesh of 12 × 12 × 12, for a 16-atom cubic cell. Some of the results and figures were obtained using the MedeA® software environment [21]. Most of the calculations were performed using Extreme Science and Engineering Discovery Environment (XSEDE) resources located at the Pittsburgh Supercomputing Center (PSC) [22], and the resources of the Center for Functional Nanomaterials (CFN) at Brookhaven National Laboratory (BNL).

III. Results and discussion

(i) Computational results

Figure 1 shows calculated element- and spin-resolved density of states of CoFeVGe (a), $CoFe_{0.75}VGe$ (b), $Co_{0.75}Fe_{1.25}VGe$ (c), and $Co_{1.25}Fe_{0.75}VGe$ (d). Calculated lattice constants, magnetization, and spin polarization values are shown in the corresponding figures. All four considered compounds have lowest energy in the regular cubic Heusler structure in which the magnetic alignment is ferromagnetic. The main contribution to the total magnetization comes from Co and Fe, with the local magnetic moments of approximately 1.1 μ_B / Co, and 0.8 μ_B / Fe. The magnetic moment of V is small (approximately 0.1 μ_B per atom), while Ge is non-magnetic.

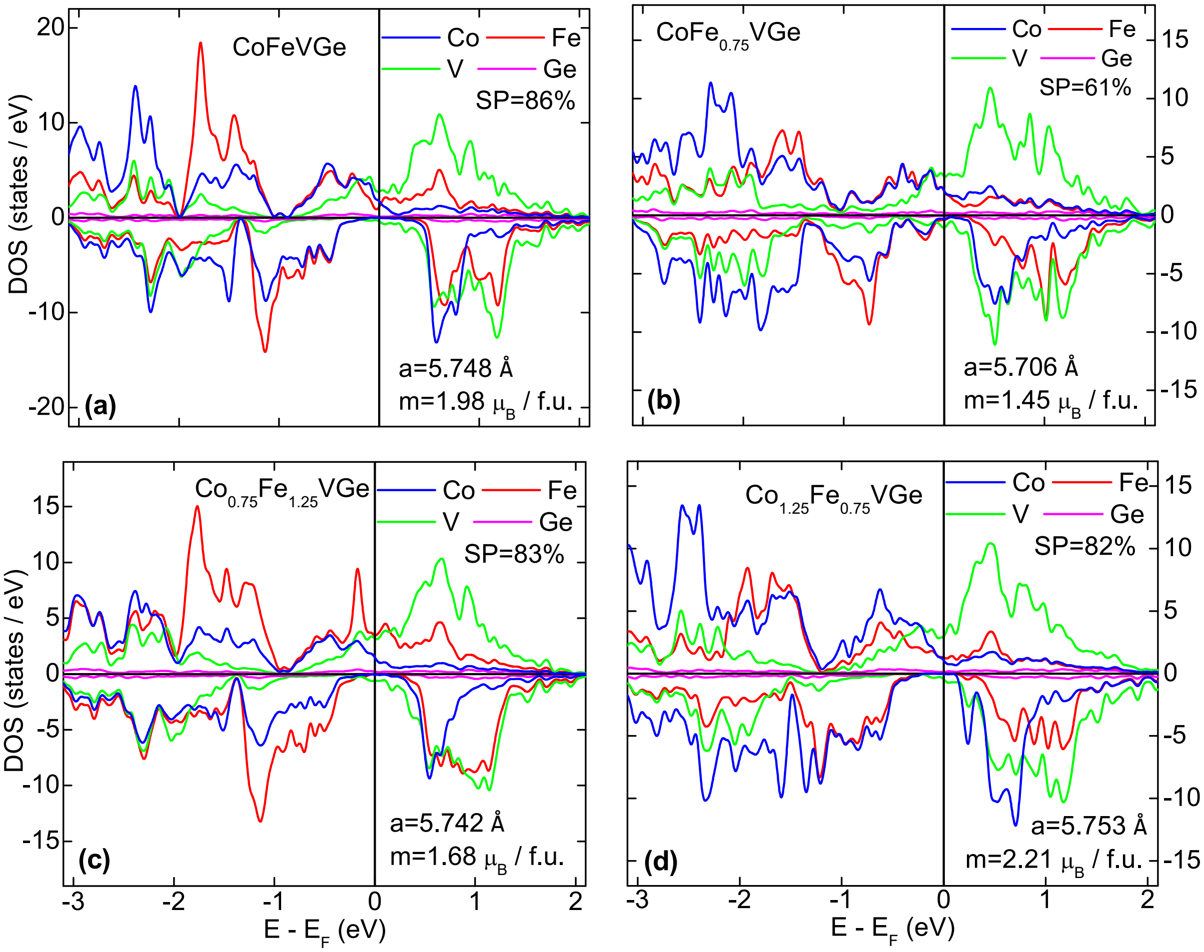

Figure 1: Calculated element- and spin-resolved density of states of CoFeVGe (a), $CoFe_{0.75}VGe$ (b), $Co_{0.75}Fe_{1.25}VGe$ (c), and $Co_{1.25}Fe_{0.75}VGe$ (d). Elemental contributions are colored as indicated in the figure: Co – blue, Fe – red, V – green, Ge – magenta. Positive and negative DOS represent majority- and minority-spin, correspondingly. Vertical line indicates position of the Fermi level. Calculated lattice constants, magnetization, and spin polarization (SP) values are shown in the figure.

