ZnRE (RE=La and Ce) intermetallics: A first-principles investigation

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Abstract: ZnRE (RE= La and Ce) intermetallics were investigated with respect to their electronic properties using first principles tight binding linear muffin tin orbital method. Electronic band structures, partial and total densities of states have been derived. The band structures show metallic character; the conductivity is mostly governed by Zn-3d and RE-4f states. The thermodynamical properties like Debye temperature and Grüneisen constant are estimated using Debye-Grüneisen (DG) model. The value of Debye temperature is calculated to be 193 K for ZnLa and 191 K for ZnCe. The Co-efficient of electronic heat capacity is also estimated and discussed. It is found to be 4.97 mJ/K^{2}mol for ZnLa and 29.29 mJ/K^{2}mol for ZnCe in calculations. The estimation of cohesive energy revealed the bond strength between Zn and RE. These estimated values are found to be 753.6 KJ/mol and 812.5 KJ/mol for ZnLa and ZnCe, respectively.

Keywords: TB-LMTO, Inter-Metallic Compounds, ZnRE, Electronic Structure, Thermal Properties

1. Introduction

Intermetallics constitute a significant class of materials, which are generally brittle and have high melting point and crystallize in cubic cesium chloride structure (B$_2$-phase, *Pm-3m*, Space Group, *221*) [1,2]. This class of materials falls in the category of ceramic and metallic materials whose hardness and/or resistance is important at high temperatures. They can also display desirable magnetic, superconducting and chemical properties, due to their strong internal ordering and bonding (metallic and covalent/ionic), respectively. Many intermetallic compounds are of great technological interest due to their physical and mechanical properties, including high temperature [3], low density and good oxidation or corrosion resistance. This has led to their utility and scope in many non-structural applications, but success in structural applications has, so far, been limited. However, a number of studies have been reported for Iron aluminides [4,5], which is a class of iron-based alloys that offers excellent high temperature oxidation and sulfidation resistance. Secondly, it is a low cost alternative to stainless steel. Similarly, titanium aluminides are used in aerospace and turbine blade applications [6]. Magnetic and superconducting materials like Fe-Al, Nb-Al, Heusler alloys are used for superconducting applications.

Looking at and considering all the aspects of intermetallics, two species, Zn and rare earth (RE) are form a new group of intermetallic compounds due to the presence of *f*-electrons in RE specie. Henceforth it becomes imperative to understand the electronic properties of this group of intermetallics. The literature reveals that the role of *f*-electrons in RE-ion with Zn on the structural and electronic properties at normal as well as at high pressure has not been extensively studied and it is yet to be explored fully. Nevertheless, recently, some of the binary intermetallics [7-12] and intermetallics involving RE specie [13-16], have been explored with respect to their structural, electronic, elastic and thermodynamical properties. Our interest in ZnRE is encouraged due to interaction of Zn-d and RE-f orbitals and we aim to provide the insight into the electronic structure of ZnRE. This is accomplished to some extent by performing electronic band structure calculations using first principles tight binding-linear muffin tin orbital method similar to our earlier work on CdRE Intermetallics [16]. In order to understand electronic contribution to ZnRE system, molar heat capacities, Debye temperature and

Grüneisen constant are calculated for the first time.

A methodical study focusing on structural, electronic and thermodynamical properties of ZnRE is organized as follows: Section 2 describes the method of calculation of band structure and density of states and its computational details. In Section 3, striking results with prophecy are discussed. The corresponding subsections 3.1, 3.2 and 3.3 deal with the structural, electronic and thermodynamical properties of ZnRE Intermetallics.

2. Method of Calculations

The structural, electronic and thermodynamical properties of ZnLa and ZnCe intermetallics were calculated using TB-LMTO method [17,18] within the local-density approximation (LDA) [19]. This method has been used for wide class of intermetallics [16, 20]. von-Barth and Hedin [21] parameterization scheme has been used for exchange correlation potential.

2.1. Computational Details

The ZnRE intermetallics crystallize in the B_2-phase (BCC structure, Figure 1), and positioned at Zn: (0, 0, 0) and RE: (0.5, 0.5, 0.5). The Wigner-Seitz sphere was chosen in such a way that the sphere boundary potential was minimum and the charge flow between the atoms was in accordance with the electro-negativity criteria. The calculations were performed for 512 k-points (8×8×8 k grid) in the Brillouin zone for B_2 phase. The E and k convergence were also checked. The tetrahedron method [22] of Brillouin zone integration has been used to calculate the total density of states, $N(E_f)$. The total energy was computed by reducing the volume from 1.05 V_0 to 0.65 V_0, where V_0 was the equilibrium cell volume. The calculated total energy was fitted to Birch equation of state [23] to obtain the pressure volume relation. The pressure was obtained by taking volume derivative of the total energy. The bulk modulus B = -V_0 dP/dV was also calculated from pressure-volume relation.

