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Energy band structure, elastic and optical constants of the filled skutterudite $CeRu_4As_{12}$

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ABSTRACT

The energy band structure and the optical response of the filled skutterudite $CeRu_4As_{12}$ have been studied using the full-potential linearized augmented plane wave (FP-LAPW) method within the local density approximation (LDA). The analysis of the region close to the Fermi energy level suggests the narrow band gap (0.18 eV) semiconducting nature of the material. The new approach of the exchange-correlation functional called the modified Becke Johnson potential used in the treatment of the material gives an enhanced band gap value of ~0.2 eV. The elastic parameters are also estimated at the ambient condition, which indicates the brittle nature of the studied material. The study of the optical spectra suggests the metallic behavior of the material in the far infrared region, which indicates that it acts as an opaque material with superluminal behavior in the ultraviolet frequency.

1. Introduction

The presence of strongly correlated electron phenomena of the lanthanide filled skutterudites (RM_4X_{12}, R=rare earth; M=Fe, Ru, Os; X=P, As, Sb) has attracted much attention to the lanthanide filled skutterudites in the physics and material science research. The various interesting properties such as the heavy fermion behavior [1], ferromagnetism [2–5], antiferromagnetism [6], small hybridization gap semi-conductivity (also known as the "Kondo Insulator" behavior) [7] make these compounds interesting for study. The low temperature properties of the materials also make them favorable candidate for thermoelectric application [8,9].

Among the ternary RM_4X_{12} compounds, the cerium based skutterudite, CeM_4X_{12} compound is the subject of numerous experimental and theoretical works which focus on the structural, electronic and optical properties. Depending on the constituent atoms M and X, such compounds exhibit a large variety of electronic properties and their properties are summarized as follows. For M=Fe, Ru and Os and with X=P, the three compounds exhibit semiconductor behavior with different energy gaps of 130 meV, 90 meV and 40 meV, respectively. These energy gaps are estimated from the hall coefficient experiment, electrical resistivity and optical conductivity spectra [10–13] and the values are confirmed by previous theoretical calculations [14–17]. On the other hand, for X=As, these compounds are semiconductors with energy gap between 5 meV to 10 meV as suggested by the X-ray diffraction measurements and optical conductivity spectra [13,18,19]. In addition, these measurements indicate a large variation in the conductivity spectra due to the choice of pnictogen and indicate an intermediate characteristic of the $CeRu_4As_{12}$ compound which is in between the $CeRu_4P_{12}$ and $CeRu_4Sb_{12}$ compounds in the value of the narrow band gap. Conversely, Sekine and co-authors [20], Sato and co-workers [21] as well as Maple et al. [22] have reported metallic characteristic for these compounds. Furthermore, first principle full-potential linearized augmented plane wave (FP-LAPW) method reports the semiconducting nature of the $CeRu_4As_{12}$ [23] and $CeFe_4As_{12}$ [24] compounds.

The $CeRu_4As_{12}$ compound was synthesized by Dieter J. Braun and Wolfgang Jeitschko [25] and the crystal growth and thermoelectric properties of the $CeRu_4As_{12}$ compound was reported by Henkie and co-authors [26]. The magnetization measurement on the $CeRu_4As_{12}$ compound [27] reflects the transition from the weak insulator to the semi-metallic nature of the polycrystalline to the single crystal of the material. In addition, the $CeRu_4As_{12}$ compound exhibits low thermal conductivity which makes it a promising candidate for thermoelectric application, and it also shows a transition from the hybridized gap insulator to the Kondo

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semiconductor with an increase in temperature [28]. Conversely, for X=Sb, these compounds exhibit metallic behavior [29–32] and at low temperatures, they display strong non Fermi liquid (NFL) properties [33,34]. Moreover, the semi-metallic nature of the hybridized 4*f*-valence band just below the Fermi energy of the $CeRu_4Sb_{12}$ compound which has been reported by the UHRPE spectroscopy measurement [35,36], is consistent with the previous report of heavy-fermion semi-metallic behavior of this compound [37]. Similarly, the semiconductor-like behavior of the $CeOs_4Sb_{12}$ compound has also been reported [38,39] at low temperatures. The extended Huckel tight-binding, the FP-LAPW and the full-potential linear muffin tin orbital (FP-LMTO) calculations show that the $CeOs_4Sb_{12}$ and $CeFe_4Sb_{12}$ compounds are narrow indirect band gap semiconductors [40–42].

From the above it is clear that there exist several experimental and theoretical works devoted on ternary cerium based skutterudite compounds but there are very few reported theoretical and experimental studies on the electronic properties of $CeRu_4As_{12}$. There is also some controversy on the nature of the band gap of this compound (direct, indirect or metal). Moreover, there are no reported theoretical or experimental data in the literature on the first order elastic constants for the compound of interest. Neither experimental nor theoretical details regarding the optical properties are available. We should also mention that the calculations of the band structure are crucial for understanding of the electronic and phonon properties of such kind of materials for their further use as photo induced nonlinear optical compounds [43] and thermoelectric materials [44]. The reasons mentioned above have drawn our attention and provided motivation to perform these calculations, using the newly recommended technique called modified Becke-Johnson (mBJ) potential in order to provide another reference data for the existing theoretical and experimental works on this compound. The paper is organized as follows. Section 2 briefly describes the computational techniques used in this work. Results and discussions of the structural, elastic, electronic and thermodynamic properties are presented in Section 3. Finally, conclusions and remarks are given in Section 4.

