Magnetic and Electronic Properties of Strongly Correlated SmX(X=S, Se): A High Pressure Study

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Abstract—*Sm–chalcogenides in the stable Fm-3m and high pressure Pm-3m phases have been studied using ab-initio pseudo-potential method with spin-polarized GGA for exchange–correlation energy optimization. The phase stability has been determined from the total energy optimization in non-magnetic and magnetic phases clearly indicating that these compounds are ferro-magnetically stable. Sm ion is considered to have both five and six localized f electrons and these chalcogenides undergo a first-order transformation from Sm^{2+} to a stable valence state (Sm^{3+}) with delocalization of the 4f electrons into the 5d states of Sm which is further followed by another transition from Fm-3m to Pm-3m state under compression. The structural parameters, i.e. equilibrium lattice constant, bulk modulus, its pressure derivative, transition pressure and volume collapse are in closer agreement with the experimental results. We have also computed the electronic structure at different volumes.*

1. INTRODUCTION

Rare-earth compounds (RECs) have attracted experimental [1-8] and theoretical attention [9-16] due to the presence of strongly correlated electrons in them. They possess interesting structural, mechanical, magnetic, magneto-optic and electronic properties which make them a candidate for industrial and technological applications. Out of these RECs, Samarium mono-chalcogenides SmX (X=S, Se, Te) have been investigated in greater detail in view of their technological applications [1,2] in spintronics and spin filtering devices. Synchrotron radiation and X-ray diffraction (XRD) studies on these compounds show that they crystallize in the Fm-3m (B1) structure and their lattice parameter 'a' increases with increasing anion size [1,2,6]. These compounds undergo a pressure induced structural transformation from B1 to Pm-3m structure. Besides, it has also been found [2,4,5] that some of these compounds show an iso-structural valence transition from divalent (2+) to trivalent (3+) states due to promotion of highly correlated f electrons into the 5d conduction band states of the Sm ion. These compounds are semiconducting if Sm is divalent and become metallic if its nature is trivalent. The semiconducting SmS and SmSe have an unusual gap as the fundamental excitation is f to d. It gives rise to excitation of localized f electrons, which are predominantly of rare-earth d character.

SmS undergoes structural phase transformation from B1 to B2 phase at 42-54 GPa while SmSe at 25 GPa [6]. This B1 to B2 transition is accompanied by an electronic collapse at 6.5 kbar for SmS and in the range of 1-50 kbar for SmSe [2] while similar transformation is observed in the pressure range of 0.65 and 3.4 GPa [4], and 1.24 and 3-9 GPa [6] for SmS and SmSe, respectively.

The phase-transition properties have been computed by SIESTA [16] with spin-polarized generalized gradient approximation (GGA) because these materials are strongly correlated in nature and hence spin is considered for magnetic properties. The results obtained are in good agreement with the experimental data [3,6] and better than those obtained by others [10].

2. THEORY AND METHOD OF CALCULATION

The present ground state calculations are based on the first-principles pseudo potential method within the density functional formalism and spin-polarized GGA using the Perdew, Burke, and Ernzerhof functional [17] for the exchange-correlation energy and standard norm conserving pseudo potential of Troullier-Martins [18] in relativistic form. All calculations are performed by using the SIESTA code which is appropriate for electronic structure calculations of large systems [19 and the references therein]. In SmSe and SmTe, the Sm atom occupies (0, 0, 0) while the Se and Te atoms are at (0.5, 0.5, 0.5) positions. The valence configuration of Sm ($5d^0\ 4f^6$), Se ($4s^2\ 4p^4\ 4d^0$) and Te ($5s^2\ 5p^4\ 5d^0$) is used which represents the basis set for our calculations. Atomic basis set, double-ζ with perturbative polarization for Sm-6s, Se-4s and Te-5s states while double-ζ for Sm-5p, 5d, 4f, Se-4p and Te-5p states has been used. To solve the self-consistent Kohn-Sham equations, we have performed convergence test for mesh cut-off and k-point up to a energy difference of 25meV. We have used the basis of plane waves up to kinetic energy of 124.2 and 109.6 Ry for SmSe and SmTe, respectively. We have used 10x10x10 k-grid (1000 k points) in the Brillouin-zone (BZ). The cut-off radius used for pseudo potential for Sm is 3.06, 4.00, 3.06 and 3.06 Bohr for

