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Structural and electronic properties of rare earth skutterudites $EuRu_4P_{12}$: a first principle study

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Abstract. Ternary skutterudites materials exhibit a large variety of electronic properties due to the unpaired 3d and 4f electronic configuration of the transition and rare-earth elements respectively. In this communication we have performed structural optimization and electronic structure calculation of the Rare Earth Skutterudite $EuRu_4P_{12}$, using FP-LAPW method. The optimized lattice parameter is in good agreement with the available experimental value. No band gap between the valence band and the conduction band has been observed which indicates that its character is metallic.

1. Introduction

Recently, the utilization of industrial waste heat into electrical energy from the thermoelectric materials has been a growing research interest [1]. These materials exhibit a large variety of electronic and magnetic properties, which are determined by the unpaired 3d and 4f electronic configuration of the transition and rare-earth elements respectively. The strongly correlated electron phenomena at low temperatures and potentially useful thermoelectric properties at high temperatures of these materials have attracted much attention of researchers over the last few years [2]. The materials with dense energy band and low energy gap at EF are the key features of thermoelectric materials, which can be achieved by either doping of heavy elements or from a thin film by controlling the lattice vibration (decreasing the thermal conductivity) [3-5]. This can also be achieved by the structural optimization of binary skutterudites MX_3 (M = Fe, Ru or Os; X = P, As or Sb) filled with rare earth elements, which gives ternary skutterudites RM_4X_{12} (R = rare earth) belonging to the space group *Im-3* (No. 204) [6,7]. In their structure the M ions are located inside the cages formed by X ions, and the M ions are believed to show random motion (rattling) around the equilibrium positions [8,9]. Bauer et al. [10] have reported the ferromagnetic behavior of some of the Nd and Eu-filled Skutterudites and Krishnamurthy et.al. [11] have reported the ferromagnetic nature of $EuFe4Sb_{12}$. Their FP-LAPW [12] study suggests the ferromagnetic nature of the ground state of $EuFe_4Sb_{12}$. The experimental study suggest the anti-ferromagnetic nature of $GdOs_4P_{12}$ [13], whereas the theoretical study by Kihou et al. [14] indicates the ferromagnetic ground state with magnetic moment 8.54 μB. Because of the technological importance of $EuRu_4P_{12}$ in various devices it is worthwhile to present detailed structural and electronic properties of this material. Thus, in the present work, we have performed the structural and electronic properties of $EuRu4P_{12}$ using the concept of the density functional theory.

2. Computational details

All the calculation of present work is carried out within the DFT framework. We use the self-consistent full potential linear augmented plane wave (FP-LAPW) method to solve Kohn-Sham equation as implemented in the Wien-2k code.$EuRu_4P_{12}$ compounds crystallize in a unique body centered cubic (BCC) structure with *Im-3* space group (No.204), where one Eu atom takes the atomic position of 2a (0, 0, 0) and one Ru atom located at 8c (0.25, 0.25, 0.25), while one P atom is located at the position of 24g (0, 0.35, 0.16). The positions of the remaining atoms in the unit cell are determined by symmetry operations associated with the space group. The unit cell crystal structure of $EuRu_4P_{12}$ is presented in Fig. 1. In this paper all the calculations performed within the density functional theory implemented in the WIEN2k code work. The exchange correlation potential is treated within the generalized gradient approximation (GGA) by the density functional of Perdew–Burke–Ernzerhof (PBE) for the calculation of structural and electronic properties. The energy eigenvalues are converged expanding the wave function in the interstitial region and the plane wave cut-off was $RMT \times Kmax = 7$, where R_{MT} is the smallest atomic muffin-tin sphere radius and K_{max} is the maximum value of the wave vector in the plane wave expansion. The R_{MT} (muffin tin radii) were selected to be 2.31, 2.10 and 1.9a.u.for Eu, Ru and P, respectively. The self-consistent potentials were calculated on a $10 \times 10 \times 10$ k-mesh in the Brillouin zone which corresponds to 1000 k points in the irreducible Brillouin zone and the convergence criterion is set to 10^{-4} Ry.

