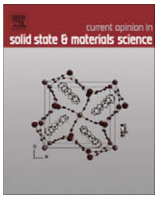
Current Opinion in Solid State and Materials Science 13 (2009) 105–111

Contents lists available at ScienceDirect

Current Opinion in Solid State and Materials Science

journal homepage: www.elsevier.com/locate/cossms



FP-APW + lo study of the elastic, electronic and optical properties of the filled skutterudites $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$

M. Hachemaoui [a], R. Khenata [a,*], A. Bouhemadou [b], Ali H. Reshak [c,*], D. Rached [d], F. Semari [d]

[a] Laboratoire de Physique Quantique et de Modélisation Mathématique (LPQ3M), Département de Technologie, Université de Mascara, 29000 Mascara, Algeria
[b] Laboratory for Developing New Materials and their Characterization, Department of Physics, Faculty of Science, University of Setif, 19000 Setif, Algeria
[c] Institute of Physical Biology, University of S. Bohemia, Zamek 136, Nove Hrady 373 33, Czech Republic
[d] Physics Department, Faculty of Science, University of Sidi-Bel-Abbès, 22000, Algeria

ARTICLE INFO

Article history:
Received 8 February 2009
Accepted 27 April 2009

Keywords:
Skutterudites
FP-APW + lo
Electronic structure
Elastic properties
Optical properties

ABSTRACT

Using a full-relativistic version of the full-potential augmented plane wave plus local orbitals (FP-APW + lo) method within the local density approximation (LDA), we have studied the elastic, electronic and optical properties of the filled skutterudites $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$. Structural parameters, including lattice constant, internal free parameters and, bulk modulus and its pressure derivative were calculated. We have determined the full set of first-order elastic constants, Young's modulus, Poisson's ratio and the Debye temperature of these compounds. Band structures, density of states, pressure coefficients of energy band gaps are also given. It is found that both $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$ are indirect band gap semiconductors. The valence band maximum (VBM) is located at Γ point, whereas the conduction band minimum (CBM) is located at N point. Optical constants, including the dielectric function, optical reflectivity, refractive index and electron energy loss were calculated for radiation up to 30 eV. This is the first quantitative theoretical prediction of the elastic and optical properties for these compounds, and it still awaits experimental confirmation.

1. Introduction

The filled skutterudite compounds have attracted a great deal of interest because they exhibit a wide variety of strongly correlated electron phenomena and are potential candidate materials for thermoelectric applications. The filled skutterudites have the formula AB_4C_{12} (A = alkali metal, alkaline earth, lanthanide, actinide; B = transition metal, and C = P, As or Sb). Many of the extraordinary properties of these compounds are associated with the A ion that occupies the atomic "cage" in the binary ("unfilled") BC_3 type-skutterudite structure. A variety of interesting phenomena, including superconductivity [1–3], small hybridization gap semiconductivity (also known as: "Kondo insulator") [4], magnetic order [5–8], valence fluctuation and heavy fermion behavior [9–11], non-Fermi liquid behavior and metal insulator transition material [12] have been displayed in the filled skutterudite. Many of these phenomena can be traced to hybridization of the localized *f*-electron states of the A ions with conduction electron states. Skutterudites have received particular attention these last years. This is not only for their interest as engineering materials in thermoelectric devices operating above room temperature, but also because they present interesting physical features from a fundamental point of view [13]. In particular, some skutterudites exhibit superconductivity and long-range magnetic order as well as rather exotic electronic-state features [1,14,15]. Electronic devices based upon spin control (spintronics) [16] and materials with a high degree of spin polarization, e.g., half-metallic ferromagnets [17,18] have evolved as topics of particular attention in recent years.