6s, 5p, 5d and 4f states, respectively. For Se, 3.56 Bohr for 4s and 2.35 Bohr for 4p state while for Te, 3.56 Bohr for 5s and 2.35 Bohr for 5p state is used. All the atoms are allowed to relax until a force tolerance of 0.01 eV/Å and stress tolerance of 0.01 GPa is reached, while restricting their structure to be cubic only.

3. RESULTS AND DISCUSSION

3.1 Magnetic State Stability

We have carried out self-consistent calculations of total energy in non-magnetic (NM) and magnetic (M) states in B1 phase. The variation of total energy with cell volume for non-magnetic and magnetic states in B1 phase for Sm-compounds is shown in figures 1 and 2. It is seen from these figures that non-magnetic-to-magnetic transition does not occur in these compounds (the curves for NM and M states do not intersect). The energy remains lower in magnetic phase. Therefore, ferromagnetic state is more stable than the non-magnetic state at ambient as well as at high pressures.

3.2. Phase Transition Properties

For computing the phase transition properties, we have performed self-consistent calculations of total energy at room temperature as a function of volume in all the phases. The calculated results in B1 and B2 phases are plotted in figures 3 and 4. It is seen from these figures that these compounds are stable in B1 phase at ambient conditions and undergo an iso-structural valence transition from Sm^{2+} to Sm^{3+} state followed by a more compressed B2 phase which is consistent with experiments [1-2,4-6].

Under ambient conditions, the energy of the B1 phase with divalent Sm is minimum than that of trivalent Sm in the same phase. On further compression, beyond B1→B2 transformation, the energy of B2 phase becomes more minimum as compared to that of B1 phase which fulfils the required criterion for relative stability of the competitive phases. It is clear from figures 3 and 4 that convergence occurs at a value close to the experimental lattice constant.
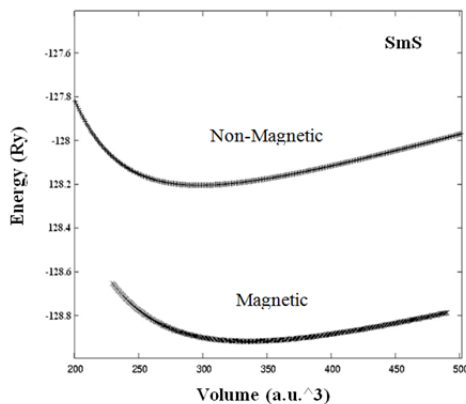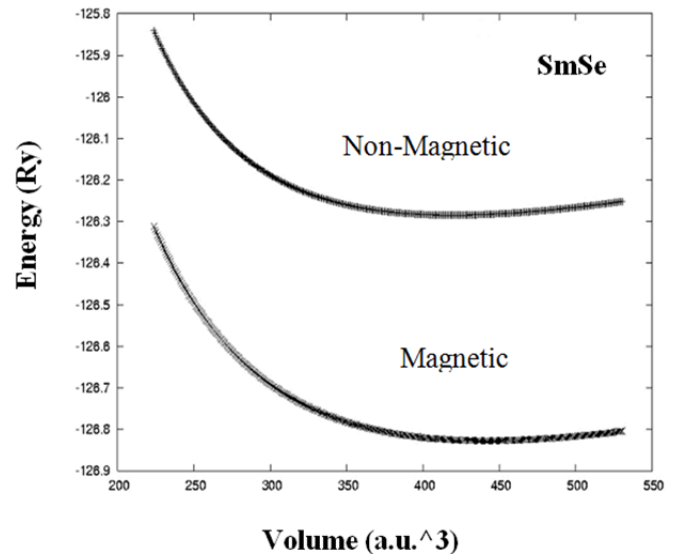

Fig. 2: Total energy vs. cell volume for both the NM and M states of the B1 phase for SmSe.

