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Structural, Electronic, Thermal, Mechanical and Elastic Properties of RPd_3 (R = La & Y) Compounds Based on *Ab-initio* Calculation

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Abstract
The structural, electronic, thermal, mechanical and elastic properties of cubic non magnetic RPd_3 (R = La &Y) compounds which crystallize in the $AuCu_3$ structure have been studied using *ab-initio* full potential linearized augmented plane wave (FP-LAPW) method within density functional theory (DFT) using generalized gradient approximation (GGA) for exchange correlation potential. The ground states properties such as lattice parameter (a), bulk modulus (B) and pressure derivative (B') have been obtained using optimization method. The elastic properties such as Young's modulus (E), Poisson's ratio (σ) and anisotropic ratio (A) and thermal are predicted for first time. The ductility of these compounds has been analyzed using Pugh criteria.
Keywords: *Ab-initio*; Density functional theory; Elastic constants; Ductility.

1 Introduction

The large success achieved by *ab-initio* electronic structure methods, in the framework of the Kohn–Sham (K–S) scheme of the Density Functional Theory (DFT) [1] has brought a quality jump into many related research fields, since it turned into reality the dreamed promise of Quantum Mechanics to explain macroscopic properties from atomic constituents and spatial arrangements [2]. The benefit brought by the introduction of state of the art *ab-initio* calculations and of user-friendly computer packages, the impulse of this area has introduced many new researchers, non-experts, into the field.

In valence fluctuation (VF) rare earth compounds, nearly-localized rare earth 4*'f'* electrons hybridize with the conduction electron. Because the 4*'f'* have a small radial extent, the overlap with the conduction electrons is weak and the hybridization is small. There are two important classes of VF materials: intermetallics valence (IV) and Heavy Fermions (HF) compounds [3]. The structure of RPd_3 (R = La & Y) belongs to the $AuCu_3$ type (space group *Pm3m*, No. 221) with lattice parameter slightly larger than 4Å for all lanthanides [4]. *Ab-initio* electronic structure calculations, within the Kohn–Sham scheme of the density functional theory, are often considered reliable and a powerful tool to provide ground state information on intermetallic compounds. Low-temperature heat capacity data are presented for a series of $AuCu_3$ type RPd_3 compounds (R = Ce, La, Lu, Y and Sc). Gardner *et al*. have made measurements of the magnetic susceptibility in a large range of temperature for a complete series of RPd_3 compounds (*R*=rare earths). Some band structure calculations exist on $LaPd_3$ and $CePd_3$. Self-consistent band structure calculations for $LaPd_3$, $CePd_3$, $PrPd_3$, and $NdPd_3$ [5] they found that magnetic ordering only in $PrPd_3$ and $NdPd_3$ and hence are consistent with the experimental findings. The value of lattice parameter for RPd_3 and RPd_3B are presented by Malik *et.al* [6]. Neither $LaPd_3B$ nor $LaPd_3$ are non magnetic compounds [7].The lattice parameter for $ScPd_3$ and YPd_3 are: 3.9595 Å and 4.0727 Å [8] respectively. $CePd_3$ is one of the most investigated compounds with intermetallic valence (IV) [9]. Very recently Rettori and coworkers published a paper on the Er, Yb and Dy resonance in YPd_3 [10]. The study of $ScPd_3$ and particularly YPd_3 is as interesting initial step to understand the physical properties of intermetallic compounds with heavier rare earth elements which have been extensively studied because of the heavy fermions [11]. The photoemission (XPS) and the Bremsstrahlung Isochromat Spectroscopy (BIS) measurements have been performed on YPd_3 [12] and a good agreement with the calculated density of states of the occupied and empty states has been obtained [12, 13]. The optical absorption of YPd_3 has been measured [14, 15] and in the high energy range the structures due to interband transitions have been confirmed. The electronic structures of $ScPd_3$ and YPd_3 are calculated self- 3 consistently by the method of linear-Muffin-tin-0rbitals (LMTO) [16]. Holland-Moritz *et.al* have studied this compound together with YPd_3 and $LaPd_3$ as diamagnetic reference compounds and $TbPd_3$ and $ErPd_3$ [17, 18] as representative magnetic RPd_3 compounds with a stable 4*'f'* shell. The electronic, structural, thermal, elastic and mechanical properties of RPd_3 (R = La & Y) compounds are investigated using first principle full potential-linearized augmented plane wave method within density functional theory.

