Structural and electronic properties of Cd-rich lanthanide intermetallics

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Abstract. The structural and electronic properties of B2-cadmium lanthanide (RE), CdLn (Ln=La, Ce and Pr) intermetallics have been calculated at T=0K at ambient and at high pressure by using tight binding linear muffin tin orbital method. We have estimated lattice parameter, bulk modulus, density of states for the three CdLn intermetallics. The \textit{f}-electrons present in the \textit{Ln}, play important role. The variation in density of states under compression is calculated due to Pr-\textit{f} effect in CdPr, which opens a possibility of structural instability.

1. Introduction.
Recently, in material design, intermetallics and alloys has a consideration for their significant application due to their ductile, high tensile strength and other properties [1-7]. The AB intermetallics, where 'A' is 'metal' and 'B' is either Lanthanide (Ln) or Actinide (Ac) or 'transition metal' (TM) are formed as unique class of materials. Particularly, Aluminium with -Ln and -TM systems have received a great attention due to their application in metallic glass technology [6,7]. The CdLn (Ln= La, Ce and Pr) intermetallics crystallize in body centered cesium chloride structure (B2-phase, \textit{Pm}3\textit{m}, Space Group, 221) [8, 9]. These intermetallics are very important with respect to their structural and electronic properties. One another interesting aspect of these materials is that they are having partially filled \textit{f}-state. Those may get delocalized and give further possibility of phase change under pressure. Therefore, it becomes important to understand the electronic properties of this class of intermetallics. To the best of our knowledge the structural and electronic properties of CdLn intermetallics at normal and as well as at high pressure, have not been extensively studied and it is yet to be explored in details. We have, therefore, explored the structural and electronic properties of CdLn intermetallics under normal and compression by employing the non-spin polarized first-principles tight binding linear muffin tin orbital (TB-LMTO) method.

2. Method of calculations
The total energy, band structure and density of states for CdRE are calculated in a manner similar to our previous work [10-12] using TB-LMTO method [13,14] within the local-density approximation (LDA) [15]. von-Barth and Hedin [16] parameterization scheme was used for exchange correlation potential. The CdRE intermetallics crystallize in the B2-type structure, and
positioned at Cd: (0, 0, 0) and RE: (0.5, 0.5, 0.5). The tetrahedron method [17] of Brillouin zone integration was used to calculate the density of states. The total energy was computed by reducing the volume from 1.05 \(V_0\) to 0.65 \(V_0\), where \(V_0\) is the equilibrium cell volume. The calculated total energy was fitted to Birch equation of state [18] to obtain the pressure-volume relation. The pressure was obtained by taking volume derivative of the total energy. The bulk modulus, \(B = -V_0 \frac{\partial P}{\partial V}\) was also calculated from P-V relation.

3. Results and discussion

3.1 Lattice parameter
Total energy is calculated under compressions using TB-LMTO method for CdLn intermetallics and is plotted in figure 1. The minimum of all the curves defines the equilibrium volume, \(V_0\) corresponding to lattice parameter \(a_0\) for CdLn. The present calculated values of lattice parameters are in good agreement with the Wycoff values [9], although the reported values of lattice parameters of CdLn intermetallics are slightly higher as compared to our results. This is due to usage of local density approximation (LDA) [15] in the present calculation. The bulk modulus for CdLa, CdCe and CdPr are calculated to be 64.77, 65.25 and 57.46 GPa, respectively.

Figure 1. Variation of total energy as a function of relative volume for CdLn

3.2 Band structure and density of states
The band structures along the high symmetry directions for all the CdLn are shown in figure 2. The lowest energy bands are due “Cd-d” states. In CdLa, some of La-d states hybridize with Cd-p states, but small amount of La-f can be seen above Fermi level, but for Ce and Pr f-states can be seen at Fermi level clearly and hybridize with ‘Cd-p’ states, which shows increased metallic character.

Figure 2. Band structure along the high symmetry directions at ambient pressure for CdLn intermetallics

To obtain clear picture of individual states, we have plotted partial and total density of states (DOS) for all CdLn intermetallics in figure 3. The ‘Cd-d’ states can be seen near energy value of -10eV. On the other hand, ‘La-f’ states can be seen in the region of 0-5eV in the figure 3. Localized ‘Ce-f’ and ‘Pr-f’ can be seen at Fermi level, which hybridizes with ‘Cd-p’ states.
From the calculations, we have found that number of states increases as we go from La to Pr. In figure 4 we have plotted the variation in total DOS under compression for three CdLn intermetallics. From this figure one can notice a linear decrease in DOS at $E_F$ as we compress. The value of total DOS at $E_F$ for CdLa decreases and suddenly increases at $V/V_0 = 0.70$. In case of CdCe only decrease in DOS between compression value of $V/V_0 = 1.05$ to 0.65. As far as, such variation for CdPr is concerned, an increase in DOS is noticed at $V/V_0 = 1.05$ to 0.90 then decrease. Such interesting feature could be the indication of structural instability under compression. The variation of DOS under compression strongly related to the $f$-states of lanthanum atom. To understand such variation of DOS under compression in CdLa and CdPr, we have estimated the electronic DOS of $f$ states and found variation in Pr-$f$ states under compression. The reason can be understood that $f$-like electrons may get delocalized. The delocalization of the Pr-$f$-like states could be the reason of variation in total DOS at $E_F$ under compression, which has been justified by calculating electron localization function (ELF) ranging here 0.5-0.6.

4. Conclusion
The CdLn intermetallics have been investigated theoretically with respect to their electronic aspect such as band structure, density of states, partial number of electrons, and other ground
state properties in B$_2$ Phase also. It is found from present study that CdLn intermetallics are metallic in nature and metallicity increases from – La to –Pr. The variation in DOS number is noticed in CdLa and CdPr under compression, which may be due to the delocalization of ‘f’ electrons under pressure.

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