

Elastic and electronic properties calculations of the filled skutterudite $\text{CeOs}_4\text{P}_{12}$

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Abstract. The full-potential linear muffin-tin orbital method (FP-LMTO) within the local density approximation (LDA) using the Perdew-Wang parameterization is used to calculate the structural, electronic and elastic properties of the filled skutterudite $\text{CeOs}_4\text{P}_{12}$. The results of the electronic properties show that this compound is an indirect band gap material (Γ -N). A special interest has been made to the determination of the elastic constants since there have been no available experimental and theoretical data. The energy band gaps and their volume and pressure dependence are also investigated.

Keywords: Skutterudite, FP-LMTO, electronic properties, elastic constants.

1. Introduction

The pursuit of new and interesting strongly correlated electron phenomena has led to a systematic investigation of the rare earth-based filled skutterudite compounds. This pursuit has been driven by the remarkable fact that one can observe metal insulator transitions [1], magnetic order [2], heavy fermion behaviour [3], superconductivity [4, 5, 6, 7], quadrupolar ordering [8, 9, 10], Kondo insulating behaviour [11], non-Fermi liquid behaviour [12], quantum critical points [13, 14], and heavy fermion superconductivity all in the same family of compounds [3]. The filled skutterudite compounds have the general formula MT_4X_{12}

(M = alkali metal, alkaline-earth, lanthanide, or actinide; T = Fe, Ru, or Os; and X = pnictogen such as P,

As, or Sb) with the $\text{LaFe}_4\text{P}_{12}$ -type structure ($\text{Im}\bar{3}$ space group) [15]. These compounds are interesting materials on the viewpoint not only of strongly correlated electron systems but also for industrial application [16]. Recently, these compounds attracted renewed attention due to their potential application as thermoelectric materials (TE) [17, 18]. TE performance is characterized by a dimensionless figure of

merit : $ZT = \frac{\sigma S^2 T}{\kappa}$, where σ is the electric conductivity, S is the thermopower, and κ is the thermal

conductivity; ZT up to 1.4 at 600 K has been measured in skutterudites.

The compound $\text{CeOs}_4\text{P}_{12}$ belongs to the family filled skutterudites, which have exhibit several physical characteristics, $\text{CeOs}_4\text{P}_{12}$ is a narrow gap semiconductor with a gap of ≈ 0.036 eV (≈ 400 K) estimated from resistivity data [19]. The room temperature resistivity is $\approx 10^{-2}$ $\Omega - \text{cm}$ increasing to $\approx 10^4$ $\Omega - \text{cm}$ at 2 K. The magnetic susceptibility is similar to that of $\text{CeRu}_4\text{P}_{12}$ [19]. The as-grown samples are p-type with a room temperature Hall mobility of 73 $\text{cm}^2 / \text{V} - \text{sec}$ for a carrier concentration of 5.10^{19} cm^{-3} . The room temperature values of the Seebeck coefficient and thermal conductivity are $147 \mu\text{V} / \text{K}$ and $105 \text{mW} / \text{cmK}$, respectively [20].

For this compound, there exist a few experimental data for the electrical, magnetic and thermoelectric properties [19, 20]. Point of view theoretical, there are no available calculations for this



compound. We therefore think that it is worthwhile to perform these calculations using the full-potential linear muffin-tin orbital (FP-LMTO) method in order to complete the exciting experimental works for this compound. In this work, we present the results of a theoretical investigation of electronic and elastic properties for filled skutterudite compounds $\text{CeOs}_4\text{P}_{12}$. The organization of the paper is as follows: we explain the computational method in Sec. 2. The results are presented and discussed in Sec. 3 for structural, electronic and elastic properties and a brief conclusion is drawn in the last section.

2. Calculations:

The atomic positions in the ternary skutterudite $\text{CeOs}_4\text{P}_{12}$ are as follows: the Ce atoms are located at (0, 0, 0), Os atoms at (1/4, 1/4, 1/4) and the phosphide atoms at (0, u , v). The calculations reported in this work were carried out by means of the full-potential linear muffin-tin orbital (FP-LMTO) [21, 22] within the framework of density functional theory (DFT). In this method, the space is divided into an interstitial region (IR) and non-overlapping (MT) spheres centered at the atomic sites. In the IR region, Fourier series represent the basic functions. Inside the MT spheres, the basis sets are described by radial solutions of the one-particle Schrödinger equation (at fixed energy) and their energy derivatives multiplied by spherical harmonics.

