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First Principles Study of Electronic, Elastic and Thermal Properties of B_2-type RECd (RE =La, Ce and Pr) Compounds

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Abstract
The electronic, elastic and thermal properties of RECd (RE =La, Ce and Pr) intermetallic compounds crystallizing in B_2-type structure have been studied using first principles density functional theory within generalized gradient approximation (GGA), and the local spin density approximation (LSDA) for the exchange correlation potential. From energy band structure and density of states we found that these intermetallics are metallic in nature. The thermal and mechanical properties are predicted from the calculated values of elastic constants. The ductility of these compounds is determined by calculating the bulk to shear ratio B/G_H. Our calculated results indicate that PrCd is most ductile amongst all the RECd compounds. To the best of our knowledge this is the first theoretical prediction of the elastic properties of these compounds.
Keywords: Intermetallics, Density Functional Theory, Elastic Constant, Ductility.

1. Introduction
Rare earth intermetallics that contain rare earth element and transition element have been extensively studied for several decades because of their appealing mechanical properties such as high oxidation resistance, high stiffness, high strength, ductility and attractive high temperature [1-5] which makes them promising high temperature structural material for automobile, aviation and aerospace application. The energy dispersive powder X-ray diffraction measurements of some LnM (Ln=La, Ce, Nd and Gd; M= Cu, Ag and Zn) compounds have been performed by Degtyareva et a.l [6]. Fujii et al. [7] have studied the magnetic properties of CeCd single crystal. Sousa et al. [8] have explained that there are three kinds of phase transition in PrCd: a structural phase transition at T_s= 125 K, an antiferromagnetic to paramagnetic transition at T_N =40 K and an unknown phase transition at T_t =20K Magnetic and structural phase transition of CeCd at hydrostatic pressure has been studied by Kadomatsu et al. [9]. 1ndelli et al. [10] have studied experimental lattice parameter of LaCd, CeCd and PrCd by X-ray diffraction technique. The RECd (RE=La, Ce and Pr) intermetallics crystallize in cubic cesium chloride structure (B_2–phase, Pm3m, Space Group, 221) [11]. In the B_2 RECd intermetallics *f*–electrons present in RE specie, play a vital role in exploring structural and electronic properties. Therefore, it becomes significant to understand the electronic properties of this class of intermetallics. To the best of our knowledge the structural and electronic properties of RECd intermetallics at normal as well as at high pressure have not been extensively studied and are yet to be explored in detail. We do not find any comprehensive study related to elastic, mechanical and thermal properties such as Young modulus and Poisson ratio, Debye temperature etc in the literature so far. So a comprehensive theoretical calculation of the electronic structure and elastic properties for this RECd (RE =La, Ce and Pr) compounds based on density functional theory (DFT) is performed in the present work.
In the present work, non spin polarized calculations are performed to investigate the fundamental properties of the LaCd, while spin polarized calculations are done for CeCd and PrCd compounds with B_2 structure using generalized gradient approximation (GGA) of PERDEW, BURKE and ERNZRHOF (PBE) [11] and Local spin density approximation LSDA approximations[12]. The rest of the paper is organized as follows: section 2 deals with the method of calculations which is employed for the electronic and elastic properties of the RECd intermetallic compounds. In Section 3, we present the results and compared them with the other experimental results. Finally, we present the conclusion in Section 4.

2. Method of Calculation
The calculations are performed using the full potential linearized augment plane wave method as implemented in WIEN2k package [13]. In order to achieve the energy eigen value convergence, we expand the basis function up to $R_{MT}*K_{max}$= 7 where R_{MT} is the smallest atomic sphere radius in the unit cell and K_{max} gives the magnitude of the largest *K* vector in the plane wave expansion. The valence wave functions inside the spheres are expanded up to l_{max} =10 while the charge density is Fourier expanded up to G_{max}= 12. A dense mesh of 1000 **k** points is used and the tetrahedral method has been employed for the Brillouin zone integration. The total energies are calculated as a function of volume and fitted to Birch equation of state [14] to obtain the ground state properties.
The elastic constants play an important role in determination of the strength, brittleness/ductility, and hardness of materials. The traditional mechanical stability conditions in cubic crystals on the elastic constants are known as

C_{11} - C_{12} > 0, C_{11} >0, C_{44} > 0, C_{12} < B < C_{11}. Our calculated elastic constants presented in Table 1 obey these stability conditions. In the present study the elastic constants are calculated by using the method developed by Charpin and integrated incorporated in WIEN2k package [13].

One of the standard methods to calculate the Debye temperature is from elastic constants data, since θ_D may be estimated from the following equation [15, 16]:

$$\theta_D = \frac{h}{K_B}\left[\frac{3n}{4\pi V_a}\right]^{1/3} v_m$$

where h is a Plank's constant, k_B is Boltzmann's constant; V_a is the average atomic volume.