Our calculations indicate that CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, and $Co_{0.75}Fe_{1.25}VGe$ are highly spin polarized, with the spin polarization values of over 80%, as shown in Fig. 1 (a, c, d). Here, the spin polarization is calculated as $P = \frac{N_{\uparrow}(E_F)-N_{\downarrow}(E_F)}{N_{\uparrow}(E_F)+N_{\downarrow}(E_F)}$, where $N_{\uparrow\downarrow}(E_F)$ is the spin-dependent density of states at the Fermi level, E_F [23]. Even though the calculated spin-polarization values of CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, and $Co_{0.75}Fe_{1.25}VGe$ are large, these materials are not half-metallic, mainly due to the presence of the minority-spin vanadium states around Fermi level (see Fig. 1). However, the large calculated spin polarization shows that these materials have potential for spintronic applications. The calculated spin polarization of $CoFe_{0.75}VGe$ in regular cubic structure is only 61%, i.e. reducing the content of Fe without increasing Co results in reduced spin polarization.

(ii) Experimental results

Figure 2 shows the x-ray diffraction patterns recorded on the powder samples of $Co_{1.25}Fe_{0.75}VGe$, CoFeVGe, $CoFe_{0.75}VGe$ and $Co_{0.75}Fe_{1.25}VGe$ alloys at room temperature. The XRD patterns can be indexed with the cubic Heusler structure with disorder. The absence of superlattice peaks (111) and (200) suggests that the samples have A2 type disorders. In addition, the patterns of $CoFe_{0.75}VGe$ and $Co_{0.75}Fe_{1.25}VGe$ show weak peaks from unknown impurity.

