A FP-LAPW Study on Ground State Electronic Nature of RESn₃ (RE= La, Ce, Pr and Nd) Intermetallic Compound

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Abstract

First principles study of structural and electronic properties of non- magnetic LaSn₃ and CeSn₃ as well as ferromagnetic PrSn₃ and NdSn₃ rare-earth intermetallic compounds, which crystallize in AuCu₃-type structure, is performed using density functional theory based on full potential linearized augmented plane wave (FP-LAPW) method. The ground state calculations are carried out within PBE-GGA and LSDA approximations for the exchange correlation potential. Lack of availability of data regarding the above properties of RESn₃ motivated us to perform systematic study of these compounds. The ground state properties such as lattice parameter are found to be in good agreement with the available experimental data. The electronic band structure calculations for the studied RESn₃ compounds show metallic character in both majority and minority spin channels.
Keywords: Rare-earth; Density functional theory; Metallic.

1. Introduction

Intermetallic compounds consist of two or more metals bonded with specific stoichiometries by mixed metallic, covalent and ionic bonding. They are formed according to the thermodynamic stability of certain types of crystal structures. The rare earths show a regular change of their properties, especially of atomic dimensions and electro negativities, due to their particular electronic structure. Moreover, some of them exhibit different valence states in compounds with metallic character, which give rise to interesting structural, electronic and magnetic properties. Many rare earths (*RE*) and group IIIA or IVA elements (*X*) form stable *REX₃* compounds which crystallize in the AuCu₃ structure. *REX₃* compounds with the AuCu₃-type cubic structure exhibits a variety of phenomena [1 - 4]. Compounds of this family are investigated because of phenomena such as magnetic moment formation, crystal field and Kondo effect or multiaxial magnetic structures, due to their incomplete 4*f* shell.

La being the first and the lightest member of the lanthanide series has unfilled '4f' shell. The number of '4f' electrons increases gradually along the period from La to Lu. Presence of 4f $^{1-14}$ electrons in rare earth elements and its compounds attract considerable attention due to the intricate electronic properties. These compounds exhibit a variety of phenomena like heavy-fermions [5, 6], mixed-valency [7] and Kondo behavior [8, 9]. An experiment has been carried out by Miller and Hall [10] to synthesize heavy rare-earth element tristannide compounds using a high pressure technique, where LnSn₃ (Ln = Tb, Dy, Ho, Er and Y) compounds were successfully prepared. A theoretical study of structural, electronic, elastic and mechanical properties of nonmagnetic rare-earth intermetallics LaX₃ (X = In, Sn, Tl and Pb), which crystallize in AuCu₃-type structure, has been performed using first principles density functional theory by Abraham et.al. [11]. CeSn₃ has however been categorized as a dense Kondo compound exhibiting valence fluctuations [12]. The ambient and high pressure behavior of CePd₃, CeSn₃ and CeIn₃ compounds have been discussed by computing electronic structures using TB-LMTO method by Shekar et. al. [13]. YbSn₃ single crystals have been synthesized by the Bridgman technique [14]. YbSn₃ shows a super conducting transition at around 3.6K [15]. Magnetic and elastic properties in the paramagnetic state of antiferromagnetic NdIn₃ have been studied by Amara et.al [16].

The rare earth intermetallics RESn₃ compounds crystallize in cubic AuCu₃-type structure (space group symmetry of Pm3m (No.221)). In the present work, we report the structural and electronic properties of RESn₃ (RE= La, Ce, Pr and Nd) compounds using density functional theory using PBE-GGA and LSDA as exchange correlation functionals. Lack of availability of data regarding the above properties of these compounds motivated us to perform this systematic study of these compounds. A brief description of the computational details is outlined in Section 2 while Section 3 covers the results, followed by discussion.

2. Computational Method.

Accurate first principles calculations using full potential linearized augmented plane wave method (FP-LAPW) [17] as implemented in WIEN2k code [18] have been performed by us for the present compounds. In this method, the basis set is obtained by dividing the unit cell into non-overlapping spheres and an interstitial region. The effects of exchange–correlation interaction are treated within the generalized gradient approximation (GGA) of Perdew, Burke and Ernzrhof (PBE) [19] and LSDA [20]. The values of $K_{max} \times RMT = 7.0$ and $l_{max} = 10$ are kept throughout the calculation. A dense mesh of $10 \times 10 \times 10$ k points is used and tetrahedral method [21] has been used for the Brillouin Zone integration. The calculations are iterated until the total energies are converged below 10^{-4} Ry. The total energies are calculated as a function of volume and fitted to Birch-Murnaghan equation of state [22] to obtain the ground state properties like zero-pressure equilibrium volume.