The calculated values of total energy are fitted to the Murnaghan's equation of state [20] to determine the ground state properties such as equilibrium lattice parameter, bulk modulus and its pressure derivative. These results are presented in Table 1 and compared with available experimental [3,6] and other theoretical [10] data.

To determine the transition pressure, the Gibb's free energy at room temperature in different B1 and hypothetical phases can be expressed as

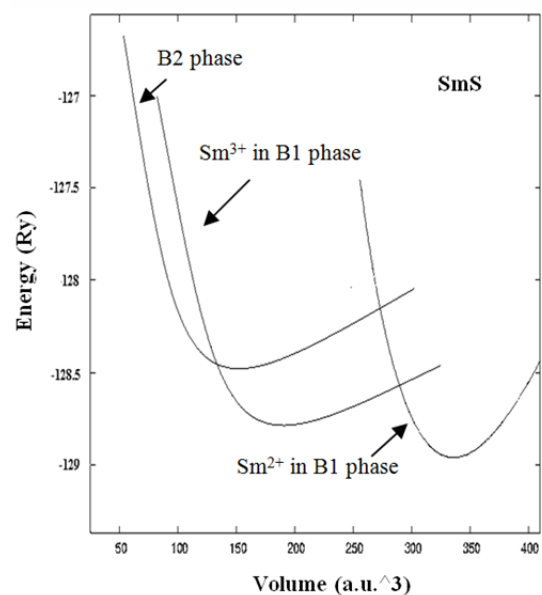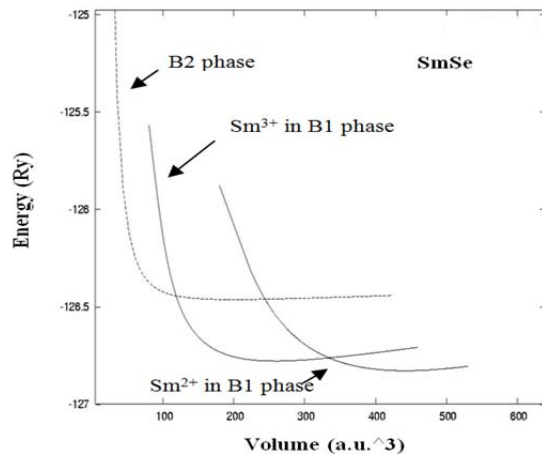$$G_{B1} = E_{B1} + PV_{B1} \text{ and } \qquad G_{Hypo} = E_{Hypo} + PV_{Hypo} \qquad (1)$$

Fig. 3: The variation of Energy (Ry per unit cell / atom) vs. volume for various structures of SmS.

Fig. 1: Total energy vs. ell volume for both the NM and M states of the B1 phase for SmS.

Fig. 4: The variation of Energy (Ry per unit cell / atom) vs. volume for various structures of SmSe.

It is known that Sm has partially localized f states which delocalize under pressure well before B1→B2 transition. Hence, in the present study, the fluctuation of $4f$ electrons to $5d$ states of Sm for both the compounds has been studied. The variation of the Gibb's free energy for both SmS and SmSe in Sm^{2+} and Sm^{3+} states reveals their equality at 1.05 and 3.87 GPa (not shown in figures) resulting in transformation of semiconducting Sm^{2+} into mixed valent Sm^{3+} state, which shows closer agreement with the available measured data [6] for SmS (1.24 GPa) and SmSe (3-9 GPa). Beyond this pressure, these compounds remain stable in B1 phase with trivalent state of Sm because the free energy in this state is lower as compared to the energy of its divalent state. The variation of Gibb's free energy in B1 and B2 phases with pressure is shown in figures 5 and 6. It may be seen from these figures that the free energy in parent (B1) phase is minimum at ambient conditions and remains minimum up-to 45.08 for SmS and 21.39 GPa for SmSe. At 45.09 and 21.4 GPa, the free energy in both the phases becomes equal showing that both the phases are in equilibrium at this pressure and hence structural phase transformation in SmS and SmSe occurs at this point. On further increasing the pressure, the Gibb's free energy minimizes in B2 phase as compared to that in B1 phase, i.e., the B2 phase becomes stable with more minimum free energy.