2. Computational details

Unlike other members of the filled skutterudites, $CeRu_4As_{12}$ also crystallizes in the unique body centered cubic (BCC) structure with $Im\,\bar{3}$ space group, as shown in Fig. 1. The Ce atom takes the atomic position 2a (0,0,0), the metal Ru is located at 8c (0.25,0.25,0.25) and the As atoms are at the position of 24 g (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 calculations presented in this work have been performed by a semi-relativistic version of the FP-LAPW method as implemented in the Wien2k [45] program, which is one of the most efficient method for the calculation and simulation of the ground state properties of materials [46,47]. From the previous literature [48], we found that the presence of localized electrons and the inclusion of spin-polarized calculation have negligible effects as compared to the hybridization of Ce and Ru in the compound. We therefore treated the exchange-correlation effect with the LDA which neglect the Coulomb interaction and spins of the electrons in our study. The energy eigenvalues are converged by choosing the wave function as plane waves with a cut-off, $K_{max}=7/R_{MT}$, where R_{MT} denotes the smallest atomic sphere radius and K_{max} is the maximum value of the wave vector in the plane wave expansion. For the correct description of the wave functions in the interstitial region, the spherical harmonics have been expanded up to $l_{max}=6$, while the charge density and the potential were expanded as a Fourier series with wave vectors up to $G_{max}=12$ (a.u.)$^{-1}$. The sets of valence orbital in the calculations were selected as 4*f*, 5*d*, 6*s* for Ce; 4*d*, 5*s* for Ru and 4*s*, 4*p* for As. All lower states were treated as core states. The multiple expansion of wave function as well as electron density and the potential inside the muffin-tin (MT) spheres were cut at $l=10$. The various MT sphere radii (R_{MT}) used were 3.2 a.u., 2.3 a.u. and 1.8 a.u. for the Ce, Ru and As atoms, respectively. The self-consistent potentials were calculated on a $17\times17\times17$ *k*-mesh in the Brillouin zone (BZ) which corresponds to 249 k points in the irreducible BZ and the convergence criterion is set to 10^{-4} Ry.

3. Results and discussions

3.1. Structural optimization and elastic constants

The structural optimizations of $CeRu_4As_{12}$ have been performed within the frame work of the PBE-GGA as the exchange correlation potential and by fitting the total energy as a function of volume to the Murnaghan's equation of state [49]. The equilibrium lattice constant that minimizes the total energy (as shown in Fig. 1) is found to be 8.62 Å. The estimated lattice constant is in close agreement with the experimental value of 8.4908 Å [9, 25]. It is known that PBE-GGA often over corrects the approximation by predicting the values by 1–2% higher than the experimental ones as seen in our result.

The elastic constants of a solid play an important role to understand the basic structural, mechanical and thermodynamic

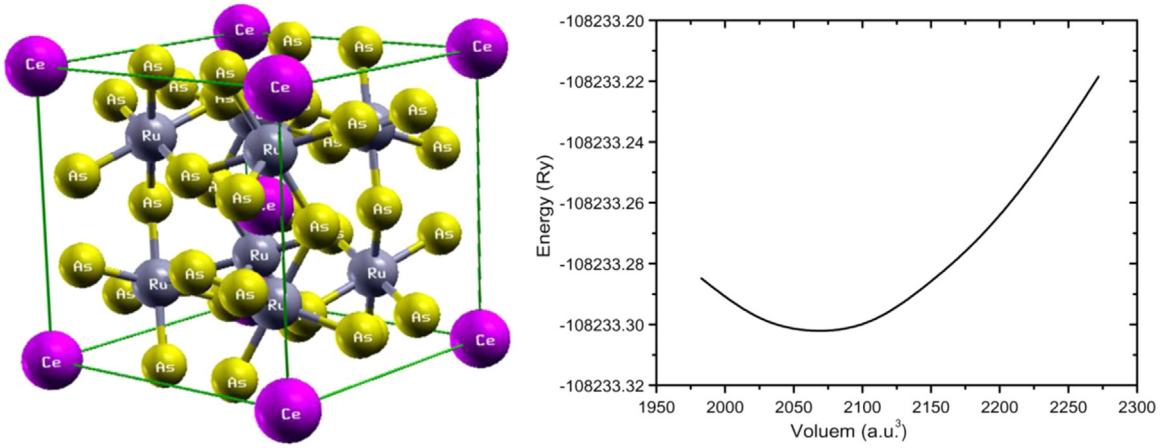

Fig. 1. (left) Unit cell structure and (right) volume optimization plot of $CeRu_4As_{12}$.