2.2. Debye-Grüneisen Model and Molar Heat Capacity

The Debye-Grüneisen (DG) model [24] was used to calculate Debye temperature Θ_D. According to this model, Θ_D can be calculated using the scaling factor in equation 1

$$\Theta_D = 41.63\sqrt{\frac{r_0 B}{M}} \qquad (1)$$

where r_0 is the Wigner-sietz radius in a.u. at equilibrium, B is bulk modulus in kbar and M is the average atomic weight, which is the weighted arithmetical average of the masses of the species for compounds. Grüneisen constant α is calculated by

$$\alpha = \frac{\partial \ln \Theta_D}{\partial \ln V} \qquad (2)$$

where V is the volume of the solid.

Coefficients of electronic heat capacity γ

$$\gamma = \frac{\pi^2 K_B^2 N(E_f)}{3} \qquad (3)$$

Where K_B is Boltzman constant and $N(E_f)$ is total DOS at E_f.

3. Results and Discussion

3.1. Structural and Ground State Properties

The lattice parameter, bulk modulus and total energy of two ZnRE intermetallics are estimated using the methodology described in the above Section. The structural optimization is depicted in Figure 1 by calculating total energy of ZnLa and ZnCe.
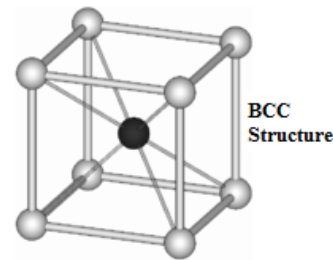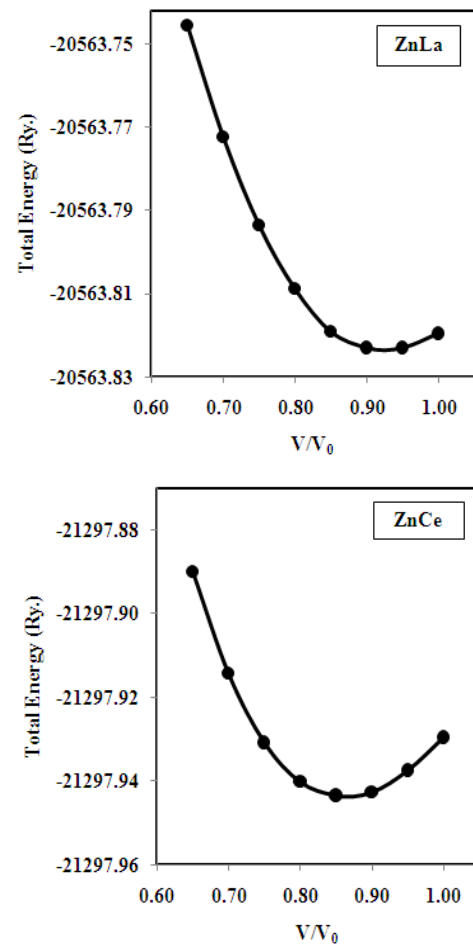

Figure 1. Variation of total energy as a function of relative volume for ZnLa and ZnCe intermetallics.

From the total energy calculations equilibrium volume, V_0 is found to be 48.69 Å³ for ZnLa and corresponding lattice parameter 3.65 Å, which is underestimated by 2.6 % with the experimental data [2]. Similarly, the equilibrium volume at 43.61Å³ and corresponding lattice parameters value of 3.52 Å is estimated for ZnCe.   The experimentally reported values of lattice parameters are little higher as compare to our results due to the convention of local density approximation (LDA)

[19] in the present calculation. Regarding the LDA contraction, it is often found that the LDA leads to some overbinding which yields lattice parameters that are somewhat smaller when compared with experiment. Furthermore, we have calculated equilibrium bulk modulus summarized in Table 1. The values of bulk modulus (B) for these intermetallics have not been reported so far by others; hence a comparison was not possible.

Table 1. *Calculated lattice parameter a_0 (a.u.), bulk modulus B_0 (GPa), first derivative (B'_0), equilibrium energy E_{tot} (Ry.), density of states $N(E_f)$ (states/eV/f.u.).*

Solid	a_0	B_0	B'_0	E_{tot}	$N(E_f)$
ZnLa	6.90 / 7.08[a]	64.68	4.28	-20563.82148	2.11
ZnCe	6.65 / 6.99[a]	66.22	4.13	-21297.94415	4.14

[a] Ref.[2].