3. Results and Discussions

3.1 Structural Properties

The non-magnetic based calculations have been carried out for non-magnetic $LaSn_3$ as well as $CeSn_3$ compounds whereas spin polarized electronic band structure calculations have been done to obtain the total energy of the magnetic $PrSn_3$ as well as $NdSn_3$ intermetallics using the first principles FP-LAPW method. The three different forms of generalized gradient approximations i.e. PBE-GGA [19], WC-GGA [20] and PBE-sol GGA [21] for non-magnetic calculations and PBE-GGA [19] as well as LSDA [22] are used for ferromagnetic calculations. In order to calculate the ground state properties, the total energies are calculated in $AuCu_3$ type structure for different volumes around the equilibrium cell volume V_0. The calculated total energies are fitted to the Birch-Murnaghan equation of state [23] to determine the ground state properties like lattice constant (a_0), bulk modulus (B) and its pressure derivative (B') at minimum equilibrium volume V_0 using exchange correlation as PBE GGA [19] and LSDA [22].

$$E(V) = E_0 + \frac{BV}{B'}\left[\frac{(V0/V)^{B'}}{(B'-1)} + 1\right] - \frac{BV}{B'-1} \tag{1}$$

Pressure is obtained by taking volume derivative of the total energy

$$P(V) = \frac{B}{B'}\left[\left(\frac{V}{V_0}\right)^{B'} - 1\right] \tag{2}$$

The calculated ground state properties of these compounds are given in Table 1, and compared with the available experimental data [23]. It is seen from Table 1 that our calculated ground state properties such as lattice parameters are in good agreement with the available experimental results. Furthermore, as, to our knowledge, no experimental data for the bulk modulus and its derivative have been reported yet, our results can serve as a prediction for future studies. The calculated total magnetic moment (μ_{tot}), magnetic moment of Pr as well as Nd and that of Sn are also calculated and given in Table 1.

3.2 Electronic Properties

The electronic band structures calculations of non-magnetic $LaSn_3$ and $CeSn_3$ have been carried out along symmetry directions using PBE-GGA while self consistent spin polarized band structures (BS) along the high symmetry directions for majority and minority spins for $NdSn_3$ using LSDA are presented in Figure 1(a) - (f). The valence and conduction bands overlap considerably and there is no band gap at the Fermi level for all these compounds. As a result, it is deduced that both non-magnetic and ferromagnetic $RESn_3$ compounds may exhibit metallic properties. The Fermi level is shown at the origin. It is clear from the electronic band structures that the lowest lying bands are due to Sn 's' like states in $RESn_3$. The bands which lie above this are due to RE 'p' like

states. The band structures appear to be almost similar for all the studied compounds except in the position of '*f*' like states of RE. The delocalized '*f*' like states lie above the Fermi level in $LaSn_3$ where as for $CeSn_3$, they lie slightly above the Fermi level. There is a flat band at the Fermi level in the majority spin channel of $NdSn_3$ as well as in $PrSn_3$, which are mainly due to '*f*' states of Nd and Pr in majority spin which gets shifts above the Fermi level in minority spin for both the compounds. The bands just below the Fermi level are due to Sn '*p*' and RE '*d*' states in all the studied $RESn_3$ compounds. The strong hybridization of Sn '*p*' and '*d*' states of Nd and Pr at the Fermi level shows the metallic character of these compounds.

The density of states (DOS) plot provides an even more comprehensive picture of the elemental contributions to the electronic structure of $RESn_3$ compounds. The total and partial densities of states (DOS) for these compounds at ambient pressure are also calculated and presented in Fig. 2(a) - (f) in both majority and minority channels. We have calculated the DOS at Fermi level for these compounds. The metallic character of the compound is clearly seen from the finite DOS at the Fermi level. Due to this metallic character, we found finite DOS at the Fermi level for $RESn_3$ in which major contribution is due to delocalized '*f*' states of RE. We can see a decrease in finite DOS in minority spin due to delocalization of RE 'f' states.

