First Principles Study of the Electronic and Magnetic Properties of $PrVSb_3$ and $PrSrVSb_3$

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Abstract

Electronic and magnetic properties of lanthanide antimonide $LnTSb_3$ *(where Ln = Pr and T = V, Sr) has been studied by using full-potential linearized augmented plane wave (FP-LAPW) method based on the density-functional theory (DFT). For the exchange-correlation potential, generalized gradient approximation (GGA) has been used. Based on our DFT calculations,* $PrVSb_3$ *is found to have antiferromagnetic (AFM) ground state in agreement with the experimental measurement. Within GGA, it is found to be metallic with finite density of states (DOS)at the Fermi level in both spin channel contributed mostly by Pr-4f and V-3d states. DOS result shows the strong hybridization between V-3d and Pr-4f states with large exchange-splitting. They are found responsible for the AFM ground state behavior in* $PrVSb_3$*. Inclusion of U (3 eV for V and 5 eV for Pr) shows semi metallic behavior.* $PrSrVSb_3$ *on the other hand, is found to have ferrimagnetic (FiM) ground state with half metallic (HM) character. Preliminary investigation on* $PrSrVSb_3$ *shows finite (DOS) at the Fermi level in one spin channel depicting possible candidate of half-metallic ferrimagnet suitable for spintronic device applications. The effective moments of* $PrSrVSb_3$ *is found to be ~3μB per formula unit while that of* $PrVSb_3$ *is zero respectively. Upon hole doping further, we expect* $PrVSb_3$ *to be a candidate of compensated HMs.*

KEYWORDS: Half metals •Ferrimagnetion •Spintronics •Spin-orbit coupling •First-principles calculations

1. Introduction

Over the past decade,a new series of the rare-earth (R) families of binary and ternary antimonides have been of substantial interest due to a wide assortment of electronic and magnetic phenomena associated with reduced dimensionality of the unit cell and point symmetry of the local moments. Lanthanide antimonides have the chemical formula $LnTSb_3$ (Ln= Lanthanides and T= Transition elements). In the cubic phase, the oxygen atoms form a cubic lattice of corner-sharing octahedra with the T cations at their centers, while the Ln cations form a second interpenetrating cubic sublattice located at the 12-fold co-ordinated sites between octahedra. The co-existing localized and itinerant spins of rare-earth antimonides $LnTSb_3$ (where Ln = Pr and T =V, Sr) compounds have attracted interest for their major technological applications in spin electronics, Read Head, magnetic RAM, nano-particles etc. They crystallize in orthorhombic phase with space group Pbcm. $LnTSb_3$ have been reported with unique first order phase transition due to the coupling between 3d and 4f moments of T and rare earth elements in terms of de-Gennes factor. The itinerant electron ferromagnetic behaviour is theoretically studied which is found to be due to strong electron correlation in the T-3d bands. Studies of the anisotropic properties in single-crystal form include those of the R-diantimonide crystal series of RSb_2 (R = La–Nd, Sm) (Budko et al., (1998); Canfield et al., (1991)) on the ternary $RAgSb_2$ (R = Y, La–Nd, Sm, Gd–Tm) (Myers et al., (1999); Sologub et al., (1995)) and on the $RTSb_3$ (R = La, Sm, Gd) series with chromium and vanadium (Jackson et al., (2001, 2007); Deakin et al., (2003)) transition metals (T). As part of our effort to discover and understand new magnetic and electronic behavior in lanthanide based systems, we focus our work on two types of lanthanide based systems.

Numerous studies on the phase transition of $RCrSb_3$ compounds have been reported experimentally (Glasso et al., (1965); Hartjes et al., (1997)) but the theoretical investigation is very much limited. Raju et al., (1998) found that the itinerant electron ferromagnetic behavior rises due to strong electron correlation in the Cr d bands (Richter et al., (2004)). They suggested the band structures to be comprised of Cr–Sb and Sb–Sb layers interacting weakly along stacking direction a-axes.Granado et al., (2002) have also studied $LaCrSb_3$ where both itinerant and local moments of Cr come into play. Choi et al. (2006) studied $LaCrSb_3$, $LaVSb_3$ and $YbCrSb_3$ using the linear muffin-tin orbital (LMTO) method in which their observation showed that LMTO fails to explain the rigid band model of $LaCrSb_3$ and $YbCrSb_3$. This is because Yb^{2+} ions are in a divalent state with fully occupied 4f bands in $YbCrSb_3$, unlike trivalent La^{3+} in $LaCrSb_3$.