Table 1: The values of lattice parameter (a), bulk modulus (B_0) and its pressure derivative (B_0') of SmS and SmSe in B1 and B2 phases.

| Properties	SmS		SmSe		
	B1 phase	B2 Phase	B1 phase	B2 Phase	
a (Å)	5.84	3.51	6.22	3.88	**Present**
	5.97	-	6.20	-	Expt.[3,6]
	5.96	-	6.19	-	Others[10]
B0 (GPa)	52.61	59.06	43.12	71.09	**Present**
	42±3		40±5	-	Expt.[3,6]
	53.40		43.9	-	Others[10]
B0'	4.79	5.60	3.30	3.77	**Present**

3.3. Electronic Transition Properties

The electronic structure of mixed valent SmX along the directions of high symmetry in the BZ has been studied. We have performed fully relativistic spin-polarized calculations treating $4f$ electrons as itinerant, at equilibrium lattice constant, in B1 phase. These results have been plotted for spin-up and spin-down channels at ambient conditions. The overall band profiles are quite similar for all the three compounds, with a small difference in detail

The spin-polarized electronic structure of mixed valent SmX treating $4f$ electrons as itinerant along high symmetry directions in the BZ in B1 phase are shown in figures 7 (a) and (b). In this case, although the spin-up and spin-down states are close to each other but they occur at different values due to itinerant electrons. In these figures, solid line represents the spin-up band structure (BS) while dotted line represents the BS in spin-down channel in B1 phase. The region around -11.8 eV for SmS and -12 eV for SmSe is mostly due to chalcogen s character and the next higher region is due to chalcogen p character. The region above the Fermi level up to 3 eV is mainly due to unoccupied $5d$ states of Sm.
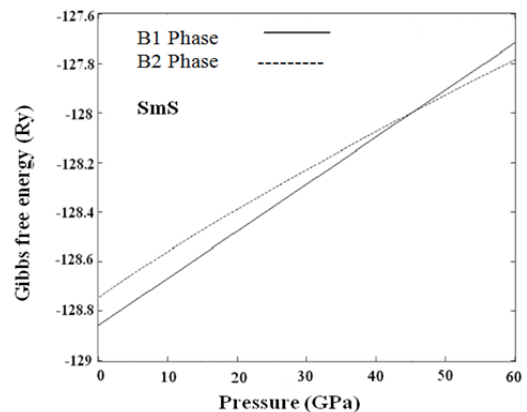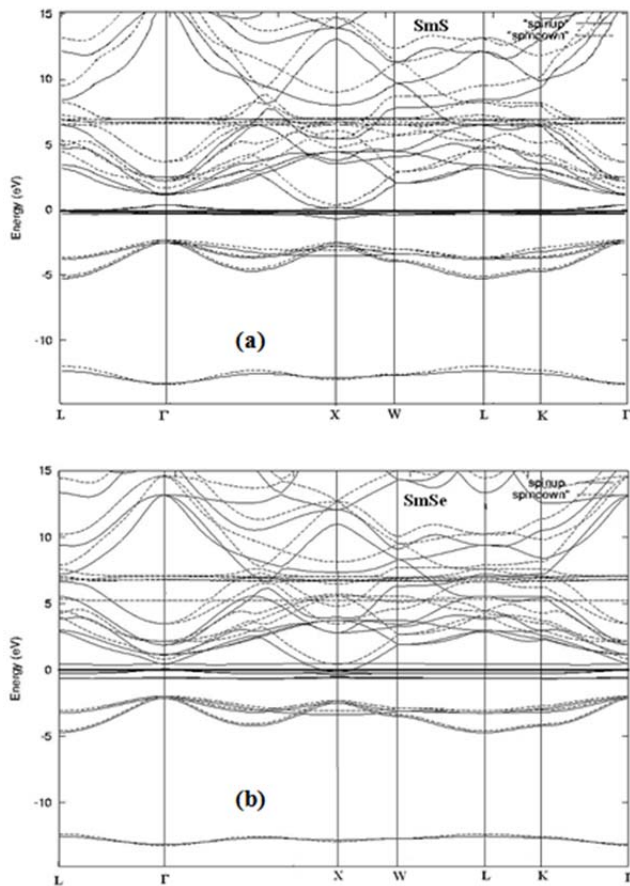