Conclusion

In conclusion, the ground state electronic nature of non- magnetic $LaSn_3$ and $CeSn_3$ as well as ferromagnetic $PrSn_3$ and $NdSn_3$ rare-earth intermetallic compounds, which crystallize in $AuCu_3$-type structure, is performed using density functional theory based on full potential linearized augmented plane wave (FP-LAPW) method. Our calculated results on the ground state structural properties such as bulk moduli and lattice parameters for these compounds are in agreement with available theoretical and experimental results. The electronic properties of these compounds are studied by calculating band structures and its corresponding density of states. The significant value of density of states at the Fermi level of the studied compounds reveals the metallic nature of these compounds at ambient conditions.

Acknowledgements

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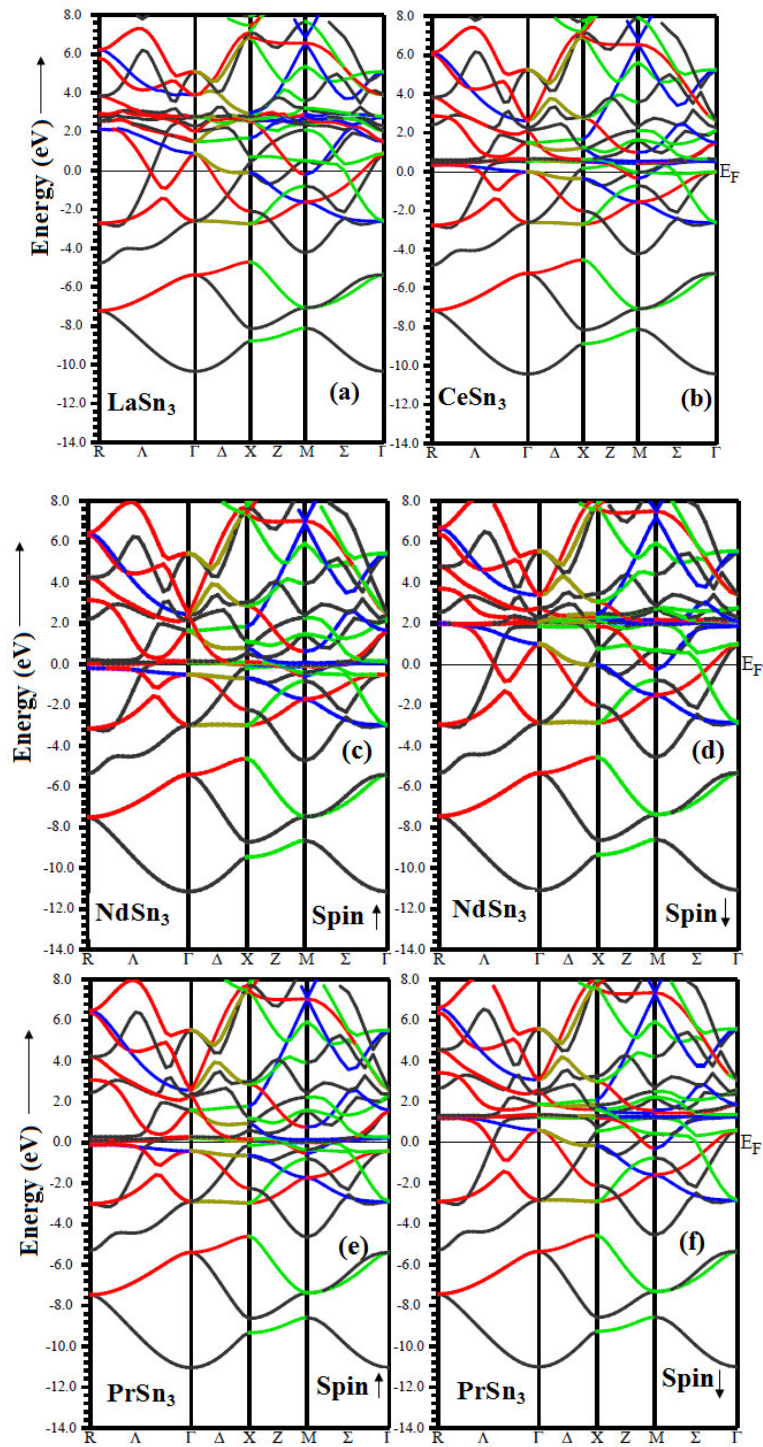
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Fig. 1 (a) – (f): Electronic Band Structures of RESn$_3$ compounds at ambient pressure.
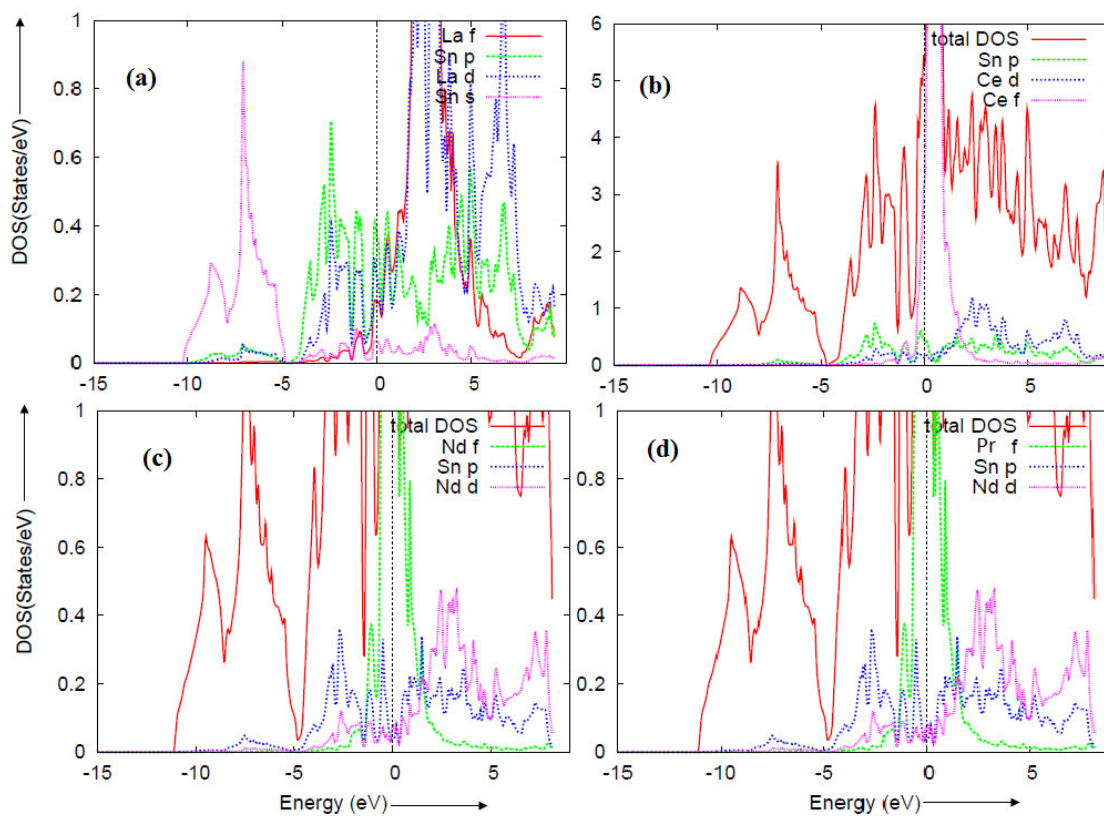
Fig. 2 (a) – (d): Density of States of RESn$_3$ compounds at ambient pressure.