Sandeep et al., (2010, 2011) have investigated the electronic and magnetic properties of layered $LaCrSb_3$. The coexistence of local and itinerant Cr - t_{2g} states suggests the double exchange mechanism for the ferromagnetic ordering. They have also studied the magnetic properties of $GdCrSb_3$, $TbCrSb_3$ and $DyCrSb_3$ and suggested that the moment contribution in these systems due to Cr-d states is absent. Richter et al.,(2004) first studied $LaCrSb_3$ and have provided its itinerant magnetic characteristic on the basis of electronic structure calculation. Ghimire et al.,(2011, 2017) have studied $LnCrSb_3$ where both itinerant and local moments of Cr come into play. According to them, $LnCrSb_3$ displays a rich magnetic structure due to complex magnetic interaction between 3d moments of Cr and 4f moments of rare earth ion.The electronic density of states (DOS) and magnetic moments of rare-earth antimonides ($NdVSb_3$) has been studied by Sandeep et al., (2015) by the first principles full-potential linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT). The exchange-splittings of V-3 dstate electrons and 4f-states of Nd atoms were analyzed to explain the magnetic nature of these systems. The V atom plays a significant role on the magnetic properties due to the hybridization between V-3 dand Sb-5p state orbitals.

Like wise, another study made by Sandeep et al. (2011) on the density of states (DOS) and the magnetic moments of $SmCrSb_3$ and $GdCrSb_3$ have been reported that DOS result shows the exchange-splittings of Cr-3d and rare-earth (R) 4f states electrons, which are responsible for the ground state ferromagnetic (FM) behavior of the systems. The FM behavior of these systems is strongly influenced by the average number of Cr-3d and Sm (Gd) 4f-electrons. The Cr atom plays a significant role on the magnetic properties due to the hybridization between Cs-3d and Sb-5p states. A report by Ghimire et al.(2010, 2011) on oxide material CrO2, and Heusler families such as NiXSb and Co_2XAl (where X=3d transition metals) identified half metallic ferromagnetism (HMF) which has potential applications in the field of spin electronics due to their important properties like half-metalicity, high magnetic ordering temperature and magneto-dielectricity (Mugavero et al., (2010); Kohn et al., (1965)). Half metals (HMs) are one class of promising materials which are metallic in one spin channel, while insulating inthe opposite spin channel due to the asymmetric band structure. HMs can generate spin-polarized currents without any external operation, leading to 100% spin-polarization and thus are very useful for spintronic applications (Ghimire et al., (2015)).

Ghimire et al., (2015, 2016) studied the electronic and magnetic properties of a material of double perovskite $[Pr_{2-x}Sr_xMgIrO_6]$2 by first-principles density functional approach. Under the cooperative effect of spin-orbit coupling (SOC) and Coulomb interactions of Ir-5dand Pr-4f electrons, they reported that half metallic ferrimagnetism (HMFiM) with the total angular moment $\mu_{tot} = \pm 3\mu_B$ per unit cell for x = 0.5 and 1.5, desirable for spintronic applications. HMFiM is fully retained in presence of SOC due to the large exchange splitting between spin-up and spin-down bands at the Fermi level.
Although a number of theoretical studies are found, there is limited report on $LnTSb_3$ and its doped allies. The researcher, therefore, intends to carryout the calculations of density of states (DOS), band structures, and magnetic properties to investigate $LnTSb_3$ by using the first-principles density functional theory (DFT) to cover the lack of experimental data and to propose further if the material is suitable for spintronic applications. For this FP-LAPW based GGA method will be used. Computations will be carried out by using WIEN2k code.