Fig. 5: Variation of Gibbs free energy with pressure for SmS.
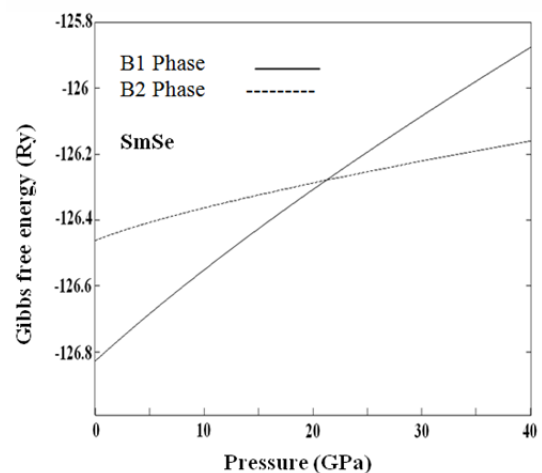
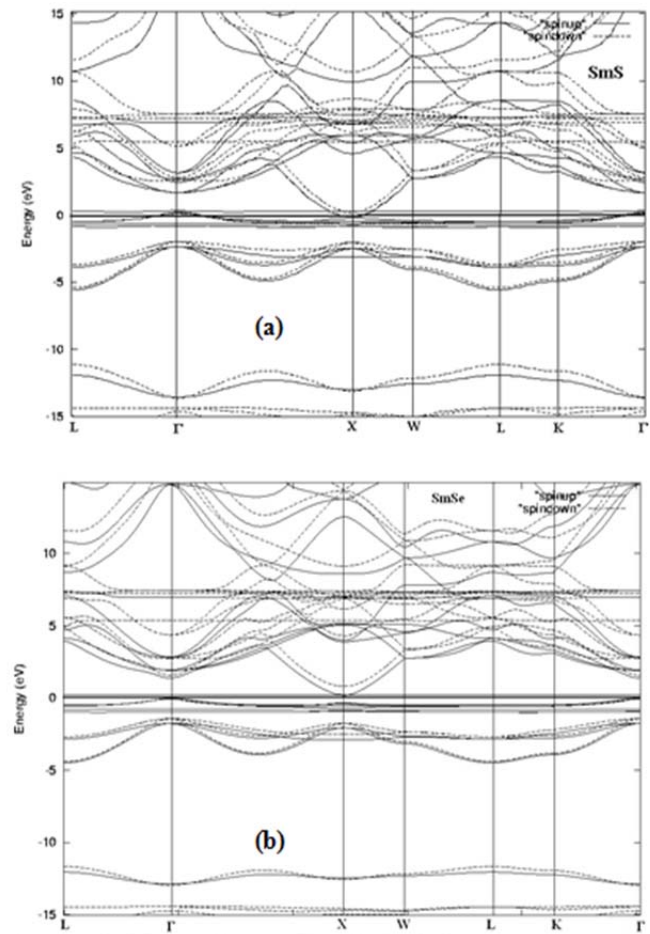**Fig. 6: Variation of Gibbs free energy with pressure for SmSe.**