In order to achieve energy eigenvalue convergence, the wave functions in the interstitial region were expanded in plane waves with a 110.0345 Ry energy cut-off and a number of plane waves equal to 34412. The muffin-tin spheres radius is taken to be 3.733, 2.317 and 2.145 a.u. for Ce, Os and P respectively. The valence wave functions inside the spheres are expanded up to $l_{\text{max}} = 6$. The exchange-correlation (XC) effects are treated by the local density approximation (LDA) [23]. The integrals over the Brillouin zone (BZ) are performed up to (6, 6, 6) grid in the irreducible Brillouin zone (IBZ), using the tetrahedron method [24].

3. RESULTS AND DISCUSSIONS

3.1. The ground states

The internal parameters u and v , which define the position of pnictogen atoms, are determined by minimizing the total energy while keeping the volume fixed at the experimentally observed value. The optimized u and v values are found to be equal 0.3589 and 0.1424, respectively. In order to calculate the ground state properties of $\text{CeOs}_4\text{P}_{12}$ the total energies are calculated in skutterudite structure for different volumes around the equilibrium cell volume V_0 . The plot of calculated energies versus reduced volume for this compound in this structure is given in Figure. 1. Fitting of the Birch equation of state [25] to the total energies versus lattice parameters, yields the equilibrium lattice parameter a_{eq} , the bulk modulus B_0 and its pressure derivative of the bulk modulus B'_0 .

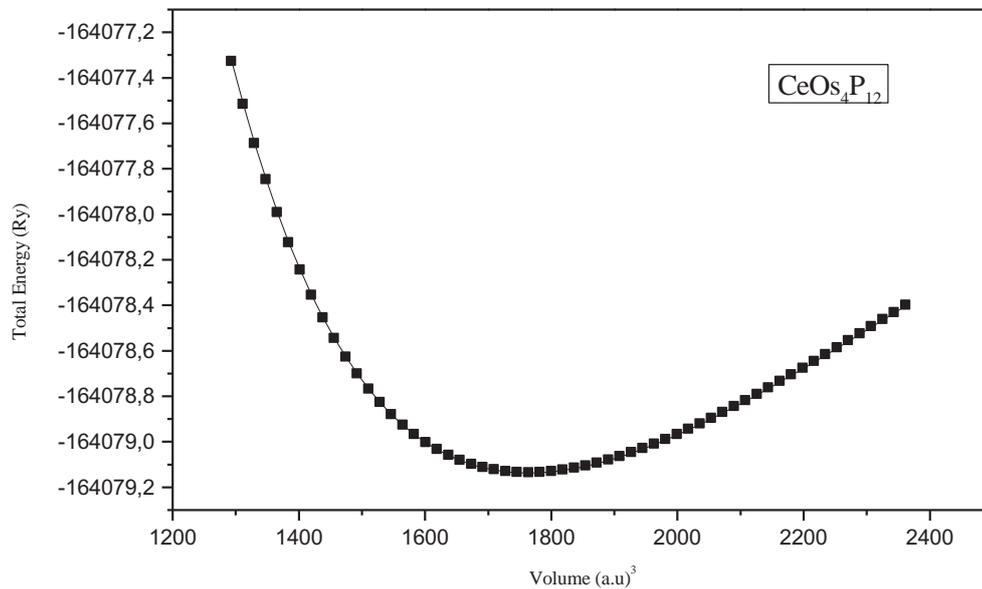


Figure 1: Calculated total energy as a function of volume

The optimized value of the lattice constant turns out to be 8.053 \AA , as compared to the experimental value of 8.0626 \AA [15], Our calculated values of a_0 is within 0.11% of the corresponding experimental value. This is due to the use of LDA which known to underestimate this quantities in comparison to experiment. The values of the bulk modulus and its pressure derivative (B_0 and B_0') evaluated at zero pressure are predicted to be (208.92 GPa and 5.87802). Our calculated value of the bulk modulus is overestimated compared to those obtained by the x-ray diffraction (150 ± 5) [26]. This overestimation is generally attributed to the use of LDA.