3.2. Band Structure and Density of States

The electronic band structure calculations (based on LDA) for ZnRE in CsCl-type structure are performed. The electron dispersion curve along the high-symmetry directions in the Brillouin zone for ZnLa in the B_2 phase is shown in Figure 2. As mentioned, the band-structure calculations of ZnLa and ZnCe have not been reported in literature; however, the overall profiles are found to be similar to the band structure of other intermetallics [16, 25]. The Fermi energy (E_f) is shown by the dotted line.
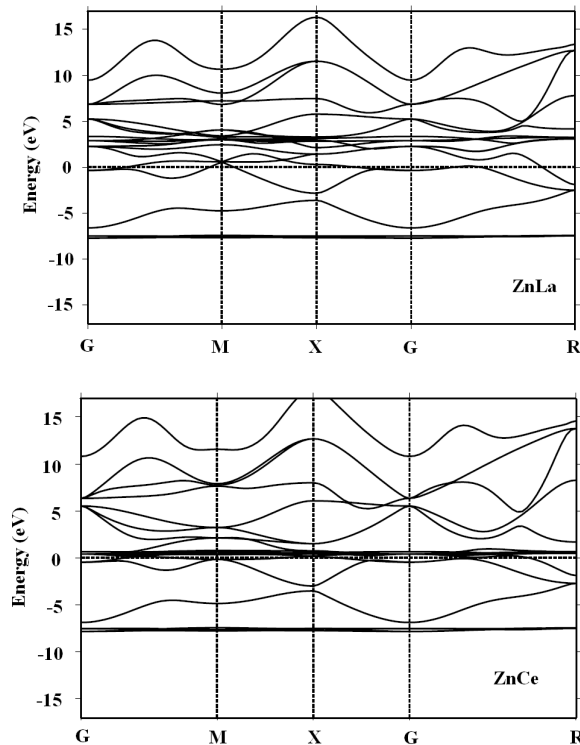

Figure 2. *Band structure along the high symmetry directions at ambient pressure for ZnLa and ZnCe intermetallics .*

It is clear from the figure that in the valence-band region just below E_f, the lowest-lying bands are due to Zn-'d' states, while 'd'-states of La, Ce can be seen above the Fermi level, which hybridize with Zn-'p' states near the Fermi level and shows metallic behavior, which can be clearly seen in total density of states (DOS) plot in Figure 3. In Figure 3 we have plotted total DOS at E_f for ZnLa and ZnCe under ambient conditions. The hybridization of Zn-'p' with La-'d' and Ce-'d' states can be seen near E_f.
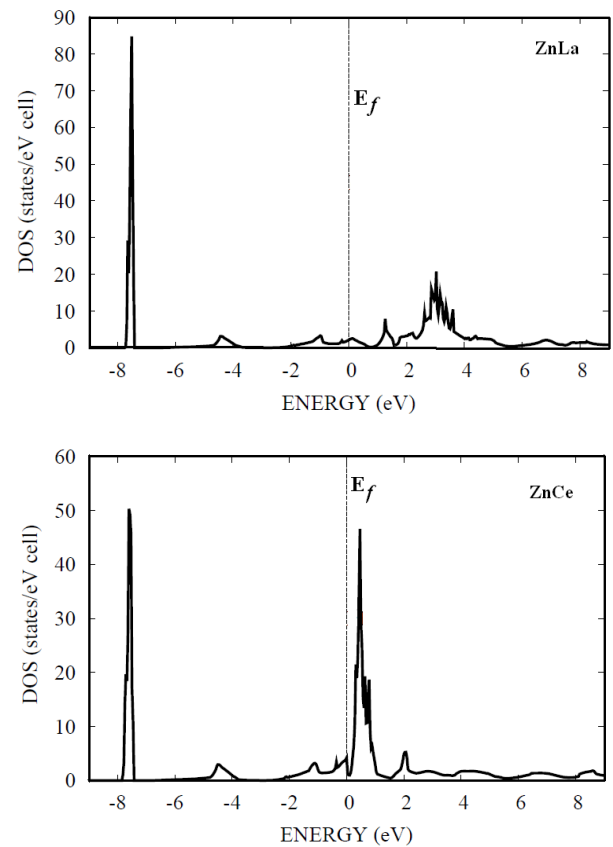