2 Calculation method

The electronic, structural and mechanical properties of RPd_3 (R = La & Y) compounds are investigated using first principle full potential-linearized augmented plane wave method within density functional theory. We used

Perdew and Wang-generalized gradient approximation, which is based on exchange correlation energy [19]. The following atomic states of La [Xe] $4f^0$, $5d^1$, $6s^2$, Y [Kr] $4d^1$, $5s^2$ and Pd [Kr] $4d^{10}$, $5s^0$ were considered as valence states. The wave vector cut-off for the plane wave expansion of the wave function in the interstitial region was chosen, $R_{MT}*K_{max}= 7$ where R_{MT} is the smallest muffin-tin radius in the unit cell and K_{max} is the maximum of reciprocal lattice vector. A dense mesh of 10×10×10 k points is used and tetrahedral method [20] 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-Murnagan equation of state [21] to obtain the ground state properties like zero-pressure equilibrium volume. Information on the influences of pressure and temperature on the elastic moduli and related aggregate properties of single crystals plays an essential role in predicting and understanding the interatomic interactions, strength, mechanical stability, phase transition mechanisms and dynamical response of materials. For a cubic crystal, the three elastic moduli C_{11}, C_{12} and C_{44} fully describe its elastic behavior. C_{11} and C_{12} can be determined from the bulk modulus B and shear constant Cs.

3. Result and discussion

3.1 Structural properties

The *Ab-initio* study of ground state properties for RPd_3 have been carried out using the Wien2k code based on the full potential linearized augmented plane wave (FP-LAPW) method. The total energies are calculated for these compounds for different volumes around the equilibrium cell volume V_0. The calculated total energies are fitted to the Birch-Murnagan equation of state 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.

$$E(V) = E_0 + \frac{BV}{B'}\left[\frac{(V_0/V)^{B'}}{(B'-1)} + 1\right] - \frac{BV}{B'-1}$$

Pressure is obtained by taking volume derivative of the total energy

$$P(V) = \frac{B}{B'}\left[\left(\frac{V}{V_0}\right)^{B'} - 1\right] \quad \text{and} \quad B' = \partial B / \partial P$$

The calculated values of a_0 are found to be 4.239 and 4.124 for $LaPd_3$ and YPd_3 respectively. The calculated values of B are found to be 110.08 and 127.53 for $LaPd_3$ and YPd_3 respectively. The values of pressure derivative of bulk modulus (B′) are found to be 4.21and 5.13 respectively. It is seen from Table 1 that our calculated values of a_0 are in good agreement with the experimental results and other theoretical work.

3.1 Electronic properties

The self consistent non-spin polarized electronic bands structure of RPd_3 compounds are investigated using generalized gradient approximation (GGA) and presented by Figure 1. We have also plot total and partial densities of states (DOS) for these compounds at ambient pressure and which are presented in Figure 2. The Fermi level is considered at the origin. From Figure 1, the delocalized bands in the energy range between -5eV to 0 eV below the Fermi level are mainly due to the Pd *'d'* likes states. From Figure 2 for $LaPd_3$, the localized peak is observed near -16eV is mainly due to La *'p'* like states with little admix of hybridized '*d*' and '*s*' states of Pd. A peak is observed around 4eV above the Fermi level which is due to *'f'* state of La. The metallic character of $LaPd_3$ mainly due to hybridization of La *'p'* and *'f'* states and Pd *'d'* states at the Fermi level. Similarly, for YPd_3 compound the delocalized bands below the Fermi level in the energy range between -5 eV and 0 eV due *'d'* likes states of Pd. A peak is observed around -2.5eV due to Pd *'d'* likes states below the Fermi level. There is hybridization of *'d'* likes states of Pd and *'d'* and *'s'* likes states of Y due to which these compound exhibit metallic character. The value of density of state at the Fermi level $N(E_F)$ 1.33 States/eV and 1.00 States/eV for YPd_3 and $LaPd_3$ respectively. The metallic character of these intermetallics is clearly seen from the finite DOS at the Fermi level. It is clear from the figures that the total DOS at the Fermi level is the highest for YPd_3 as compared to $LaPd_3$. The reason might be due to presence of unoccupied single '*d*' electron in outermost orbit of Y.