3. Results and Discussions

3.1 Electronic Properties

For the ground state properties of RECd (RE=La, Ce and Pr) intermetallic compounds the total energies are calculated as a function of volume in B_2 phase. The calculated total energies are fitted to the Birch equation of state [14] to determine the ground state properties like lattice constant (a_0), bulk modulus (B), its pressure derivative (B')and magnetic moments (μ_B) which are listed in Table 1 and compared with the available experimental results. We have calculated partial density of states (DOS) along with the total DOS at Fermi level (E_F) for all the RECd (RE= La, Ce and Pr) intermetallics under ambient conditions and depicted in Fig. 1(a)-(e) The calculated electronic band structures (BS) along the principle symmetry directions of RECd compounds are presented in the Fig.2 (a) – (c) where Fermi level is considered at origin. For all RECd compounds the lowest lying energy bands are due to RE '*p*' states as shown in the Fig 1(a)-(e). For LaCd, the Density of states (DOS) at the Fermi level is mainly due to the '*d* ' states of La, which hybridize with '*s*' and '*d'* states of Cd. However, '*f* ' states of La can be seen above the Fermi level near 2 eV, which might be due to the charge leakage during the hybridization of '*d* ' states of La, with '*s*' and '*d'* states of Cd.

As CeCd and PrCd being the magnetic compound, we performed spin polarized ferromagnetic calculations for them. For CeCd the '*f*' like states of Ce in majority spin channel are located at the Fermi Level. For minority spin channel, this state get shift above to the Fermi level near 0.45eV in conduction band. Similarly for PrCd, we get a finite DOS at the Fermi level which is due to the mixing of '*f*' states of Pr with the '*p*' state of Cd and '*d*' state of Pr for spin up channel while for spin down these states are situated near 1.4eV above the Fermi Level. From DOS and BS it is clear that metallic behaviour in CeCd and PrCd are mainly due to the 4*f* orbital electrons of Ce and Pr while in LaCd it is due to 5*d* orbital electron states. The number of density of states at Fermi level N (E_F) for LaCd CeCd and PrCd are 0.06, 7.75 and 28.709 states /eV respectively.

3.3 Elastic Properties

The elastic constants are important characteristic parameters of solids. The investigation of them is essential to understand many of their physical properties. We have calculated the elastic constants of the RECd compounds at ambient pressure by using the method developed by Charpin and integrated it in the WIEN2k package [13]. It is noticeable from Table 1, that our calculated elastic constants satisfied the stability criteria. To the best of our knowledge, no experimental or theoretical values of elastic moduli for the studied compounds are available in literature

3.4 Mechanical properties

Elastic constants can be used to determine mechanical properties such as Young's modulus (E), shear modulus (G), Poisson's ratio (σ), anisotropic ratio (A), for useful applications. We have calculated these properties of RECd compound and presented in Table 3. The shear modulus G_H describes the material's response to shearing strain using the Voigt- Reuss-Hill (VRH) method [16-18], the effective modulus for the polycrystals could be approximated by the arithmetic mean of the two well known bounds for monocrystals. The bulk modulus and Hill shear modulus G_H is defined as:

$$B = \frac{1}{3}(C_{11} + 2C_{12}) \quad \text{and} \quad G_H = \frac{\frac{C_{11} - C_{12} + 3C_{44}}{5} + \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}}{2}$$

where Hill shear modulus G_H is the average sum of Voigt shear modulus (G_V)and Reuss shear modulus (G_R) The Young's modulus (E) describes the material's response to linear strain, such that,

$$E = \frac{9\,BG_H}{3B + G_H}$$

The Poisson's ratio (σ) is given as:

$$\sigma = \frac{3B - 2G_H}{2(3B + G_H)}$$

The calculated value of Poisson's ratio for LaCd, CeCd and PrCd are 0.24, 0.28 and 0.33 respectively, and is given in Table 2. The value of Poisson's ratio (σ), found to be ≈ 0.1 in covalent material and ≈ 0.33 in metallic material [19, 21].