For the spin-up case, the Sm *f*-like states (cluster of solid lines) can be seen at E_F, showing its metallic nature, while for the spin-down case these states can be seen above the Fermi level (cluster of dotted lines), which hybridize with Sm *d*-like states, showing semiconducting nature. In spin-up case, the interaction of Sm-*f* states and chalcogenen *p* states leads to a mutual repulsion so that the chalcogen *p* states are pushed to energies above the Fermi level. These chalcogen *p* states connect with lower states and are responsible for metallic character of the spin-up BS. Since the Sm *f* levels are polarized above the Fermi level in the spin-down direction, the same interaction of chalcogen *p* and Sm *f* states presses the chalcogen *p* levels below the Fermi level to open a gap, and produces semiconducting behaviour.

The electronic band structure with Sm in trivalent state, just after the Sm^{2+} to Sm^{3+} transition, are shown in figures 8(a and b). It is clear from these figures that as we increase the external pressure, thereby decreasing the lattice constant, the width of Sm 5*d* and 4*f* bands increases which may be responsible for decrease in the gap between *p* and *f* states. At this pressure the 4*f* electrons spill into 5*d* bands leaving $4f^5$ state behind. The ionic radius of Sm^{3+} is about 15% less than the radius of Sm^{2+}. Therefore, with more electrons in the 5*d* conduction band, the lattice will shrink, thereby giving further rise in the crystal-field splitting of the 5*d* states. This results in an avalanche effect and a first-order valence transition is observed. However, the valence transition does not go all the way to trivalency but stops where the gain in electronic energy is compensated by an increase in lattice strain energy. The initial empty 4*f* level still remains partially occupied due to pinning at the Fermi level with occupation number equal to 0.15 (valence 2.85+). This situation is typically found in mixed-valent crystals.

Fig. 7: Self-consistent spin-polarized electronic structure for (a) SmS and (b) SmSe at ambient conditions in B1 phase. The position of the Fermi level is shown by the solid horizontal line.

It is interesting to note that our calculations on electronic structure in B1 phase show an energy gap of 3.1 and 2.5 eV (figures 6(a and b) between *p* band and the bottom of conduction band for SmS and SmSe compounds. It indicates the decrease of energy gap from SmS to SmSe, the 4*f* bands of Sm approach *p* states of the legend from S to Se. This increase in the *f* band width may be interpreted as the interaction of *f* states of cation with *p* states of anion.

Fig. 8: Self-consistent spin-polarized electronic structure for (a) SmS and (b) SmSe with Sm in trivalent state. The position of the Fermi level is shown by the solid horizontal line.