3.3. Elastic properties

The elastic properties play an important role in providing valuable information about the binding characteristic between adjacent atomic planes. Anisotropic characters of binding and structural stability are usually defined by the elastic constants C*ij*. These constants have been often related to the shear modulus and Young's modulus, which are frequently measured for polycrystalline materials when investigate their hardness. The elastic moduli require knowledge of the derivative of the energy as a function of the lattice strain. We have calculated the elastic constants of the $LaPd_3$ and YPd_3 compounds in $AuCu_3$ structure using PBE-GGA as exchange correlation at ambient pressure using the method developed by Thomas Charpin and integrated it in the WIEN2k package

[22]. The calculated values of elastic constants are given in Table 2. In the absence of any available measured data in the literature, these elastic constants could not be compared. It can be noted that our calculated elastic constants satisfy the stability criterions: $C_{11}- C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, $C_{12} < B < C_{11}$, which clearly indicate the stability of these compounds in $AuCu_3$ structure.

3.4 Mechanical properties

The theoretical methods are completely independent of experiment and solve the quantum mechanical equations of DFT. Among these studies, the calculation of elastic constants based on the first principle calculation within the highly accurate all-electron full-potential (linearized) augmented plane wave plus local orbital is very attractive because many other mechanical properties such as bulk modulus, shear modulus, Young's modulus, etc., can be derived from elastic constants. The elastic constants determine the response of the crystal to external forces, as characterized by bulk modulus, Young's modulus, shear modulus and Poisson's ratio which play an important role in determining the strength of the materials.

Elastic properties play an important role in providing valuable information about the binding characteristics between adjacent atomic planes, the anisotropic character of binding and structural stability. The elastic constants of solids provide a link between the mechanical and dynamical behaviors of crystals and give important information concerning the nature of the forces operating in solids. These constants can be also predicting the structural stability of materials.

The bulk and shear modulus, defined as

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

Another important parameter is the elastic anisotropic factor A, which gives a measure of the anisotropy of the elastic wave velocity in a crystal and it is given as:

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

which is unity for an isotropic material. It also tells more about the structural stability and it is correlated with the possibility of inducing micro cracks in the materials.

The calculated elastic anisotropic factor for both the compounds is greater than 1, which indicates that these compounds are not elastically isotropic. As suggested by Pugh [23], if $B/G_H > 1.75$; a material behaves in a ductile manner. From Table 2, it can be seen that the highest value of B/G_H is 7.14 for $LaPd_3$ indicating it more ductile than YPd_3. Ganeshan *et.al.* [24] have established a correlation between the binding properties and ductility. The bond character of cubic compounds is explained with respect to their Cauchy pressure (C_{12}–C_{44}). The $LaPd_3$ has a highest positive Cauchy pressure; resulting strong metallic bonding (ductility) in it as compared to YPd_3. Young's modulus is defined as the ratio of stress and strain, and is used to provide a measure of the stiffness of the solid, *i.e.,* the larger value of *E*, the stiffer is the material. It can be seen from Table 2 that the highest value E occurs for YPd_3 implying it to be stiffer as compared to $LaPd_3$.

Young's modulus (E) is given by

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

The Poisson's ratio (σ) is given by

$$\sigma = \frac{(3B - E)}{6B}$$

The value of Poisson's ratio, found to be 0.433 for $LaPd_3$ compound and 0.27 for YPd_3 compound.

3.5 Thermal properties

Once we have calculated the Young's modulus E, Bulk modulus B and shear modulus G_H we may obtain the Debye's temperature is by using the average sound velocity v_m. At low temperature the vibrational excitations arise solely from acoustics vibrations. Hence at low temperature the Debye temperature calculated from elastic constants. We have calculated the average sound velocities and Debye temperatures as well as densities for RPd_3 compounds by using the calculated elastic constants which are given Table 3. In the absence of any measured data in the literature, they could not be compared. Hence, our result can be considered as a prediction for these properties of $LaPd_3$ and YPd_3 compounds and it will testify future experimental work.

Conclusion

In conclusion, the structural, electronic, thermal, mechanical and elastic properties of cubic non magnetic RPd_3 (R=La &Y) compounds which crystallize in the $AuCu_3$ structure have been studied using *ab-initio* full potential linearized augmented plane wave (FP-LAPW) method. The ground states properties such as lattice parameter (a), Bulk modulus (B) and its pressure derivative (B') have been obtained using optimization method. The value of lattice parameter for these two compounds is in good agreement with the experimental data. The electronic band

structure of $LaPd_3$ and YPd_3 exhibit a metallic character. In the present study we found $B/G_H > 1.75$ and C_{12}-$C_{44}>0$; which implies that these two compounds are ductile in nature. We also report the mechanical and thermal properties for these compounds and it will be tested in the future experimentally and theoretically.