3.2. Elastic constants

The elastic properties define the properties of a material that undergo stress, deform and then recover and returns to its original shape after stress ceases. These properties play an important part in providing valuable information about the binding characteristic between adjacent atomic planes, anisotropic character of binding and structural stability. The elastic moduli require knowledge of the derivative of the energy as a function of the lattice strain. In the case of cubic system, this strain is chosen in such a way that the volume of the unit cell is preserved. Thus for the calculation of elastic constants C_{11} , C_{12} and C_{44} for this compound we have used the Mehl method [27, 28]. For cubic crystal, the bulk modulus is given by:

$$B = \frac{1}{3} (C_{11} + 2C_{12}) \quad (1)$$

C_{11} , C_{12} and C_{44} comprise the complete set of elastic constants for a cubic system and the shear modulus G , Young's modulus E , and the Poisson's ratio ν can be derived using the following standard relations:

$$E = 9BG / (3B + G) \quad (2)$$

$$G = (C_{11} - C_{12} + 3C_{44}) / 5 \quad (3)$$

$$\nu = (3B - E) / (6B) \quad (4)$$

$$A = 2C_{44} / (C_{11} - C_{12}) \quad (5)$$

The calculated elastic constants C_{ij} , the shear modulus G , the Young's modulus E and the Poisson's ratio (ν) are summarized in Table 1. To date no experimental or theoretical data of the elastic constants of these compounds are given in the literature.

Table 1: Calculated elastic constant C_{11} , C_{12} , C_{44} (in GPa), Young and shear modulus (in GPa), Poisson's ratios (ν) and the anisotropic parameter for $\text{CeOs}_4\text{P}_{12}$

C_{11}	C_{12}	C_{44}	G	E	ν	A
503.04	43.86	304.58	274.58	572.81	0.043	1.32

Furthermore, this compound exhibit small value of C_{12} . From the elastic constants, we obtain the anisotropy parameter $A=1.32$, this indicates that the elastic properties of this compound are highly anisotropic. The requirement of mechanical stability in cubic crystal leads to the following restrictions on the elastic constants, $C_{44} > 0$, $C_{11} > |C_{12}|$, and $C_{11} + 2C_{12} > 0$ [29]. The elastic constant in Table 1, obey these stability conditions, including the fact that C_{12} must be smaller than C_{11} . With these results, we conclude that the skutterudite structure is the stable ground state.

The Debye temperature (θ_D) is fundamental physical property, and is used to distinguish between high- and low temperature regions for a solid. If $T > \theta_D$ we expect all modes to have energy $k_B T$, and if $T < \theta_D$ one expects high-frequency modes to be frozen [30]. In the present case, Debye temperature (θ_D) is estimated for $\text{CeOs}_4\text{P}_{12}$ by using the calculated elastic constant data, in terms of the following classical relations [31]:

$$\theta_D = \frac{h}{k} \left[\frac{3n}{4\pi} \left(\frac{N_a \rho}{M} \right) \right]^{1/3} v_m \quad (6)$$

Where v_m is the average wave velocity, h is Planck's constants, k is Boltzmann's constant, N_a is Avogadro's number, n is the number of atoms per formula unit, M is the molecular mass per formula unit, $\rho = M/V$ is the density, and v_m is obtained from [32]:

$$v_m = \left[\frac{1}{3} \left(\frac{2}{v_l^3} + \frac{1}{v_t^3} \right) \right]^{-1/3} \quad (7)$$

Where v_l and v_t , are the longitudinal and transverse elastic wave velocities, respectively, which are obtained from Navier's equations [33]:

$$v_l = \left(\frac{3B + 4G}{3\rho} \right)^{1/2} \quad (8)$$

and

$$v_t = \left(\frac{G}{\rho} \right)^{1/2} \quad (9)$$

The calculated average longitudinal and transverse elastic wave velocities and Debye temperature for $\text{CeOs}_4\text{P}_{12}$ are given in Table 2. Unfortunately, as far as we know, there are no data available to these properties in the literature for these compounds. Future experimental work will testify our calculated results.

