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To cite this article: Himadri R Soni et al 2012 J. Phys.: Conf. Ser. 377 012077

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A first principles study of lattice dynamical and electronic properties of Yb-pnictides (YbX, X= N, P and As) compounds

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Abstract. The Yb-pnictides have drawn considerable interest in the field of solid state and material science due to it’s diverge applications in the properties like electronic, magnetic, optical and phonon. These compounds have got keen interest due to its partially filled 4f bands. In the frame work of density functional theory (DFT), we determine structural, electronic, lattice dynamical and elastic properties of Yb-pnictides (YbX, X= N, P, As) in rocksalt (RS) phase using first-principles density functional theory (DFT) simulations based with a generalized gradient approximation (GGA) of the exchange correlation energy implemented in ABINIT package.

1. Introduction

The Yb-pnictides have drawn considerable interest in the field of solid state and material science due to it’s diverge applications in the properties like electronic, magnetic, optical and phonon [1-3]. These compounds have got keen interest due to its partially filled 4f bands. Such rare earth (RE) compounds have electronic configuration such as $4f^{n-1}(5d6s)^m$, where this 4f band is partially filled. The special characteristic of these Yb-pnictides is the fluctuations in their valence electrons. The Yb ion in these compounds is predominantly trivalent with one 4f hole. All YbX (X=N, P, As) compounds are semimetallic with rocksalt (RS) structures. Because of the interesting properties which are associated with the question of the lanthanides (for instance, mixed and intermediate valency and heavy fermion behaviour). It is important to have a good understanding of what stabilizes a given electronic configuration. Furthermore, it is also observed that there is a strong electron-phonon coupling at the RE (Rare Earth) ion site due to 4f-5d hybridization giving rise to anomalies in their phonon dispersion curves [3-5]. The Yb-pnictides crystallize in rocksalt structure, while many more investigations are to be carried out to establish the physical properties of the Yb-pnictides in the present paper.

In the present paper we report the density functional theoretical study of lattice dynamical and electronic properties of such Yb-pnictides (YbX, X=N, P, As). We briefly outline the theory in section 2 and present our calculated results in section 3.

2. Computational Details

To determine the lattice dynamical and electronic properties of YbX (X=N,P and As) in RS phase, we have performed plane-waves and pseudopotentials (both norm-conserving and ultrasoft) calculations...
using ABINIT code [6]. The generalized gradient approximation (GGA) [7-8] has been used for the exchange and correlation energy density function. A fully relativistic calculation is performed for core states, whereas the valence states are treated in a scalar relativistic scheme. In order to find an appropriate energy cutoff, the total energy as a function of the energy cutoff has been calculated for 23 different energy cutoff ranging from 10 Ry to 125 Ry. The total energy converges near the energy cutoff of 52 Ry, 32 Ry and 32 Ry for YbN, YbP and YbAs respectively. Here, for the self consistency, the initial potential for the next iteration is constructed using a convergence stabilization scheme. The number of sampling k-points used in the Brillouin zone (BZ) summation of the electronic density and total energy is increased until the total energy converges to the desirable tolerance. The self consistent calculations are considered to be converged when the total energy of the system is stable within convergence of $E_{\text{tot}} < 2.73 \times 10^{-3}$ eV and forces on atoms $F_i < 0.01$ eV/ Å. To generate the $(6\times6\times6)$ mesh in the BZ, the scheme of Monkhorst-Pack [9] has been used. Further, the lattice dynamical study for YbX are performed using density functional perturbation theory [DFPT] [10]. In this method, the dynamical matrix which provides information on lattice dynamics of the system can be obtained from the ground state electron charge of the nuclear geometry. The kinetic energy cut off and numbers of k-points mentioned above are found to yield phonon frequencies converged to within 2-5 cm$^{-1}$.

| Compound | YbN | YbP | YbAs |
|----------|-----|-----|------|
| **Lattice parameter (Å)** | Present work | 4.8033 | 5.5545 | 5.7449 |
| Experimental | 4.78[11] | 5.537[11] | 5.697[11] |
| **Bulk modulus (GPa)** | Present work | 130.77 | 61.77 | 54.3363 |
| Experimental | | | | |
| Other work | 4.787[15] | 5.552[14], 5.545[15] | 6.081[14], 5.694[15] |
| Other work | 130.55[12],136[13] | 70[13], 104±3[14] | 63[13], 85±4[14] |

Table 1. Calculated equilibrium lattice constants, bulk modulus for YbN, YbP and YbAs and compared with experimental and available other calculations.