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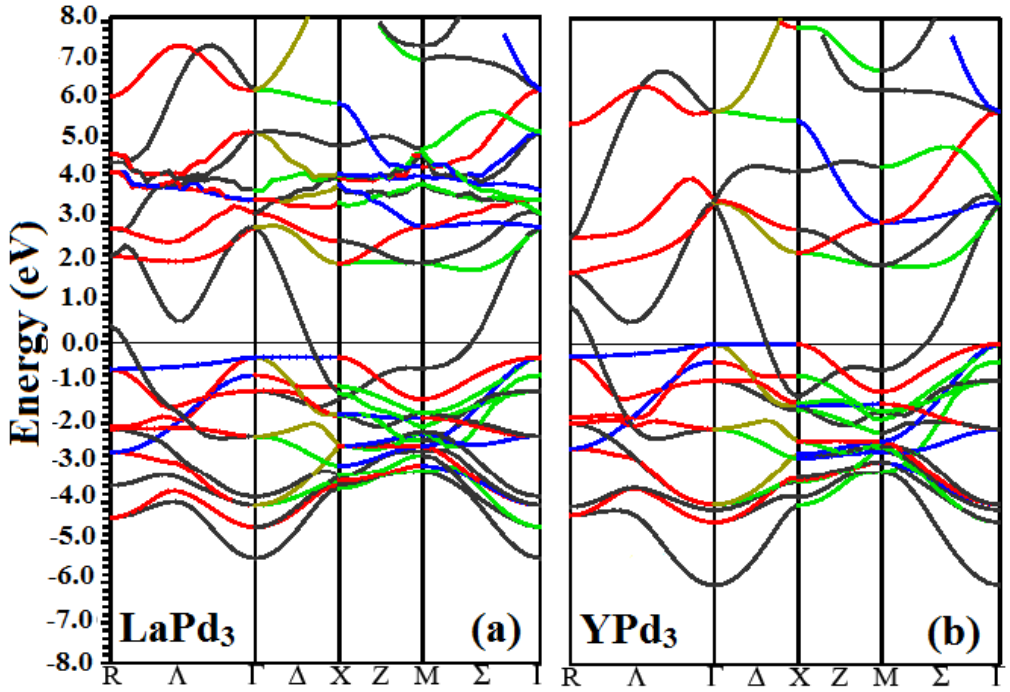
Table 1. Calculated lattice parameter a_0 (Å), Bulk modulus B (GPa), its pressure derivative (B′) and elastic constants (C_{11}, C_{12}, C_{44}) of $LaPd_3$ and YPd_3 in $AuCu_3$ structure

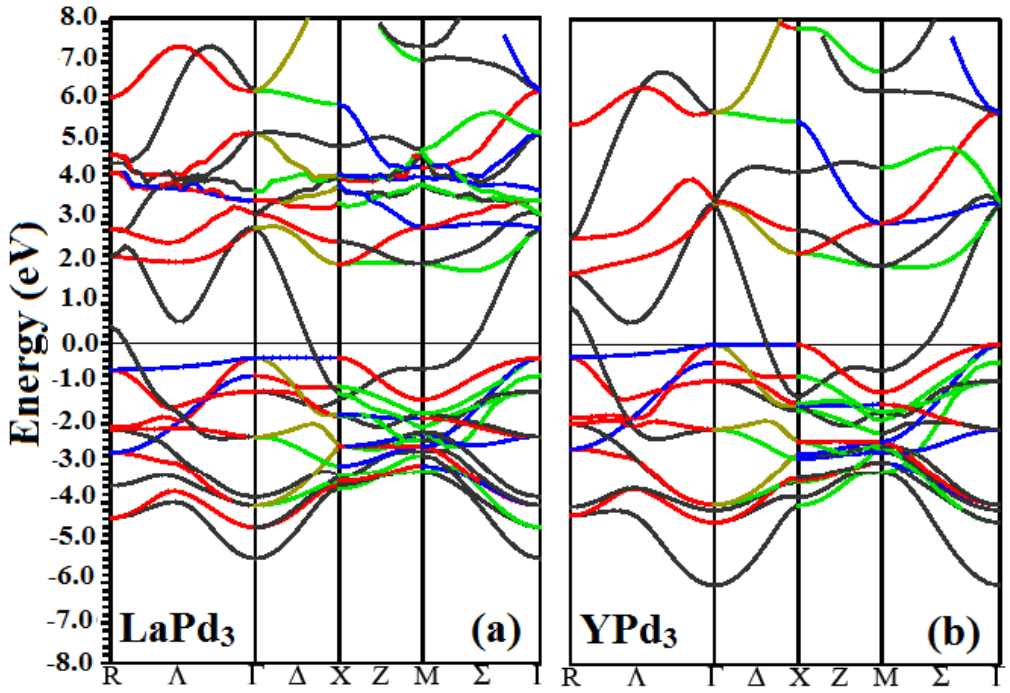
Solid	Work	a_0 Å	B (GPa)	B'	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
$LaPd_3$	PBE GGA	4.239	110.08	4.21	165.04	75.83	5.46
	Expt	4.235	-	-	-	-	-
	Other	4.229[a]	-	-	-	-	-
YPd_3	PBE GGA	4.124	127.53	5.13	195.53	97.96	87.78
	Expt	4.074		-	-	-	-
	Other	4.0727[b]		-	-	-	-