Another important parameter is the elastic anisotropic factor A, which gives measure of the degree of elastic anisotropy in solid, and is given as:

$$A = \frac{2C_{44}}{C_{11} - C_{12}}$$

For an ideal isotropic system, A is unity and deviation from unity measures the amount of elastic anisotropy. The calculated anisotropy factors for CeCd and PrCd compounds are found to be greater than one, while for LaCd it is found to be less than one, hence these compounds are not elastically isotropic. As suggested by Pugh [22], a material will be ductile if B/G_H >1.75. From Table 2, it can be seen that amongst RECd compounds, the calculated values of B/G_H for CeCd and PrCd are found to be 1.95 and 2.64, which indicate that these compounds show ductile nature while for LaCd it is found to be 1.41 indicating brittle nature. The Young's modulus (E) and Poisson's ratio (σ) are very important properties for industrial applications. The Young's modulus (E), the ratio of the tensile stress to the corresponding tensile strain, is required to provide information about the measure of the stiffness of the solids. LaCd has higher value of Young's modulus among RECd indicating LaCd is stiffer than CeCd and PrCd. The hardness of a material can be determined more accurately by using the Bulk modulus. The calculated value of Bulk moduli increases from PrCd to LaCd indicating that LaCd is hardest and least compressible than the other RECd compounds. Pettifor [23] suggested the bond character of cubic compounds with respect to their Cauchy pressure (C_{12}–C_{44}). The negative value of Cauchy's Pressure shows their brittle nature. The calculated value of Cauchy's pressure for LaCd is negative while that of CeCd and PrCd are negative.

3.5 Thermal properties

We have calculated average sound velocities, Debye temperature as well as the density for these compounds in B_2 phase by using the calculated elastic constants which are given in Table 2. The Debye temperature defines a division line between quantum mechanical and classical behaviour of phonons. In the absence of any available measured data in the literature, they could not be compared. Future experimental work will testify our calculated results.

4. Conclusion

In conclusion, we have studied the electronic, elastic and thermal properties of RECd (RE=La, Ce and Pr) using FP-LAPW method based on density functional theory. From band structure and density of states, we found that these compounds exhibit metallic behaviour. In present study we found $B/G_H > 1.75$ and C_{12}–$C_{44} > 0$ for CeCd and PrCd compounds, LaCd is found to be brittle in nature.

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Table 1. Calculated lattice parameter a_0 (A°), Bulk modulus B (GPa) its pressure derivative (B′), magnetic moment (μ_B) and elastic constants of RECd (RE= La, Ce and Pr) in B_2 phase.

Solid	work	a_0 (A°)	B (GPa)	B'	μ_B	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
LaCd	GGA	3.932	47.54	4.48	-	72.71	33.37	37.01
	LSDA	3.806	61.39	3.99	-	93.51	47.63	50.40
	Expt.	3.905[a]	-	-	-	-	-	-
CeCd	GGA	3.8408	46.19	4.73	1.34	85.49	30.09	23.01
	LSDA	3.7007	57.44	4.23	1.23	71.58	58.40	49.58
	Expt.	3.865[a]	-	-	-			
PrCd	GGA	3.8502	42.09	3.88	2.74	57.5	40.8	28.6
	LSDA	3.7079	56.22	3.74	2.63	63.28	53.98	9.79
	Expt.	3.830[a]	-	-	-	-	-	-

[a]Ref [9] Expt. –Experimental.

Table 2. The calculated Young's modulus (E), shear modulus (G_H),anisotropy factor (A), Poisson's ratio (σ), B/G_H ratio, Cauchy's pressure (C_{12}-C_{44}), longitudinal (v_l), transverse (v_t), average elastic wave velocity (v_m) and Debye temperature (θ_D) for LaCd, CeCd and PrCd using GGA approximation.

Solid	E (GPa)	G_H (GPa)	A	σ	B/G_H	C_{12}-C_{44} (GPa)	$\rho x10^3$ (kg/m^3)	v_l (m/s)	v_t (m/s)	v_m (m/s)	θ_D (K)
LaCd	79.90	32.92	2.36	0.24	1.41	-13.11	29.20	1795.65	1106.55	1219.9	147.10
CeCd	63.54	24.78	0.83	0.28	1.95	7.08	29.59	1661.99	917.05	1021.2	98.19
PrCd	46.65	17.50	3.42	0.33	2.64	12.20	29.44	1581.96	834.33	932.1	89.40