II. CRYSTAL STRUCTURES AND METHODS

$Lnvsb_3$ series of compounds crystallize in orthorhombic structure with space group Pbcm. The crystal structure consists of sheets of Sb atoms arranged in b-c plane. The rare earth ions are placed below and above these Sb sheets in a checker board pattern. Each V ion is surrounded by six Sb atoms forming a face (edge) sharing octahedra along c(b) axis. In short, it crystallizes in a quasi two dimensional structure with PrSb and VSb_2 layers stacked along an axis (Perdew et al., (1965); Granado et al., (2002) ; Inamdar et al., (2008)).Corrugated VSb_2 layers are stacked normal to [110] and are separated by R^{3+} ions and a nearly square planar Sb layer. The crystal structure consists of VSb_6 distorted octahedral in the b-c plane, which share faces along the c axis and share edges along the b axis. Separating the stacking of these octahedral is a region of Pr ions and a nearly square sheet of Sb_1. The strong crystallographic anisotropy will also present itself in the anisotropic transport properties. Bond length considerations suggest that the rare earth and V ions are trivalent, while the Sb, making up the corners of the octahedra, has a valence of 2.5 and the Sb_1 has a valence of 1.

Figure 1: Crystal structure of $PrVSb_3$ obtained using the VESTA package. The VSb_6 octahedra is formed between V-3d and Sb-6p states.

The electronic and magnetic properties of the $LnVSb_3$ compound were studied by using the FP-LAPW method, in the framework of DFT (Perdew et al., (1965)). The calculations have been performed using the experimentally determined lattice parameters and the atomic positions and WIEN2k code (Blaha et al., (2001) is used for computations. Since R 4f-orbitals are rather localized, the 4f-electron correlations are expected to be strong. Consequently, the LSDA+U calculations (Dutta et al. (2010) have been chosen to include the on-site Coulomb interaction. The on-site Coulomb energy (U) applied are 6eV and 4eV respectively for Ln and V atoms. 500k points have been used for $PrVSb_3$ in the irreducible Brillouin zone and the muffin tin radii for Ln, V, Sb_1, Sb_2, Sb_3 are 2.5, 2.35, 2.35, 2.35 and 2.35 a.u. respectively. The density plane cut-off RMTxKMAX is 7.0, where KMAX is the plane wave cut-off and RMT is the smallest of all atomic sphere radii. The self-consistency is better than 0.001 e/a.u.3 for charge and spin-density and the stability is better than 0.01 mRy for total energy per cell.

III. PARENT MATERIAL [$PrVSb_3$]AND DOPED MATERIALS [$PrSrVSb_3$]

Single crystals of rare-earth vanadium triantimonides $RVSb_3$ are grown out of solution. The substitution of heavier rare-earths makes the orthorhombic structure contract and accompanies changes in the magnetic properties throughout the series (Wu et al., (2005)). $PrVSb_3$ has an interesting feature due to anisotropy in its structure, antiferromagnetic (AFM) ordering of V and 4f moments of Pr ions(Leonard et al., (2000)). $PrVSb_3$ is determined to have antiferromagnetic ground state experimentally.The previous magnetization measurement on a $PrVSb_3$ polycrystalline sample found an antiferromagnetic ground state with TN = 7K. Field- dependent magnetization isotherms of $PrVSb_3$ along the three crystallographic axes shows features of metamagnetic transitions. The magnetic moments were determined to be 2.89 μ_B at 65kOe. This value is close to the theoretical Pr^{3+} free ionvalue of 3.2 μ_B.

In the material PrSrVSb$_3$, Pr site is doped with Sr atoms which have a charge state +2 that corresponds to whole doping to identify the possible half-metallic states. Hole doped (Sr) on PrVSb$_3$ shifts the V-3d bands in spin-down channel to cross E$_F$ generating metallic DOS while spin-up remains insulating. Doping one Sr, from the view of rigid band model, shifts E$_F$ downward to valence region such that it crosses the topmost occupied states. As shown in Fig. 2 (bottom), hole doped (Sr) to Pr-site in PrVSb$_3$ shifts the V-3d bands in spin-down channel to cross E$_F$ generating metallic DOS while spin-up remains insulating Pr nominally takes the charge state +3 with 4f^2 configuration lying deeply in the valence region. For U=3 eV, the topmost valence band in spin-up channel shifts deeper towards the valence region giving rise to an insulating state. In contrary, for spin-down channel, the metallic state is maintained, except that the DOS peak near E$_F$ is splitted due to strong electron-correlations. The effect of U is comparatively small as expected due to partial occupation of the orbitals in spin-down channel. With spin-up channel insulating and the spin-down channel metallic, PrSrVSb$_3$ is a half-metal (Fig. 2 and Fig. 3).