[a]Ref [6], [b]Ref [8]

Table 2. Calculated Young's modulus (E), shear modulus (G_H), anisotropic factor (A), Poisson's ratio (σ), B/G_H ratio, Cauchy's pressure ($C_{12} - C_{44}$) , density (ρ), longitudinal (v_l), transverse (v_t), average elastic wave velocities (v_m) and Debye temperature (θ_D) of $LaPd_3$ and YPd_3 compounds.

Solid	E (GPa)	G_H (GPa)	A	σ	B/G_H	$C_{12} - C_{44}$ (GPa)	ρ x 10^3 (kg/m^3)	v_l (m/s)	v_t (m/s)	v_m (m/s)	θ_D (K)
$LaPd_3$	42.33	14.77	0.12	0.43	7.14	70.36	7.064	4350	1729	1957	120.6
YPd_3	176.74	69.35	1.79	0.27	1.88	10.17	6.538	5888	3322	3693	233.8

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YPd3
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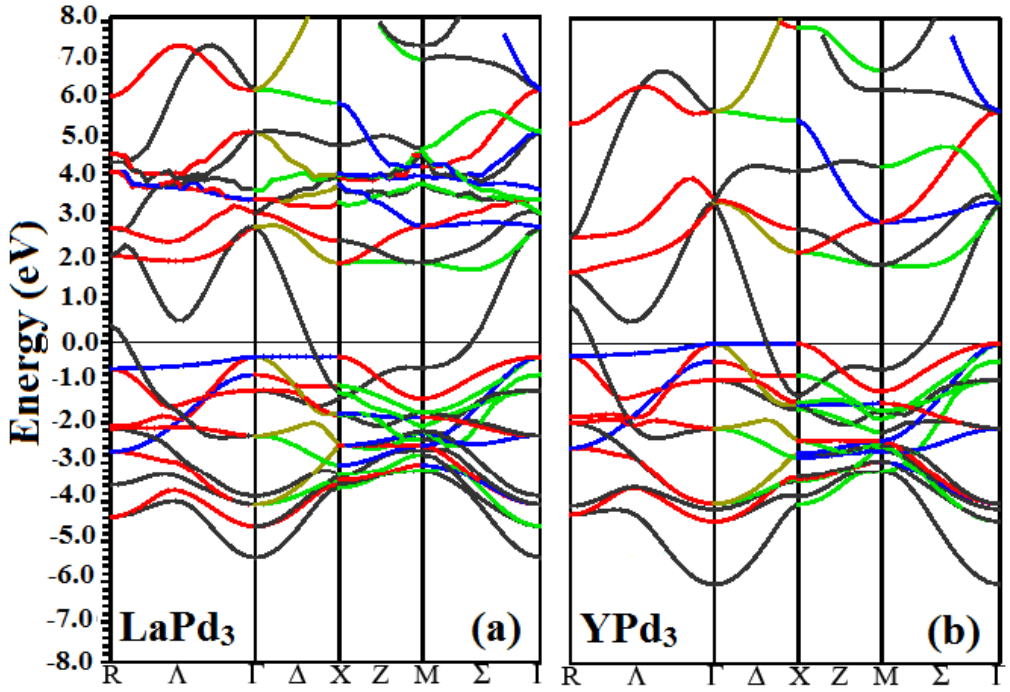