Figure 3. *Density of states at Fermi level for ZnLa and ZnCe intermetallics.*

To validate above plots, partial DOS at E_f have been plotted for the two Intermetallics and presented in Figure 4. One can clearly see such hybridization. However, La-f states are found near 0-5 eV, and sharp peak of Ce-f states can be seen at Fermi level in Figure 4.
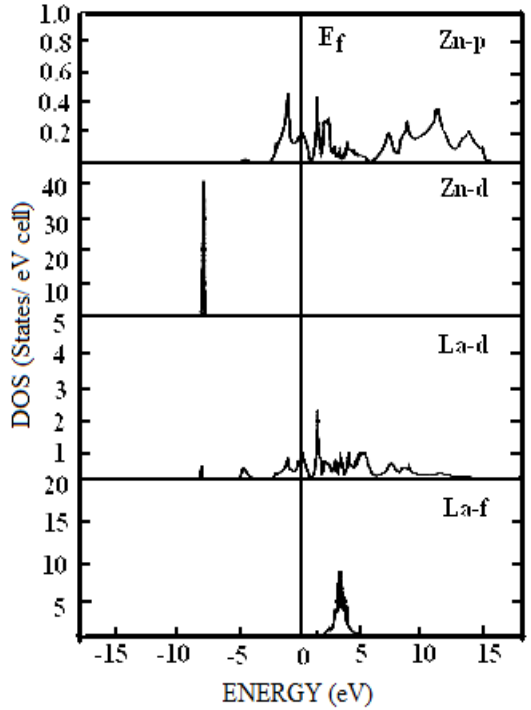
Figure 5. Total density of states at Fermi level for ZnLa and ZnCe intermetallics.

Table 2. Partial number of electrons and total density of states at Femi level for ZnLa intermetallic

V/V$_o$	Zn			La			
	s	p	d	s	p	d	f
1.00	1.132	0.87	9.915	0.527	0.509	1.765	0.279
0.95	1.128	0.874	9.911	0.520	0.507	1.772	0.283
0.90	1.122	0.877	9.908	0.514	0.504	1.787	0.287
0.85	1.108	0.880	9.899	0.500	0.500	1.812	0.298
0.80	1.095	0.884	9.891	0.485	0.496	1.836	0.310
0.75	1.085	0.878	9.880	0.469	0.496	1.864	0.325
0.70	1.066	0.874	9.868	0.451	0.498	1.897	0.344
0.65	1.045	0.869	9.855	0.430	0.499	1.932	0.368

Table 3. Partial number of electrons and total density of states at Femi level for ZnCe intermetallic

V/V$_o$	Zn			Ce			
	s	p	d	s	p	d	f
1.00	1.114	0.899	9.909	0.518	0.518	1.807	1.231
0.95	1.100	0.904	9.902	0.507	0.517	1.851	1.217
0.90	1.089	0.910	9.895	0.493	0.511	1.898	1.201
0.85	1.076	0.910	9.885	0.483	0.506	1.945	1.191
0.80	1.062	0.913	9.875	0.468	0.502	1.998	1.180
0.75	1.045	0.912	9.863	0.452	0.499	2.054	1.173
0.70	1.026	0.909	9.850	0.434	0.498	2.108	1.172
0.65	1.003	0.901	9.835	0.413	0.500	2.074	1.172

We have also calculated partial number of electrons in these states and presented in Table 2-3 under compression. Under compression transfer of electrons can be seen within the states and increment in number of electrons can be seen in Ce-f states. The total density of states is calculated to be 2.11 and 4.14 states/eV.cell for ZnLa and ZnCe, respectively.

3.3. Thermodynamical Properties

On the basis of electronic structure calculations, Debye temperature and Grüneisen constant are estimated and values are presented in Table-4 using the (1)-(3) described in Section 2.

Figure 4. Partial density of states at Fermi level for ZnLa and ZnCe intermetallics.

In Figure 5 we have plotted total density of states under compression for ZnLa and ZnCe, which shows a linear decrease in DOS at different compression values.
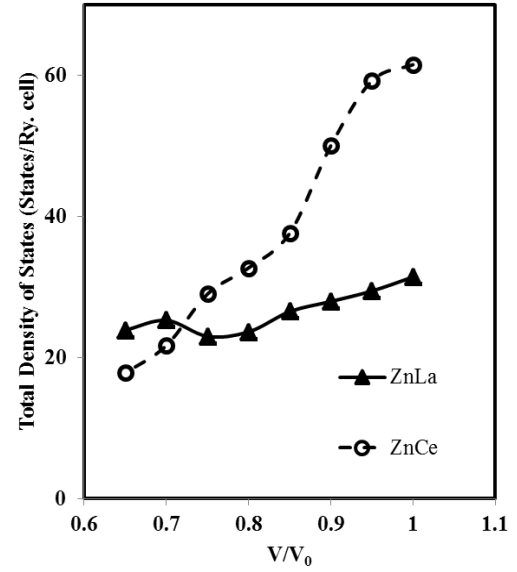
In order to understand the amount of heat required to change the temperature of solid we have obtained the Co-efficient of electronic heat capacity.