3. Results and discussions

3.1 Structural properties

We have performed the structural optimization of $EuRu_4P_{12}$ using PBE-GGA, we obtained lattice parameter (***a)***, bulk modulus (B), the equilibrium volume (V_0) corresponding to minimum energy (E_0) and the pressure (P) are calculated by fitting the total energy to the Murnaghan's equation of states [15]. All physical properties are related to the total energy. The lattice constant that minimizes the total energy is the equilibrium lattice constant of a crystal. The detailed values of the optimized lattice parameter and bulk modulus are given in table 1. The optimized equilibrium lattice parameters were slightly different than the experimental lattice parameter (in table 1). Bulk modulus is a measure of resistance to volume change by an applied pressure. A series of calculated total energies as a function of volume can be fitted to an equation of states according to Murnaghan's equation of state .

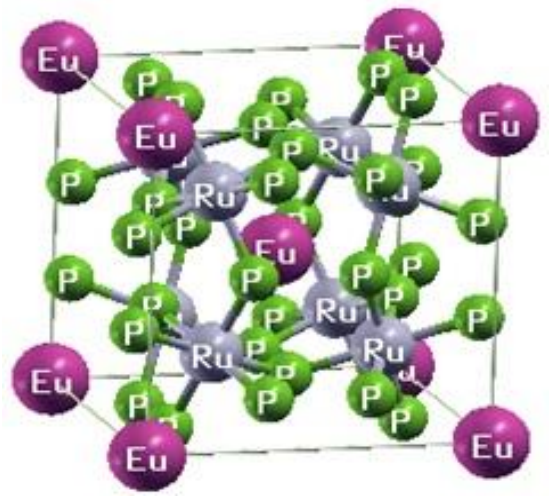

Figure 1. The unit cell structure of $EuRu_4P_{12}$ in space group *Im-3*.

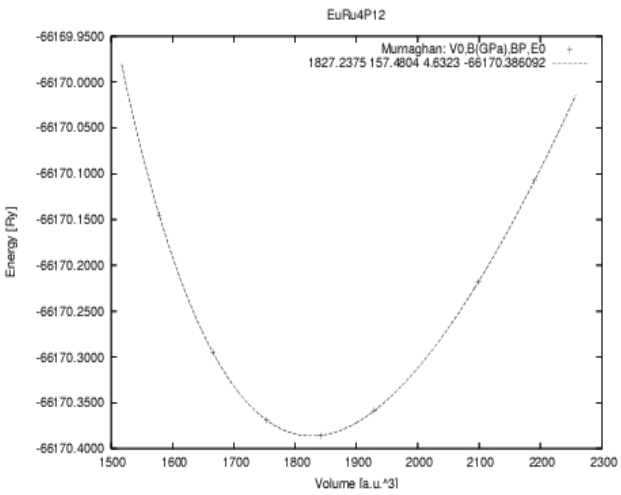

Figure 2. Plot of the total energy as a function of unit cell volume in BCC structure of $EuRU_4P_{12}$.

Table 1. Calculated equilibrium lattice parameter (a), unit cell volume (V_0), bulk modulus (B_0) and first pressure derivatives of bulk modulus (B_0') of $EuRu_4P_{12}$.

a (Å)	V_0	E_0	B_0	B'_0	Ref.
8.14	1827.2528	-66170.3864	159.8792	4.365	P.W
8.04					Exp [8]

3.2*Electronic Properties*

The energy distribution of the electron in the valance and conduction bands is important in determining the electronic properties of solids. The equilibrium lattice constant is used to calculate the electronic band structure and the density of states of $EuRu_4P_{12}$. The calculated band structure of $EuRu_4P_{12}$ is shown in figure 3. The energy band structure is calculated along the high symmetry points of the first Brillouin zone using PBE- GGA. From band structure, we observe that there is no band gap between conduction and valence band as a result $EuRu_4P_{12}$ has metallic character which is in good agreement with earlier result. In order to support band structure plots finding we have also plotted the total and partial density of states for atoms Eu, Ru and P. In PDOS plots, *d*-electrons have the highest contribution in Eu whereas *p*-electrons have highest contribution in atoms Ru and P. But DOS plots also do not show any band gap between valance and conduction bands. This supports that $EuRu_4P_{12}$ exhibit metallic nature in agreement with our band structure plots finding.

