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First-principle calculations of elastic and electronic properties of the filled skutterudite $CeFe_4P_{12}$

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Abstract

A theoretical study of elastic and electronic properties of the filled skutterudite $CeFe_4P_{12}$ is presented, using the full-potential linear muffin–tin orbital (FP-LMTO) method. In this approach the local spin density approximation (LSDA) was used for the exchange-correlation (XC) potential. Results are given for lattice constant, bulk modulus, its pressure derivative and elastic constants. Our calculations performed for band structure and density of state show that this compound is an indirect band gap material (Γ–N). The results are compared with previous calculations and experimental data.

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Keywords: Skutterudite; FP-LMTO; Electronic properties; Elastic constants

1. Introduction

The filled skutterudites, have the formula RT_4X_{12} (where R = Ca, Sr, Ba, La–U, Yb, Th, U; T = Fe, Ru, Os; X = pnictogen: P, As, Sb) and crystallize in the cubic skutterudite structure (Space group Im3) [1–3]. Many of extraordinary properties of these compounds are associated with the R ion that occupies the atomic 'cage' in the binary (unfilled) type skutterudite structure. The phenomena displayed by the filled skutterudites includes superconductivity [4,5], magnetic order [6,7], small hybridization gap semi conductivity also known as 'Kondo insulator behavior' [8], valence fluctuation and heavy fermions behavior [9,10], Non Fermi liquid behavior [11] and metal-insulator transitions [12]. Many of these phenomena can be traced to hybridization of the localized f-electron states of the R ions with the conduction electron state. Furthermore, most these compounds are characterized by the high carrier mobility, low lattice thermal conductivity and low electrical resistivity, which make them potentially candidate material in thermoelectric application [13–17].

CeF_4P_{12} compound is among the ternary filled skutterudites, characterized by its semi conducting behavior. This is confirmed by Dordevic et al. [18] by the infrared reflectance spectroscopy measurements. From the theoretical point of view, the electronic and optical properties of this compound are studies by Khenata and co-workers [19] and Nordström and Singh [20], using the full-potential linearized augmented plane wave. Except, the work reported by Khenata et al. [19] on the elastic properties of CeF_4P_{12}, these constants have been not yet calculated or measured. We therefore think it is worthwhile to perform these calculations using the full-potential linear muffin–tin orbital method which has proven to one of the most accurate method for the computation of elastic properties and electronic structure of solids within the density functional

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theory (DFT), in order to complete the exciting experimental and theoretical works for this compound.

2. Method of calculations

The atomic positions in the ternary skutterudite $CeFe_4P_{12}$ as follows: The Ce atoms are located at (0, 0, 0), Fe 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, the basis functions are represented by Fourier series. Inside the MT spheres, the basis sets is 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 eigenvalues convergence, the wave functions in the interstitial region were expanded in plane waves with a 131.4691 Ry energy cut-off and a number of plane waves equal to 39326. The muffin–tin spheres radius is taken to be 3.411, 2.049 and 2.085 a.u for Ce, Fe and P respectively. The valence wave functions in side the spheres are expanded up to $l_{max} = 6$. The exchange-correlation (XC) effects are treated by the local spin density approximation (LSDA) [23]. The integrals over the Brillouin zone are performed up to $(6, 6, 6)$ grid in the irreducible Brillouin zone (IBZ), using the tetrahedron method [24].

3. Results and discussion

3.1. The grounds 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 0.3596 and 0.1448, respectively. They are in good agreement with the experimental and theoretical results [19,20]. The total energies are computed for specified sets of lattice constants at the optimized values of the internal structural parameters. The plot of calculated total energies versus reduced volume is given in Fig. 1. Fitting of the Birch equation of state [25] to the total energies versus lattice parameters, yields the equilibrium lattice parameter (a_{eq}), bulk modulus B_0, and the pressure derivative of the bulk modulus B_0'. The obtained lattice parameter, Bulk modulus and its pressure derivative are found to be equal 7.705 Å, 168.3 GPa and 5.953, respectively. Our calculated a_0 is within 1.0% smaller to the corresponding experimental value. This is due to the use of LSDA which known to underestimate this quantities in comparison to experiment. Our calculated bulk modulus is in good agreement with those determined by the X-diffraction

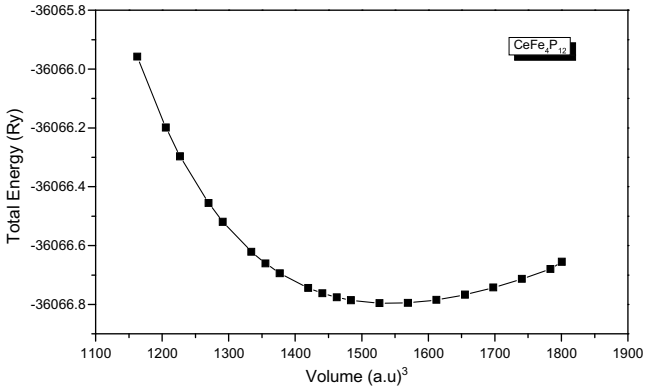

Fig. 1. Calculated total energy as a function of volume.

study (162 ± 4 GPa; Ref. [26]) and smaller than these obtained by the FP-LAPW.

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].

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 ration v can be derived using the following standard relations:

$$E = 9BG/(3B + G) \quad (1)$$

$$G = (C_{11} - C_{12} + 3C_{44})/5 \quad (2)$$

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

$$A = 2C_{44}/C_{11} - C_{12} \quad (4)$$

The calculated elastic constants C_{ij}, the shear modulus G, the Young's modulus E and the Poisson's ratio (v) are summarized in Table 1. It is clearly seen that our calculated elastic constants are relatively smaller than those calculated by using the full-potential linearized augmented plane wave

Table 1
Calculated elastic constant C_{11}, C_{12}, C_{44} (in GPa), Young and shear modulus (in GPa), Poisson's ratio (v) and the anisotropic parameter for $CeFe_4P_{12}$

C_{11}	C_{12}	C_{44}	G	E	v	A
384.21	60.345	228.61	201.93	432.72	0.07	1.41
422[a]	59[a]	183[a]	182[a]	409[a]		1.01[a]

[a] Ref. [10].