Table 2: Calculated longitudinal, transverse and average sound velocity (v_l, v_t, v_m in m s^{-1}) calculated from polycrystalline elastic modulus and the Debye temperature (θ_D in K) for $\text{CeOs}_4\text{P}_{12}$.

v_t	v_l	v_m	θ_D
8239.07	11923.09	8963.32	329

3.3. Electronic properties

The calculated band structures of filled skutterudite $\text{CeOs}_4\text{P}_{12}$ at equilibrium lattice constant along the high symmetry lines of the BZ is presented in figure 2. This figure, show clearly the semiconducting behaviour of $\text{CeOs}_4\text{P}_{12}$, which are drawn along the symmetry directions in the first Brillouin zone.

Predicting the valence band maximum (VBM) at Γ point and the conduction band minimum (CBM) at N point resulting in an indirect band gap material ($\Gamma - \text{N}$). The value of this gap turns out to be 0.218 eV.

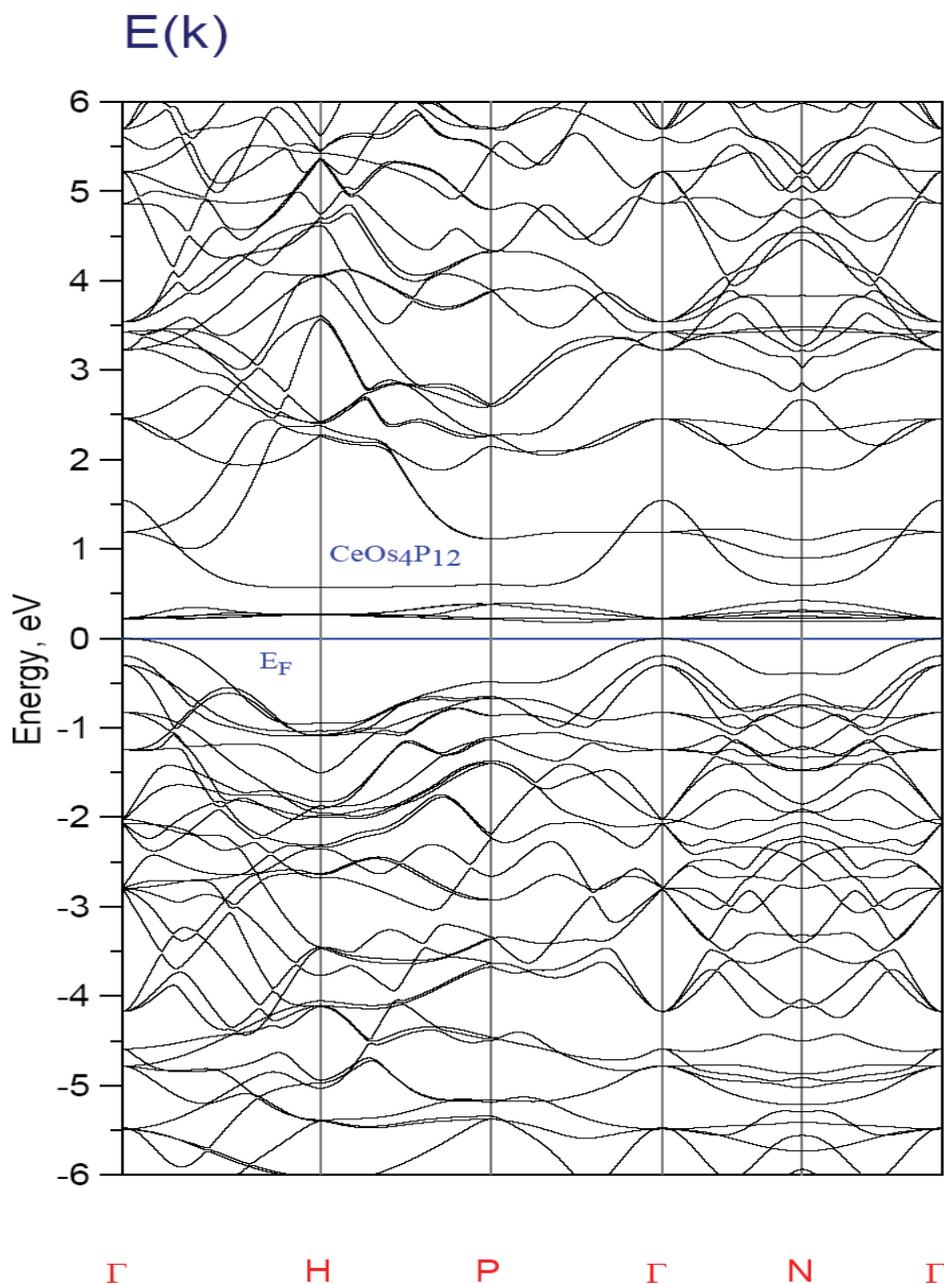


Figure 2: Band structure along the symmetry lines of the Brillouin zone at the equilibrium lattice constant. The position of the Fermi Level is shown by solid horizontal line.

From the figure the valence band is essentially dominated by the Os-5d below the Fermi energy with minor contributions of the others states of the elements forming the compound. The region including the Fermi energy arises predominately from the Ce-4f.

To further elucidate the nature of the electronic band structure, we have also calculated the total and the partial densities of states (DOS) of this compound these are displayed in Figure 3 and 4.

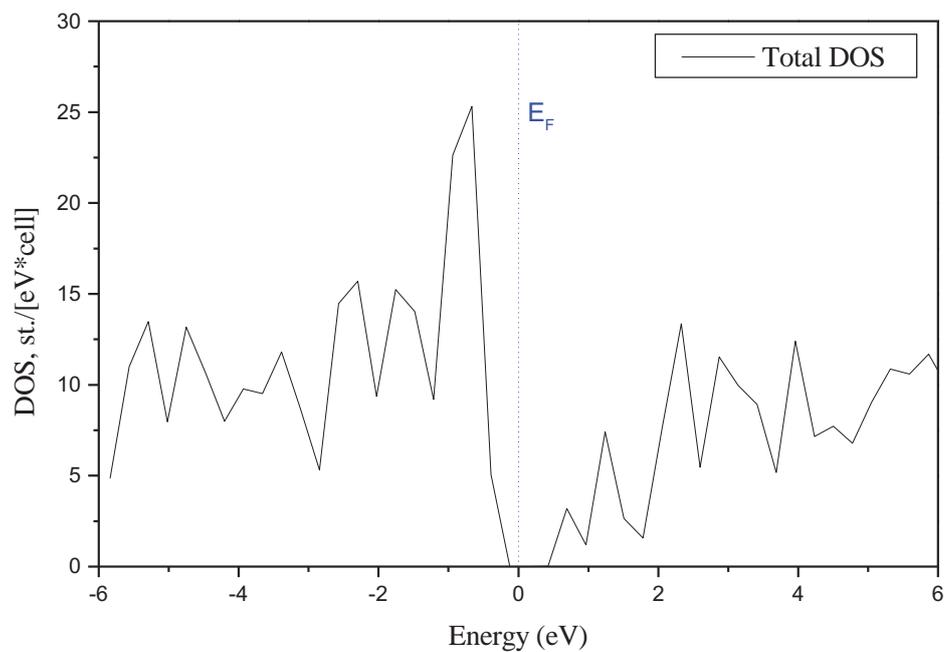
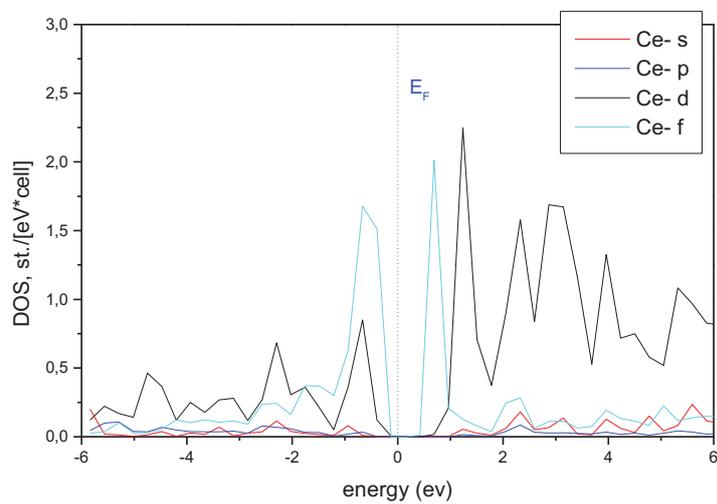
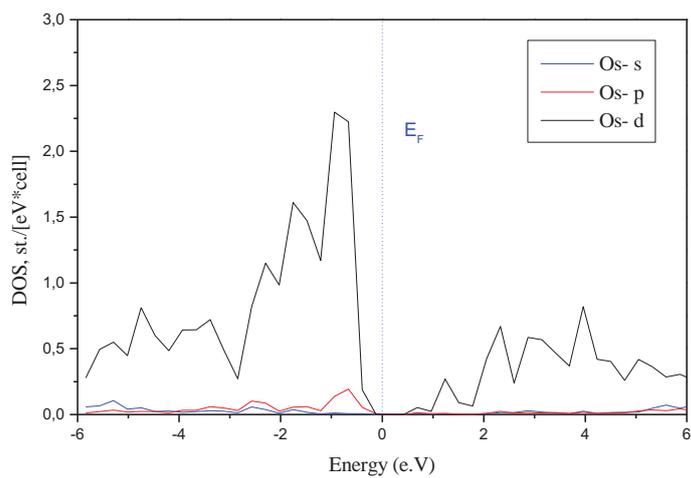