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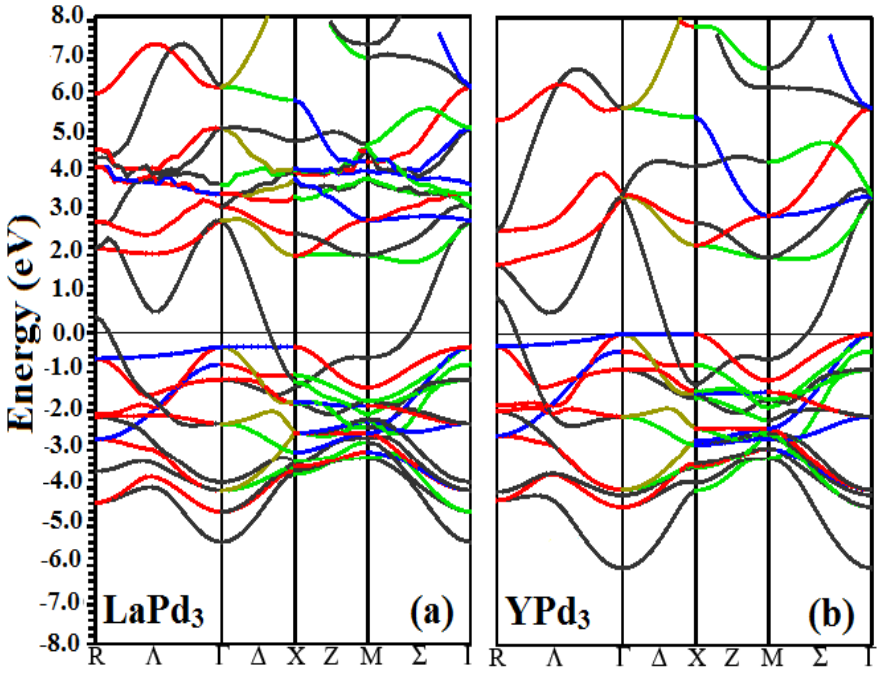
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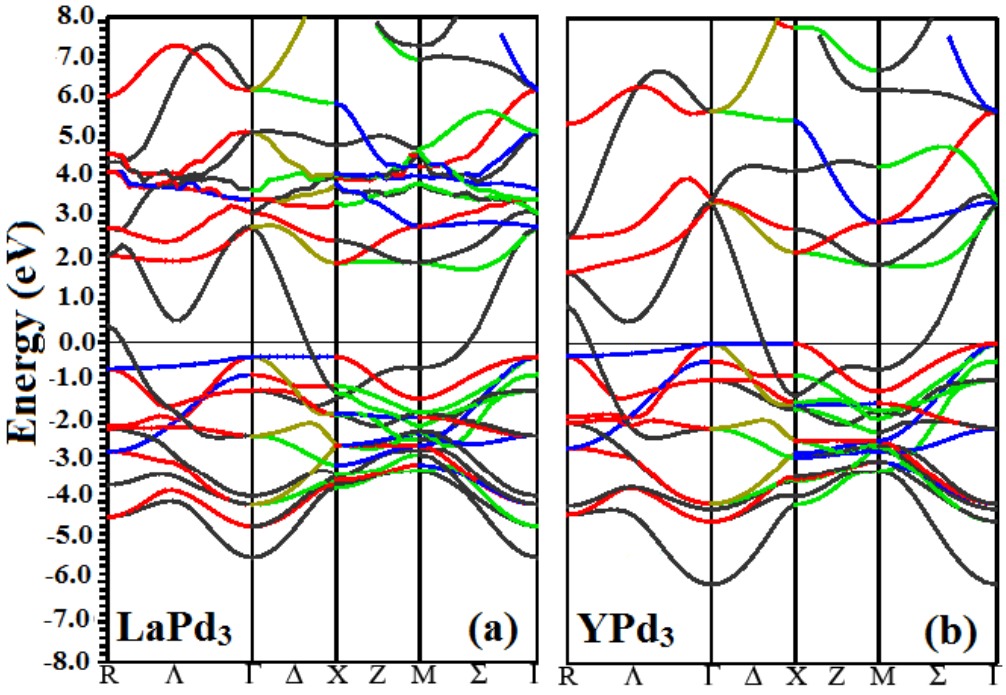
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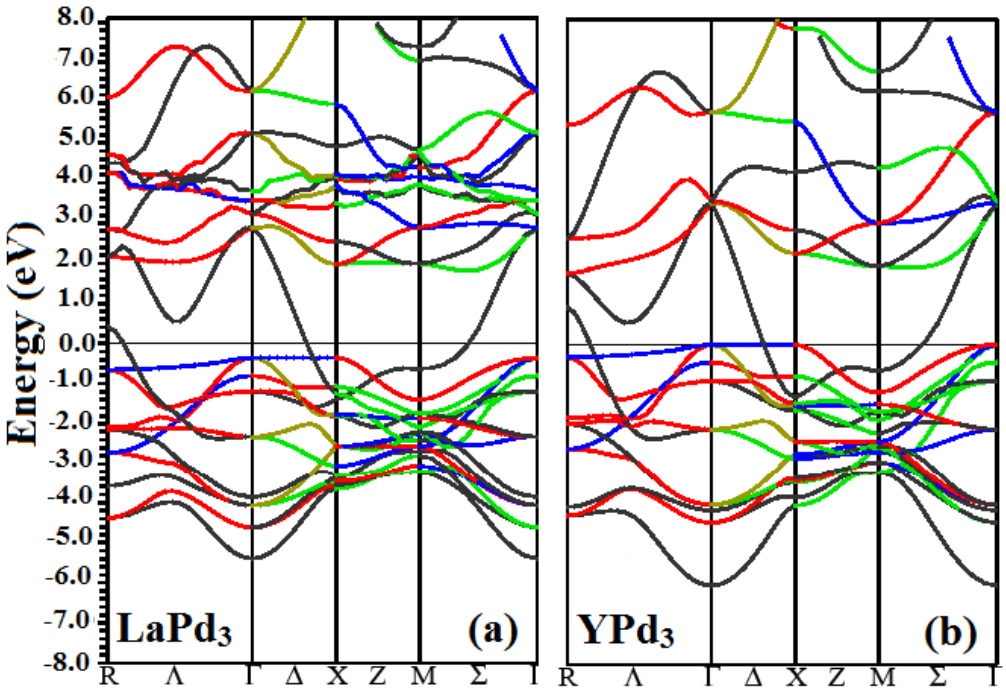
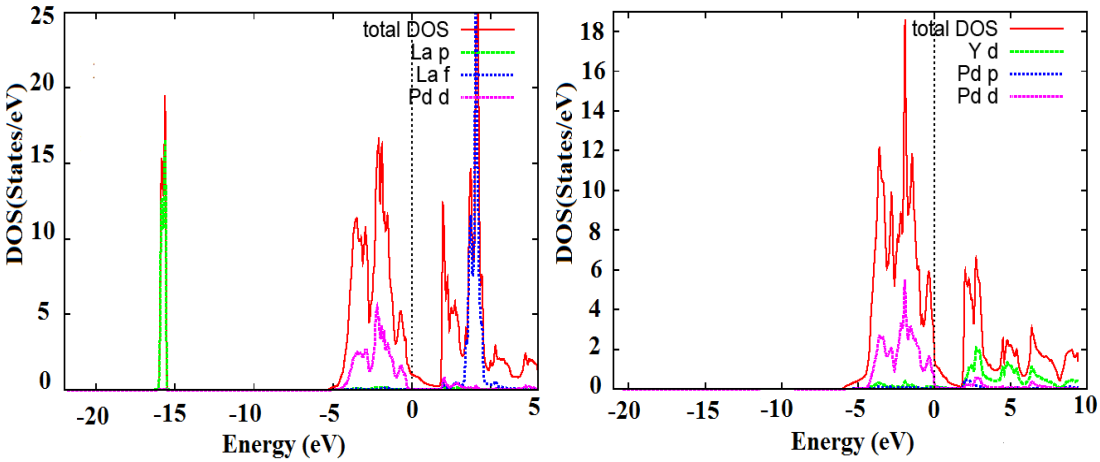


Figure 1. Band structure of $LaPd_3$ and YPd_3 compounds



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