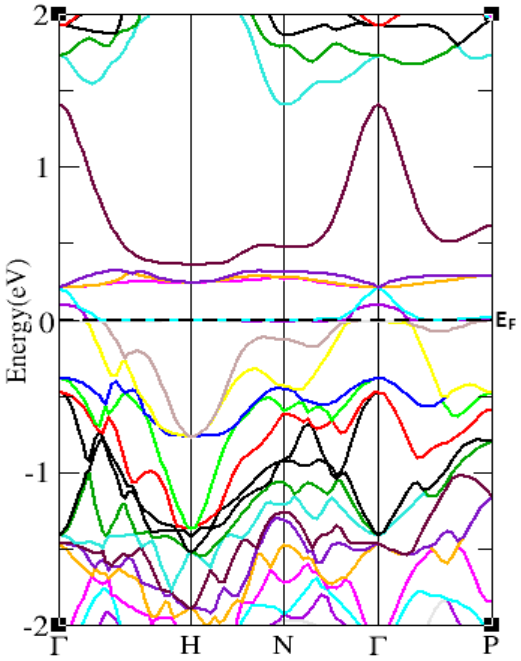

Figure 3. A plot ofelectronic bands of $EuRu_4P_{12}$ at ambient condition in bcc structure.

4. Conclusions

We have performed structural optimization and electronic structure calculation of the Rare Earth Skutterudites $EuRu_4P_{12}$, using FP-LAPW method to evaluate theoretical lattice parameter and density of electron states near Fermi energy level. The optimized lattice parameter is in good agreement with the available experimental value. There is no band gap between the valence band and the conduction band and it indicates metallic nature of this compound and likely to be the candidate for thermoelectric applications.

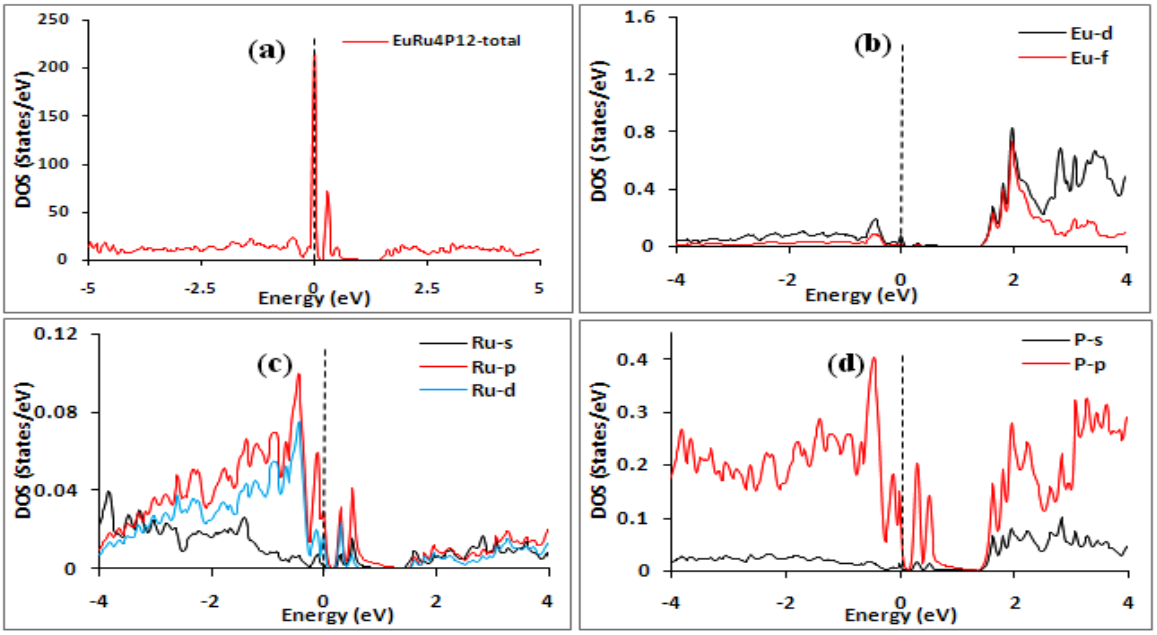

Figure 4. TDOS (a) and PDOS for (b) d and f statesof Eu (c) s, p and d states of Ru (d) s and p states of P of $EuRu_4P_{12}$.

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