Experimentally, several works have been devoted to explore the physical properties of the filled $CeFe_4Sb_{12}$; they focused on the structural properties [19,20], electrical resistivity [21–24], optical conductivity [25], transport and magnetic properties [22,26–28] and the phonon density of states [29]. The crystal structure of the $CeFe_4As_{12}$ internal free parameters u and v has been determined by Henkie et al. [30], using the X-ray diffraction measurements. Theoretically, Nouneh and coworkers [31] performed band energy calculations for the filled skutterudites $CeFe_4Sb_{12}$ and $LaFe_4Sb_{12}$, using tight-binding linear muffin-orbital (TB-LMTO) and full-potential linearized augmented plane wave (FP-LAPW) methods to clarify the origin of the thermoelectricity in these compounds. The crystal structure and electronic band structure of $CeFe_4Sb_{12}$ has been also discussed by Nardström and Singh [32], using the full-potential linearized augmented plane wave (FP-LAPW) method.

To the best of our knowledge, neither experimental nor theoretical details regarding the elastic and optical properties are

---

* Corresponding authors. Tel.: +420 777729583; fax: +420 386 361231.
E-mail addresses: khenata_rabah@yahoo.fr (R. Khenata), maalidph@yahoo.co.uk (A.H. Reshak).

1359-0286/$ - see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cossms.2009.04.004

available for $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$ compounds. Moreover, no calculations on the pressure effect have been reported in the literature. Therefore, we think that it is timely to perform first-principles calculations for the structural, elastic, electronic and optical properties for $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$ compounds, using the full-potential augmented plane wave plus local orbitals method (FP-APW + lo), based on the density functional theory (DFT), which has proven to be one of the most accurate methods for the computation of the electronic structure of solids [33,34], in order to provide reference data for the experimentalists and to complete existing theoretical and experimental works on these compounds.

The rest of the paper has been divided in three parts. In Section 2, we briefly describe the computational techniques used in this study. The most relevant results obtained for the structural, elastic, electronic and optical properties for $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$ compounds are presented and discussed in Section 3. Finally, in Section 4 we summarize the main conclusions of our work.

2. Computational method

The calculations reported in this work were carried out using a full-relativistic version of the full-potential with the mixed basis APW + lo method [35,36] as incorporated in the WIEN2 K code [37]. This is an implementation of the density functional theory (DFT) [38] with different possible approximations for the exchange-correlation (XC) potentials. The XC potential was calculated using the local density approximation (LDA) of Perdew and Zunger (PZ) [39], which is based on exchange-correlation energy optimization to calculate the total energy.

In order to achieve energy eigenvalues convergence, the wave functions in the interstitial region were expanded in plane waves with a cut-off $K_{max} = 8/R_{MT}$, where R_{MT} denotes the smallest atomic muffin-tin sphere radius and K_{max} gives the magnitude of the largest K vector in the plane wave expansion. The R_{MT} are taken to be 3.0, 1.9, 2.1 and 2.4 atomic units (au) for Ce, Fe, As and Sb, respectively. The valence wave functions inside the muffin-tin spheres are expanded up to $l_{max} = 10$, while the charge density was Fourier expanded up to $G_{max} = 12$ $(au)^{-1}$. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-5} Ry. The integrals over the Brillouin zone are performed up to 18 $\boldsymbol{k}$-points in the irreducible Brillouin zone, using the Monkhorst–Pack special $\boldsymbol{k}$-points approach [40].