3. Results and Discussion
The theoretical ground state constants such as lattice parameters and bulk modulus of the three pnictides YbN, YbP and YbAs are obtained using the method discussed in the above section and listed in Table 1, which also includes the available experimental [11] and other theoretical [12-15] data for comparison. It is clear that the present theoretical values agree reasonably well with the experimental data [11]. It is generally observed that GGA yields higher lattice constant. The total energy versus volume curve is fitted to the Murnaghan equation of state [16] to obtain the bulk modulus value as given below:

$$E(V) = E_0 - \frac{B_0 V_0}{B'_0 - 1} + \frac{B_0 V}{B'_0} \left(\frac{V_0}{V}\right)^{\frac{B_0}{B'_0} - 1} + 1$$

(1)

where $B_0$ and $B'_0$ are the bulk modulus and its derivative respectively, $E_0$ is the ground state total energy and $V_0$ is the volume. The bulk modulus so obtained is presented in Table I and compared with the available experimental [11] and other theoretical [12-15] data. There is an excellent agreement between the present and other theoretical data [12-15].

The total density of states (DOS) of these YbX (X=N, P, As) are presented in Fig. 1. One of the interesting features, which emerges from Fig. 1 is that for YbX (X=N, P, As) the Fermi level $E_F$
resides above the high dense peak which indicates instability. It is due to further filling up of \(d\)-orbitals. The additional \(d\) electrons for YbX (X=N, P, As) lead to a shift of the center of gravity of the total DOS towards lower energies. Furthermore, it is interesting to point out from Fig. 1 that, the major contribution in N(E\(_f\)) comes from the Yb-4f states which is of course shifted a bit from the Fermi level due to hybridization.

**Figure 1.** Electronics density of states of YbN, YbP and YbAs.

The phonon dispersion curves along with the phonon density of states for rocksalt YbX (Yb=N, P, As) are plotted in Fig. 2. These figures give impression that YbX compounds in rocksalt structure are dynamically stable as the frequency of phonon modes throughout the Brillouin zone is positive. It is clear from the figure that gap appears between the optical and acoustical phonon branches in the case of YbX, which is due to mass ratio of constituent atoms. We obtain the frequency of acoustic branches comparatively lower in magnitude and show a smooth variation along all the directions of the Brillouin zone. There is some anomalous behaviour for lowest TA phonon branch around zone centre in case of YbN. A systematic trend of variation of a LA phonon in all three compounds is observed. As the mass of the pnictides ion increases, a hump near the X-point from YbN to YbAs of the Brillouin zone gradually appears. This hump is maximum in the case of YbAs. No gap between LO and TO at \(\Gamma\) point indicates metallic behaviour for YbX compounds in contrast to the rigid ion model calculation [3]. The rigid ion model around the ionic behaviour for these compounds thereby indicating strong coulomb interaction for crystal cohesion.

4. Conclusions

In the present study, we reported the results of ab-initio calculations on structural, electronic and phonon properties of YbX (X=N, P, As) in rocksalt structure. There is a good agreement in the case of lattice parameter and bulk modulus. Electronic density of states and phonon dispersion curves reveal metallic nature of YbX. The slight unusual behaviour of phonon dispersion curve is observed in the case of YbAs.
Figure 2. Calculated phonon dispersion curves along with the phonon density of states of YbN, YbP and YbAs.

Acknowledgements
Financial assistance from Department of Science and Technology, Govt. of India, New Delhi and Department of Atomic Energy, Govt. of India, Mumbai.

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