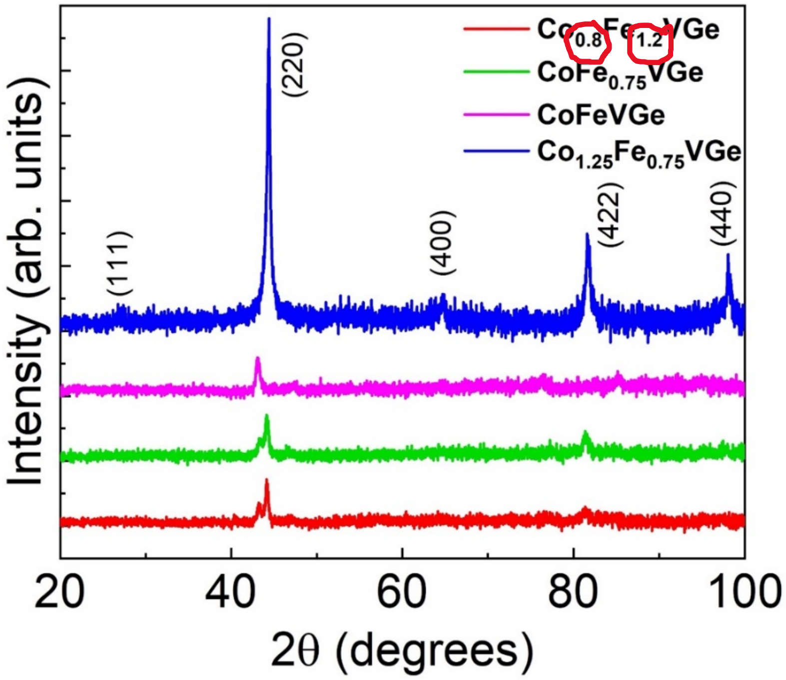

Figure 2: Room temperature x-ray diffraction patterns of $Co_{1.25}Fe_{0.75}VGe$, CoFeVGe, $CoFe_{0.75}VGe$ and $Co_{0.75}Fe_{1.25}VGe$ (bottom to top) alloys.

Figure 3(a) shows the thermomagnetic curves M(T) recorded at 1 kOe on $Co_{1.25}Fe_{0.75}VGe$, CoFeVGe, $CoFe_{0.75}VGe$ and $Co_{0.75}Fe_{1.25}VGe$ alloys. There is a smooth transition on the M(T) curves of all these alloys at their Curie temperatures. The parent alloy CoFeVGe has a Curie temperature (T_C) of 288 K which is slightly below the room temperature. Increasing Fe content at the cost of Co has decreased the Curie temperature. The T_C of $Co_{0.75}Fe_{1.25}VGe$ is 238 K. However, the T_C can be increased by reducing Fe content either keeping Co concentration constant or increasing it. The Curie temperature of $Co_{1.25}Fe_{0.75}VGe$ and $CoFe_{0.75}VGe$ are slightly above room temperature, namely 305K and 306K respectively. However, the magnetization of $Co_{1.25}Fe_{0.75}VGe$ shows very slow decrease at the Curie temperature similar to that of a ferrimagnetic material and also the magnetization has decreased drastically as compared to those of the other samples.

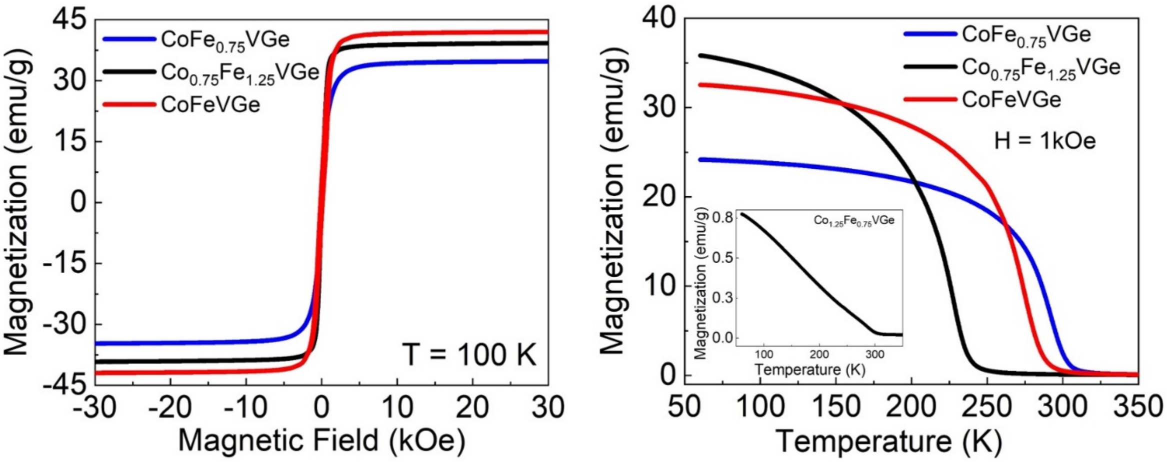

Figure 3: (a) Thermomagnetic curves M(T), and (b) isothermal magnetization curves M(H) of $Co_{1.25}Fe_{0.75}VGe$, CoFeVGe, $CoFe_{0.75}VGe$ and $Co_{0.75}Fe_{1.25}VGe$ (top to bottom) alloys.