To see the effect of high pressure on the electronic structure and phase transformation in these compounds, we have also computed the electronic structure in B2 phase (just after the B1→B2 transition) for SmX and plotted them in figures 9(a and b). It may be seen that the 4f bands of Sm lie close to Fermi level which drops down towards the chalcogen p states at point and overlap with the top of chalcogen p states at H point showing metallization. This is because there is a decrease in energy separation between the 4f states and the conduction band edge with increase in pressure. It may be due to the fractional change in the valence state of Sm during the pressure induced structural transition. Due to the decrease in energy separation with pressure, the fractional delocalization of the 4f states has been observed. Similar semiconductor to metal transition has also been observed experimentally under pressure [3]. Furthermore, as the pressure increases, the hybridization of d states of Sm and chalcogen p states increases and the lower energy bands shift towards the higher energy side. In the spin-down channel the gap between the chalcogen-p and Sm-d states reduces, while Sm-f states shift to the higher energy side and participate in the bonding with p states of anion. On the other hand, in case of spin-down channel the metallic property increases resulting in metallization in the B2 phase.
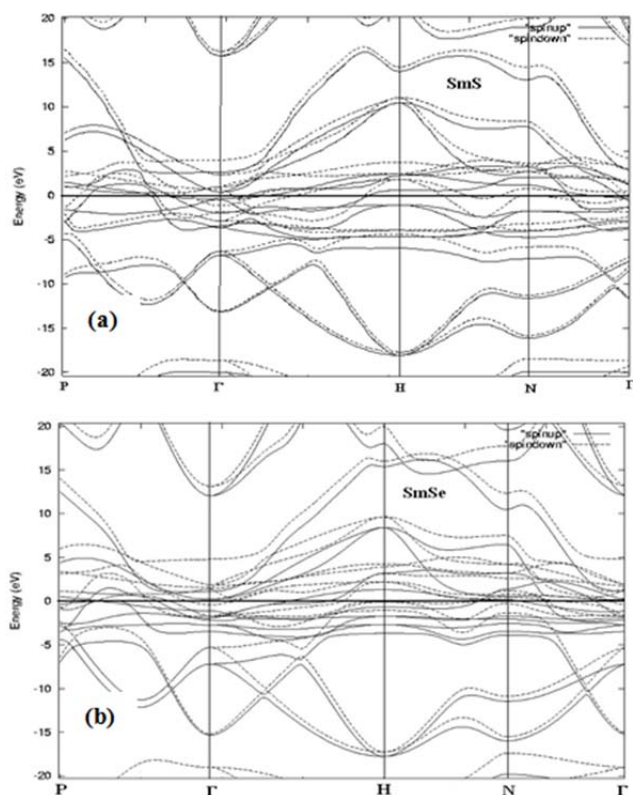
Fig. 9: Self-consistent spin-polarized electronic structure for (a) SmS and (b) SmSe in B2 phase (just after B1→B2 phase transition). The position of the Fermi level is shown by the solid horizontal line.

The spin-polarized self-consistent band-structure calculations have been very successful in calculating and predicting the magnetic moments using GGA. The calculated values of magnetic moments for SmX are listed in Table 2. It is clear that the local and total magnetic moments decrease with the increase in pressure, which is quite natural in magnetic materials. The contribution to the total magnetic moment is mainly due to Sm-4f electrons, while the contribution of chalcogen-atom is almost negligible. But it is interesting to note that the magnetic moment contributed by chalcogen-atom is negative, which indicates that the contribution from 3p, 4p and 5p states of the chalcogen atom (S and Se) is anti-parallel to the magnetic moment contributed by Sm-4f states.

Table 2: Total and local magnetic moments (in Bohr magneton μ_B) as a function of pressure (in GPa) for SmX in B1 phase.

Pressure	SmS			SmSe		
	Sm	S	Total	Sm	Se	Total
0	6.223	-0.219	6.004	6.201	-0.201	6.000
5	6.214	-0.227	5.987	6.194	-0.217	5.977
10	6.199	-0.235	5.964	6.189	-0.223	5.966
15	6.192	-0.243	5.949	6.163	-0.228	5.935
20	6.178	-0.250	5.928	6.139	-0.232	5.907
25	6.152	-0.258	5.894	6.130	-0.235	5.895
30	6.132	-0.267	5.865	6.117	-0.261	5.856

4. CONCLUSION

In the present article, we have attempted to provide a unified picture of the crystal properties of the strongly correlated systems (SmS and SmSe). For this purpose, *ab-initio* pseudo-potential calculations have been performed to obtain iso-structural valence transition, structural phase transition, electronic, and magnetic properties under pressure by employing spin-polarized GGA as implemented in SIESTA. The present calculations predict that these materials are ferromagnetic in nature and they do not show any magnetic to non-magnetic transition. They show an iso-structural valence transition due to fluctuation of electrons from f to d state of Sm [$(4f^6, 5d^0)$ to $(4f^5, 5d^1)$] followed by structural phase transformation from B1→B2 phase under pressure. The calculated properties *viz.* lattice constant, bulk modulus and its pressure derivative, Gibbs free energy, transition pressure, are in reasonably good agreement with experimental data and better than other theoretical results. The electronic structure has been computed in B1 and B2 phases to analyze the effect of f-electrons and pressure on the nature of bands in these strongly correlated compounds. The calculated local and total magnetic moment decreases with increasing pressure.

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