Table 1: Calculated lattice constant (a$_0$), bulk modulus (B), its pressure derivative (B′) and magnetic moments (μ) of RESn$_3$ at ambient pressure.

Solid	Work	Approx.	a$_0$ [Å]	B [GPa]	B′	μ$_{RE}$	μ$_{Sn}$	μ$_{tot}$
LaSn$_3$	Pre.	PBE-GGA	4.780	57.31	4.98	-	-	-
		WC-GGA	4.750	65.18	4.29	-	-	-
		PBE-sol GGA	4.749	65.03	3.95	-	-	-
	Expt.		4.768[a]	-	-	-	-	-
	Oth.	GGA	4.810[b]	-	-			
		LDA	4.700[b]	-	-	-	-	-
			4.730[c]	78.00[c]	-			
CeSn$_3$	Pre.	PBE-GGA	4.726	62.45	4.67	-	-	-
		WC-GGA	4.651	72.53	4.12	-	-	-
		PBE-sol GGA	4.642	72.67	4.69	-	-	-
	Expt.		4.721[c]	-	-	-	-	-
PrSn$_3$	Pre.	PBE-GGA	4.726	59.66	4.01	4.23	0.23	4.56
		LSDA	4.601	70.54	4.39	4.10	0.18	4.32
	Expt.		4.716[a]	-	-	-	-	
NdSn$_3$	Pre.	PBE GGA	4.728	50.50	4.19	3.288	0.037	3.77
		LSDA	4.594	66.93	4.77	3.150	0.032	3.51
	Exp.		4.706[a]	-	-	-	-	-

[a] Ref. [24]; [b] Ref. [25]; [c] Ref. [13]. Pre.-Present; Expt. Experiment

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