Figure 3(b) shows the isothermal magnetization curves M(H) of $Co_{1.25}Fe_{0.75}VGe$, CoFeVGe, $CoFe_{0.75}VGe$ and $Co_{0.75}Fe_{1.25}VGe$ alloys recorded at 100 K. All four alloys show very small coercivities with saturation magnetizations of 1.5 emu/g, 42 emu/g, 35 emu/g, and 39 emu/g for $Co_{1.25}Fe_{0.75}VGe$, CoFeVGe, $CoFe_{0.75}VGe$ and $Co_{0.75}Fe_{1.25}VGe$, respectively. The saturation magnetization of the cobalt rich sample $Co_{1.25}Fe_{0.75}VGe$ which shows ferrimagnetic like transition at the Curie temperature is very small as compared to those of other three samples. The saturation magnetizations 42 emu/g, 39 emu/g and 35 emu/g of three samples CoFeVGe, $Co_{0.75}Fe_{1.25}VGe$ and $CoFe_{0.75}VGe$ follow the trend predicted by theory (1.98 μ_B / f.u., 1.68 μ_B / f.u., and 1.45 μ_B / f.u.). However, $Co_{1.25}Fe_{0.75}VGe$ which is predicted to have the highest magnetization (2.21 μ_B / f.u.) among the studied samples shows the smallest magnetization of 1.5 emu/g. In addition, its M(T) curve is similar to that of highly disordered ferrimagnetic material. Although all studied samples are disordered, the presence of excess cobalt in $Co_{1.25}Fe_{0.75}VGe$ has shown unique magnetic behavior inconsistent with our theoretical prediction.

IV. Conclusions

We have investigated the electronic, structural and magnetic properties of CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, $Co_{0.75}Fe_{1.25}VGe$, and $CoFe_{0.75}VGe$ bulk alloys. Our first principles calculations suggest that all four alloys show ferromagnetic order, where CoFeVGe, $Co_{1.25}Fe_{0.75}VGe$, and $Co_{0.75}Fe_{1.25}VGe$ are highly spin polarized with spin polarization values of over 80% but the spin polarization of $CoFe_{0.75}VGe$ is only 61%. The samples prepared using arc-melting and annealing have crystallized in a cubic structure with A2 type disorder. The experimental (theoretical) saturation magnetizations of CoFeVGe, $Co_{0.75}Fe_{1.25}VGe$ and $CoFe_{0.75}VGe$ and are 42 emu/g (1.98 μ_B / f.u.), 39 emu/g (1.68 μ_B /f.u.), 35 emu/g (1.45 μ_B /f.u.) respectively, but that of $Co_{1.25}Fe_{0.75}VGe$ is only 1.5 emu/g irrespective of the predicted high value of 2.21 μ_B / f.u. The observed magnetic and electronic band properties indicate that the investigated materials have potential for near room temperature magnetic applications desiring low magnetization and high spin polarization.

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References

1. T. Graf, C. Felser, S. S. P. Parkin, Simple rules for the understanding of Heusler compounds, Prog. Solid. State Ch., **39**, 1-50 (2011).
2. Y. Jin, S. Valloppilly, P. Kharel, R. Pathak, A. Kashyap, R. Skomski and D J Sellmyer, Unusual perpendicular anisotropy in Co_2TiSi films, J. Phys. D: Appl. Phys. **52**, 035001 (2019).
3. Z. H. Liu, M. Zhang, Y. T. Cui, Y. Q. Zhou, W. H. Wang, and G. H. Wu, Martensitic transformation and shape memory effect in ferromagnetic Heusler alloy Ni_2FeGa, Appl. Phys. Lett. **82**, 424 (2003).
4. V. Kumar, N. Kumar, M. Reehuis, J. Gayles, A. S. Sukhanov, A. Hoser, F. Damay, C. Shekhar, P. Adler, and C. Felser, Detection of antiskyrmions by topological Hall effect in Heusler compounds, Phys. Rev. B **101**, 014424 (2020).