Table 4. *Theoretically calculated Cohesive energy E_c (kJ/mol), Wigner-sietz radius r_o (a.u.), Debye temperature Θ_D (K), Grüneisen constant α, Co-efficient of electronic specific heat γ (J/(K^{2}mol)*

Solid	E_c	r_0	Θ_D	α	$\gamma(10^{-3})$
ZnLa	753.6	3.400	193	1.031	4.97
ZnCe	812.5	3.272	191	1.052	29.29

The variation of Θ_D with pressure for the two intermetallics is plotted in Figure 6, which shows normal behavior under pressure. It is in accordance with our earlier calculations [16].
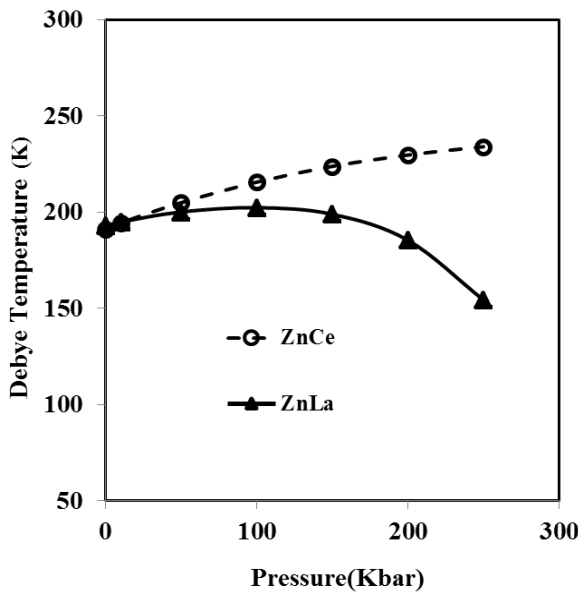

Figure 6. *Variation of total energy as a function of relative volume for ZnLa and ZnCe intermetallics.*

As it can be seen from the (3) that the Co-efficient of electronic heat capacity depends on DOS. Maximum the value of DOS, maximum the value of electronic heat capacity. Table 1 shows that DOS has the sequence in ZnRE: ZnLa<ZnCe, therefore ZnLa has the weakest metallic nature, while ZnCe has the strongest metallic nature. Since there are no experimental observations available to the best of our knowledge, a comparison is not possible.

Further, cohesive energy is the measure of the strength of the forces, which binds the atoms together in the solid state. In this connection, the cohesive energy of ZnLa and ZnCe is estimated. The cohesive energy (E_{coh}) in B$_2$ phase is defined as the difference in the total energy of the constituent atoms at infinite separation and total energy of that particular phase, such that

$$E_{coh}^{AB} = \frac{1}{m+n}[mE_{atom}^A + nE_{atom}^B - E_{total}^{AB}]$$

Where A= Zn; B=RE; and E_{total}^{AB} is the total energy of a ZnRE primitive cell that includes m Zn atoms and n RE atoms

with equilibrium lattice parameters, E_{atom}^A and E_{atom}^B are the total energy of a Zn atom and an RE (RE = La and Ce) atom. The calculated energies of Zn, La and Ce isolated atoms are eV/atoms. The calculated values of cohesive energies, E_{coh} are given in Table 4. However, a comparison could not be possible for the want of experimental data. Our calculations are a prediction and can be used as a reference for future studies.

Finally, we have performed a theoretical study on electronic and thermodynamical properties of ZnLa and ZnCe intermetallics using first principles TB-LMTO method. Electronic band structure and density of state calculations show metallic character of both the intermetallics. The thermodynamical properties like Debye temperature and Grüneisen constant are analyzed using Debye-Grüneisen (DG) model. Co-efficient of electronic heat capacity is also estimated. The estimation of cohesive energy reveals the bond strength between Zn and RE. The potential results on ZnRE intermetallics open many avenues and channels with wide scope for researchers both theoretically and experimentally.

Acknowledgements

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