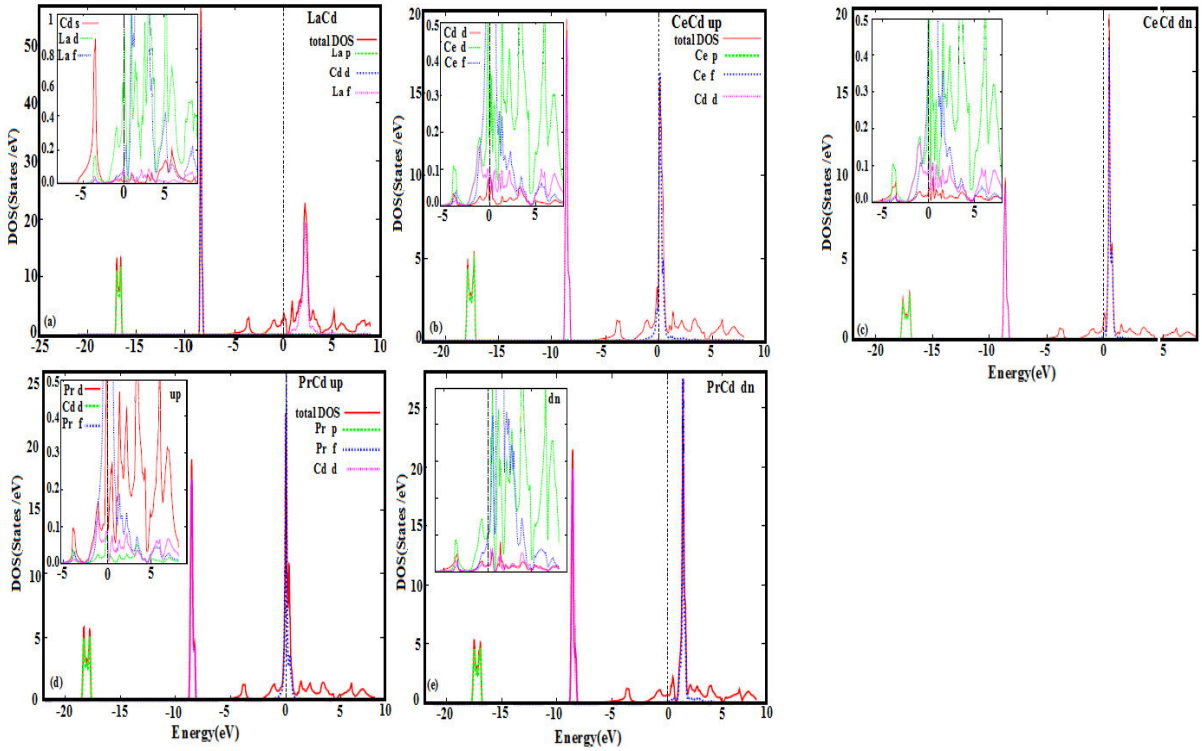

Figure 1. (a)- (e) Density of state of RECd (RE=La, Ce and Pr) intermetallics.

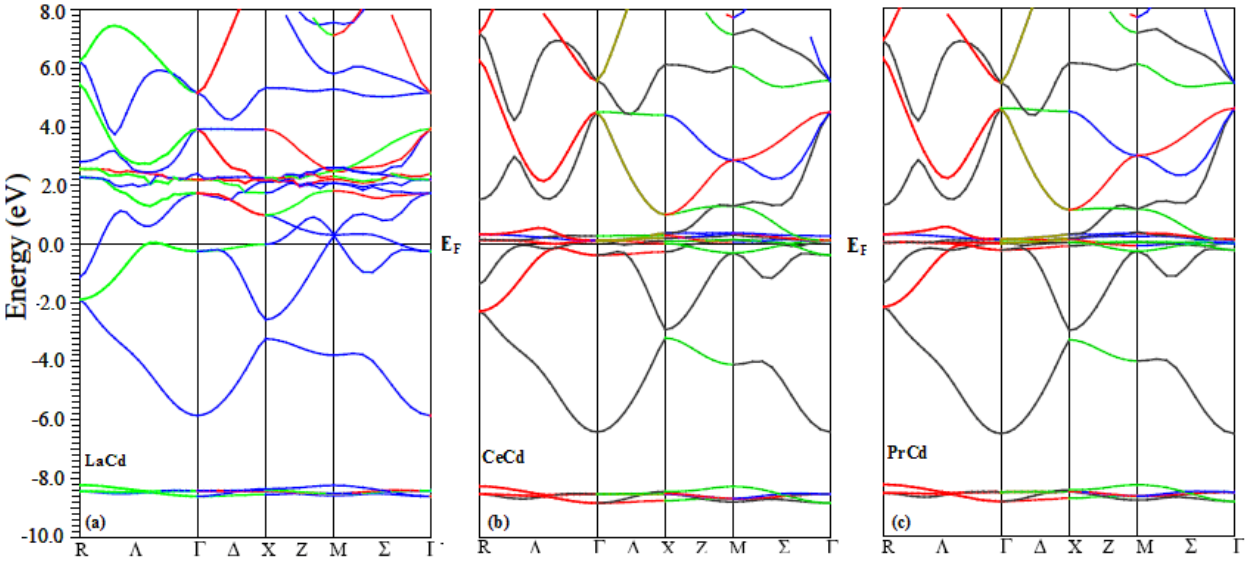

Figure 2. (a) –(c) Band structure of RECd intermetallics.

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