5. W. Zhang, P. Kharel, S. Valloppilly and D. J. Sellmyer, Large magnetocaloric effect in rapidly quenched $Mn_{50-x}Co_xNi_{40}In_{10}$ nanomaterials, J. Phys. D: Appl. Phys. **54**, 175003 (2021).
6. K. Elphick, W. Frost, M. Samiepour, T. Kubota, K. Takanashi, H. Sukegawa, S. Mitani, A. Hirohata, Heusler alloys for spintronic devices: review on recent development and future perspective, Science and technology of advanced materials, **22**, 234-271 (2021).
7. R. J. Soulen Jr., J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, A. Barry, and J. M. D. Coey, Measuring the Spin Polarization of a metal with a Superconducting Point Contact, Science **282**, 85 (1998).
8. X. L. Wang, Proposal for a new Class of Materials: Spin Gapless Semiconductors, Phys. Rev. Lett. **100**, 156404 (2008).
9. L. Ritchie, G. Xiao, Y. Ji, T. Y. Chen, C. L. Chien, M. Zhang, J. Chen, Z. Liu, G. Wu, and X. X. Zhang, Magnetic, structural, and transport properties of the Heusler alloys Co2MnSi and NiMnSb, Phys Rev. B **68**, 104430 (2003).
10. Y. Jin, J. Waybright, P. Kharel, I. Tutic, J. Herran, P. Lukashev, S. Valloppilly, and D. J. Sellmyer, Effect of Fe substitution on the structural, magnetic and electron-transport properties of half-metallic Co_2TiSi, AIP Advances **7**, 055812 (2017).
11. P. Kharel, G. Baker, M. Flesche, A. Ramker, Y. Moua, S. Valloppilly, P. M. Shand, and Pavel V. Lukashev, Electronic band structure and magnetism of $CoFeV_{0.5}Mn_{0.5}Si$, AIP Advances **12**, 035011 (2022).
12. I. Tutic, J. Herran, B. Staten, P. Gray, T. Paudel, A. Sokolov, E. Tsymbal, and P. Lukashev, Effects of pressure and strain on spin polarization of IrMnSb, J. Phys.: Condens. Matter **29**, 075801 (2017).
13. E. O'Leary, A. Ramker, D. VanBrogen, B. Dahal, E. Montgomery, S. Poddar, P. Kharel, A. Stollenwerk, and P. Lukashev, Chemical substitution induced half-metallicity in $CrMnSb_{(1-x)}P_x$, J. Appl. Phys., **128**, 113906 (2020).
14. L. Stuelke, L. Margaryan, P. Kharel, P. Shand, P. Lukashev, Electronic, magnetic, and structural properties of $CrMnSb_{0.5}Si_{0.5}$, J. Magn. Magn. Mater **553**, 169267 (2022).
15. Y. Jin, P. Kharel, S. R. Valloppilly, X.-Z. Li, D. R. Kim, G. J. Zhao, T. Y. Chen, R. Choudhary, A. Kashyap, R. Skomski, and D. J. Sellmyer, Half-metallicity in highly L21-ordered CoFeCrAl thin films, Appl. Phys. Lett. **109**, 142410 (2016).
16. L. Xiong, L. Yi, and G. Y. Gao, Search for half-metallic magnets with large half-metallic gaps in the quaternary Heusler alloys CoFeTiZ and CoFeVZ (Z=Al, Ga, Si, Ge, As, Sb), J. Magn. Magn. Mater **360**, 98 (2014).
17. G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
18. P. Blöchl, Phys. Rev. B **50**, 17953 (1994).
19. J. P. 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-2.22, Materials Design, Inc., San Diego, CA, USA, 2017.
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. J. P. Velev, P. A. Dowben, E. Y. Tsymbal, S. J. Jenkins, and A. N. Caruso, Surf. Sci. Rep. **63**, 400 (2008).