Figure 3: Total density of states (DOS) of CeOs₄P₁₂.

a)



b)



c)

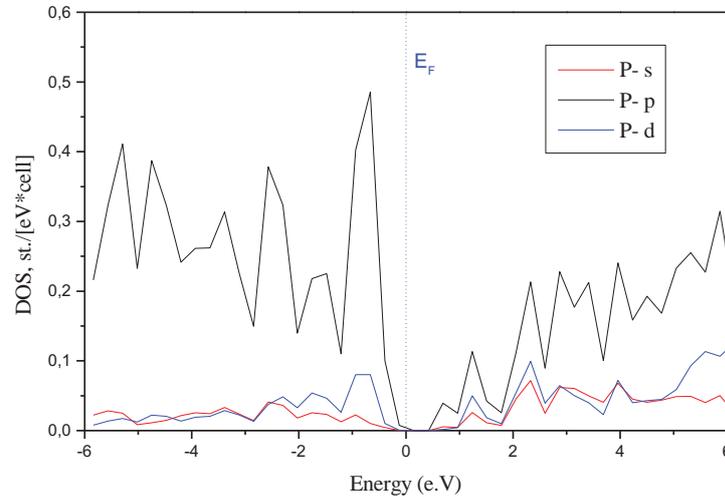


Figure 4: Partial DOS of $\text{CeOs}_4\text{P}_{12}$. (a) The states contributions of Ce, (b) the states contributions of Os and (c) the states contributions of P.

These results show that the top valence bands have characters of hybridized Os-5d and P-3p states. The low of the valence bands is mainly due to the P-3s states with a few contributions of Ce-5p. The remaining part until the Fermi energy is essentially dominated by Os-5d states with the contributions from P-3s, 3p and Ce-5d states. In conduction bands, from the Fermi energy up to strongly peak is dominated by Ce-4f states, the remaining part the conduction bands, there are mixture of the Ce-4f, Ce-5d and P-3p states.