IV. RESULTS AND DISCUSSIONS

Based on the experiment, we perform the electronic structure calculation and determine the ground state. For the AFM calculations, we generated a 2x1x1 supercell such that two Pr, four V and eight Sb atoms are identified in the new structure. With antiferromagnetic ground state, the two Pr flips antiparallel to each other. Similarly, the flipping of V is antiparallel to each other along the a-b plane.

To gain insight into the electronic and magnetic properties of the compounds, we perform the DFT calculations. The total DOS for PrVSb$_3$ and PrSrVSb$_3$ along with partial DOS of Sb-5p, V-3d and Pr-4f for spin-up and spin-down configurations are shown in Fig.3 and Fig.4 respectively. The regions are contributed by the Pr-4f and V-3d state electrons in both spin channels. In the valence regions DOS contributions were observed due to V-3d state electrons in spin-up channel. Sharp peak due to V-3d state electrons were observed at 1.5eV in the spin-down channel. At core region contribution of Pr-4f state electrons were highest in the spin-up channel. The splitting of the DOS in the spin-up and spin-down channels were found to occur for both V-3d and Pr-4f states which contribute to the magnetic nature of the compounds and were supported by the individual magnetic moments calculated. The lower magnetic moment could be explained on the basis of hybridization between the states of Sb-6p and V-3d which leads to a less prominent splitting of the 3d states giving rise to lower magnetic moment for V atoms. Hence, PrVSb$_3$ has an antiferromagnetic ground state consistent with experiment and preliminary investigation shows total DOS of PrVSb$_3$ as semi-metallic behavior with presence of small DOS at E$_F$ (Fig.2).

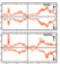

Figure 2: Total DOS for Semi-metallic PrVSb$_3$ (top) and Half metallic PrSrVSb$_3$ (bottom) within GGA+U+SOC scheme in spin-up and spin-down channels. The dashed vertical line corresponds to E$_F$ set at zero energy.

Fig- 3

Figure 3. Partial DOS of PrSr(VSb$_3$) within GGA+U+SOC scheme for Pr -4f, V-3d and Sb-5p states in spin-up and spin-down channels. The dashed vertical line corresponds to EF set at zero energy.

From the spin-resolved partial DOS shown in Fig. 3, one can understand the role played by the concerned atoms. As observed, Pr-4f states in spin-up channel lies deep in the valence region with sharp peak around -3.8 eV, and few bands lie in the conduction region above E_F with a clear indication of filling of two f-electrons. On the other hand, in spin-down channel, Pr-4f electrons lie in the conduction region indicating the empty states. V-3d state is found to play major role. In spin-up, valence region are almost empty while finite DOS peaks in the conduction region, whereas in the spin-down channel, V-3d contributed mainly in the valence region with finite DOS ranging from around -3 eV upto the conduction region (3 eV). The role played by Sb-5p state is negligible. Thus, with spin-up channel insulating and spin-down channel metallic, the material is predicted to be a half metallic ferrimagnets.

The calculated effective magnetic moments for PrVSb$_3$ are zero where two Pr and four V align antiparallel to each other which results in cancellation of total moment. However, for PrSrVSb$_3$ its effective moment is found to be $2\mu_B$ contributed mainly by the Pr-4f states. The reason is that out of four V atoms, two V flips antiparallel to other two such that their moment cancels each other while out of two Pr, one is replaced with Sr such that one Pr carries $2\mu_B$ moment.

V. CONCLUSIONS

From the investigations, it was found that PrVSb$_3$ is antiferromagnetic consistent with experimental prediction. DOS result shows the strong hybridization between V-3d and Pr-4f states with large exchange-splitting. They are found responsible for the AFM ground state behavior in PrVSb$_3$. Inclusion of U (3 eV for V and 5 eV for Pr) shows semimetallic behavior.When the parent material PrVSb$_3$ is doped with hole (Sr) to Pr-site partially, half-metallic states is achieved generating metallic DOS in spin-down channel while spin-up remains insulating. The effective moments of PrSrVSb$_3$ is found to be $\sim 2\mu_B$ per formula unit while that of PrVSb$_3$ is zero respectively. Upon hole doping further, for example with Na to Pr site, we expect PrVSb$_3$ to be a candidate of compensated HMs. Therefore, PrVSb$_3$ upon hole doping turns out to be HM ferrimagnet with one spin channel conducting, it is expected to have desirable application in spintronicsdevices

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