3. Results and discussion

3.1. Crystal structure and elastic properties

The semiconducting ternary $CeFe_4M_{12}$ (M = As and Sb) compounds crystallize in the cubic structure with the space group Im$\bar{3}$ [41,42]. The Ce atom is located at (0, 0, 0), Fe atom at (1/4, 1/4, 1/4) and the M atom at ($0, u, v$). The skutterudite structure is characterized by three lattice free parameters: the lattice constant a_0 and the two internal free parameters u and v, which are not fixed by the symmetry. For both compounds, the internal free parameters u and v have not been determined experimentally, so we have optimized them by minimizing the total energy while keeping the volume fixed at the experimentally observed value. The optimized values of u and v for $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$ are listed in Table 1. The obtained $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$ internal free parameters are in good agreement with the previously measured and calculated ones [30,32]. The optimized values of u and v are used to calculate the total energies for specified set of lattice constants. The total energies versus unit cell volumes are fitted to the Murnaghan's equation of state (EOS) [43] to determine the ground state properties such as the equilibrium lattice constant a_0, the bulk modulus B_0 and the bulk modulus pressure derivative B'. The calculated structural parameters: a_0, B_0 and B' of $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$ compound are summarized in Table 1. Results from earlier experimental and theoretical works are quoted for comparison. The obtained lattice constants for both compounds are in good agreement with experimental data. The obtained values deviate from the measured ones within 1.5%. The calculated bulk modulus of $CeFe_4Sb_{12}$ is overestimated compared to the measured one [44]. This overestimation is generally attributed to the use of LDA, which known to overestimate the bulk modulus value compared to the experimental one.

Table 1
Lattice constant a_0 (in Å), pnicogen atom free internal parameters u and v, and bulk modulus B_0 (in GPa) and its pressure derivative B'. Experimental and theoretical data are shown for comparison.

	CeFe4As12			CeFe4Sb12		
	Present work	Expt.	Other calc.	Present work	Expt.	Other calc.
a_0 (Å)	8.146	8.2959[a] 8.289[b]		8.958	9.135[a] 9.1391[c]	
u	0.341	0.3445[b]		0.333		0.333[d]
v	0.1564	0.1543[b]		0.162		0.163[d]
B_0 (GPa)	161.27			117.03	88 ± 4[c]	
B'	5.73			5.33	4 ± 1[c]	

[a] Ref. [20].
[b] Ref. [30].
[c] Ref. [44].
[d] Ref. [32].

Elastic properties of a solid are important because they are closely related to various fundamental solid-state phenomena such as interatomic bonding, equations of state and phonon spectra. Elastic properties are also linked thermodynamically with specific heat, thermal expansion, Debye temperature and Grüneisen parameter. Most importantly, knowledge of elastic constants is essential for many practical applications related to the mechanical properties of a solid: load deflection, thermoelastic stress, internal strain, sound velocities and fracture toughness. The elastic constants C_{ij} are the proportionality coefficients relating the applied strain (ε_i) to the stress (σ_i), $\sigma_i = C_{ij}\varepsilon_j$. So, the C_{ij} determine the response of the crystal to external forces. Ab initio calculation of the elastic constants requires precise methods. For obtaining the elastic constants from their known structure a popular approach [45–48], which is based on the analysis of the changes in calculated total energy values resulting from changes in the strain, is used. A cubic structure is characterized by three independent elastic constants, namely C_{11}, C_{12} and C_{44}. The present values of elastic constants for $CeFe_4As_{12}$ and $CeFe_4Sb_{12}$ are given in Table 2. A given crystal structure cannot exist in a stable or metastable phase unless its elastic constants obey certain relationship. The requirement of mechanical stability in a cubic structure leads to the following restrictions on the elastic constants, $C_{11}-C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$. These criteria are satisfied, indicating that these compounds are stable against elastic deformations.

The shear modulus G, Young's modulus E, Poisson's ratio ν and Lamé's coefficients μ and λ, which are the important elastic properties for applications, are also calculated in terms of the computed data (see Table 2) using the following relations:

$$E = 9BG/(3B + G) \tag{1}$$

$$G = (C_{11} - C12 + 3C_{44})/5 \tag{2}$$

$$\nu = (3B - E)/(6B) \tag{3}$$

$$\mu = E/(2(1 + \nu)) \tag{4}$$

$$\lambda = \nu E/((1 + \nu)(1 - 2\nu)) \tag{5}$$

We note that $CeFe_4As_{12}$ has higher values of elastic, shear and Young's moduli compared to $CeFe_4Sb_{12}$. Furthermore, these com-