In order to investigate the effects of the cell volume on the size of the energy gap of $\text{CeOs}_4\text{P}_{12}$ in the cubic skutterudite structure, the band energies at selected symmetry points are examined as a function of the cell volume. We calculated the pressure dependence of energy gap in this semiconductor using the following relation [34]:

$$\left(\frac{\partial E_p}{\partial P}\right)_T = \left(\frac{\partial E_g}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = -\left(\frac{V_0}{B_0}\right)_T \left(\frac{\partial E_g}{\partial V}\right)_T \quad (10)$$

The value of $\left(\frac{\partial E_g}{\partial V}\right)_T$ was obtained directly from the energy gap versus volume calculations and

the value of $\left(\frac{\partial V}{\partial P}\right)_T$ was obtained from the compressibility relation ship:

$$K = \frac{1}{B_0} = -\left(\frac{1}{V_0}\right)\left(\frac{\partial V}{\partial P}\right)_T \quad (11)$$

The results of our calculations for the nature of the band gap for CeOs₄P₁₂ versus the volume are shown in Figure 5.

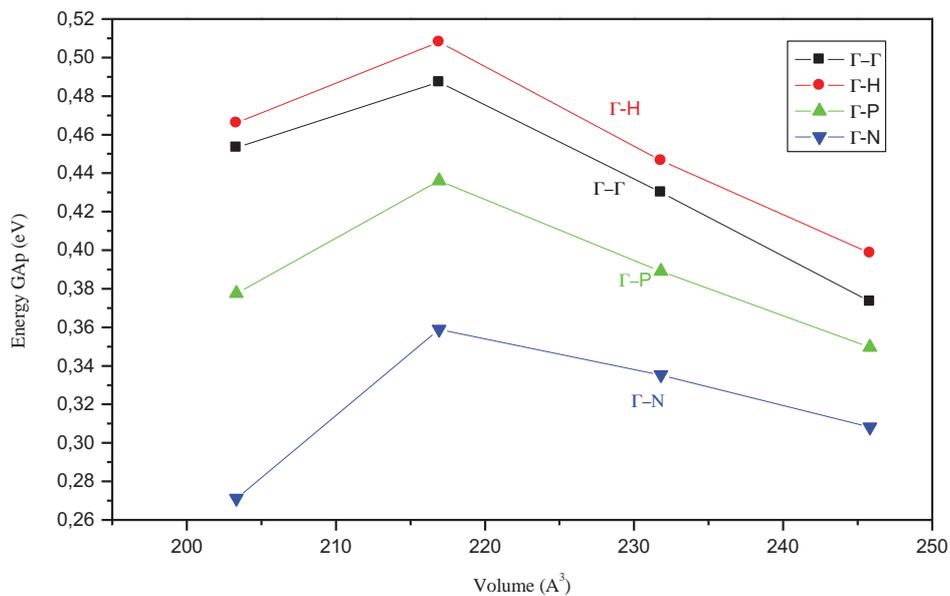


Figure 5: Calculated volume of energy gap in CeOs₄P₁₂

We notice that this compound is indirect gap (Γ-N) semiconductors at ambient conditions. Also we notice that the fundamental gaps present a nonlinear behaviour. The calculated linear pressure coefficients relative to different transitions (Γ-Γ-H-P-N) bands are listed in Table 3. The linear pressure increase with decrease of the pressure.

Table 3: Energy band gap (eV) for various points of the Brillouin zone and the calculated volume and pressure coefficients for CeOs₄P₁₂ skutterudite.

	$\Gamma - \Gamma$	$\Gamma - H$	$\Gamma - P$	$\Gamma - N$
CeOs ₄ P ₁₂	0.218	0.261	0.215	0.198
$\frac{\partial E_g}{\partial V}$ (meV/Å ³)	-3.95	-3.79	-2.99	-1.76
$\frac{\partial E_p}{\partial P}$ (meV/GPa)	4.93	4.73	3.73	2.19

4. Conclusion

We have performed first-principle FP-LMTO calculations of the elastic and electronic of filled skutterudite CeOs₄P₁₂. The ground states properties including the lattice parameter, bulk modulus and its pressure derivatives are compared with the available theoretical and experimental results. The elastic constants C_{ij} , shear modulus, Young's modulus and the Poisson's ratio for these compounds are derived. The Debye temperature is also estimated from the average sound velocity. Our results may be considered as reliable prediction of the elastic properties of this compound. Our results concerning the electronic properties show that this compound is an indirect gaps (Γ -N) semiconductor.

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