Journal of Alloys and Compounds 509 (2011) 4653–4659

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

DysB under high pressures: A full-potential study

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ARTICLE INFO

Article history:
Received 27 July 2010
Received in revised form 5 January 2011
Accepted 30 January 2011
Available online 22 February 2011

Keywords:
Rare-earth compounds
Phase transition
Electronic properties
Elastic properties
Magnetic properties
High pressure

ABSTRACT

The magnetic, structural, electronic and mechanical properties of DySb in the stable $Fm\bar{3}m$ and high-pressure $Fm\bar{3}m$ phase have been analyzed using full potential (linear) augmented plane wave method. The local spin-density approximation along with Hubbard-U corrections and spin–orbit coupling has been used for present calculations. The magnetic phase stability shows that DySb is ferromagnetically stable at ambient and high pressures. Under compression, it undergoes first-order structural transition from B1 to B2 phase at 22.2 GPa which shows good agreement with the experimental value of ~22 GPa. The elastic properties of DySb have also been computed at normal and high pressures. The structural properties *viz*, equilibrium lattice constant, bulk modulus and its pressure derivative, transition pressure, volume collapse and elastic moduli are in good agreement with the experimental data. The calculation shows DySb to be semi-metallic.

1. Introduction

In recent years, the rare-earth (RE) compounds with rock-salt structure have drawn considerable interests of materials scientists due to their diverse structural, transport, magnetic and vibrational properties [1–16]. Spurred by the search for magnetic semiconductors *i.e.*, spintronic materials, we now have a better understanding of the electronic, magnetic and transport properties of RE compounds which are, generally, semiconductors or semimetals. Despite their simple rock-salt structure, they demonstrate various types of magnetic ordering. Their electronic structures and magnetic properties are sensitive to temperature, pressure (strain) and impurity effects. The RE 4*f*–5*d* interactions and the hybridizations between the RE non-4*f* and pnictogen *p* states are responsible for many fascinating phenomena that occur in them. In contrast to the RE metals, both super exchange and indirect Ruderman–Kittel–Kasuya–Yosida (RKKY) type interactions coexist in the family of RE compounds while the former interaction is dominant in heavy RE monopnictides. It is possible that other exchange coupling mechanisms, such as direct exchange or double exchange or both may also contribute in these monopnictides.

DySb constitutes an interesting system due to strongly correlated electrons with partially filled *f* orbitals of Dy atom which is found to be responsible for its anomalous properties. The changing 4*f* occupation implies that the RE elements and hence their compounds show different magnetic properties and electronic structures. Due to the unfilled 4*f* shells of Dy atom, it is a challenging problem to obtain an accurate theoretical description of the electronic structure of DySb.

The total magnetic moments have both orbital and spin components because *f* orbital moments cannot be quenched by the crystal field, hence spin–orbital interactions are particularly strong for many of the RE elements and compounds. The inner shell magnetic moments are largely aligned through intra-atomic *s*(*d*)–*f* exchange interaction and weaker inter-atomic *s*–*s* (*d*–*d*) exchange interactions. The 4*f* bands are generally very narrow and significantly different from the bands dominated by *s*, *p* and *d* states; there exists strong on-site Coulomb repulsion between the highly localized *f* electrons [17 and references therein]. This makes the independent particle approximation no longer valid and calculations based on local spin density approximation (LSDA) fail to describe the RE 4*f* electrons correctly. To explain the behavior of RE 4*f* electrons, many-body effects must be taken into account and calculations beyond LSDA are absolutely necessary. Coulomb repulsion (U) as an additional parameter to the one particle LSDA equations for a quasi-particle band structure can be introduced for this purpose.

The high pressure structural behavior of binary RE compounds is of current interest in condensed matter research. The majority of these compounds undergo first-order structural transition from NaCl (B1 phase) to CsCl (B2 phase) structure at high pressures. Recently, Shirotani et al. [1] have investigated the high pressure structural properties in these compounds up to 60 GPa at room temperature by powder X-ray diffraction (XRD) using synchrotron radiation whose profile shows that DySb is stable in NaCl structure at ambient conditions and transform to CsCl structure at ~22 GPa.

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doi:10.1016/j.jallcom.2011.01.175

The aim of the present computation is to perform a comprehensive study of the structural, magnetic, mechanical and electronic properties of DySb. A survey of the literature reveals that no theoretical attempts have been devoted so far to predict these properties of DySb. For making a better account of the on-site *f*-electron correlations, we have adopted a suitable LSDA + U approach [18].

The present article has been organized as: A brief description of the methodology used to compute parameters has been given in the next section followed by discussion on the calculated results, on a variety of interesting physical properties, in Section 3. The paper is concluded in Section 4.

2. Theory and method of calculation

A variety of material properties of DySb have been computed by employing first principles full-potential (linear) augmented plane wave + local orbital (FP-L/APW + lo) method [19] using the WIEN2K code [20] within the frame work of density functional theory [21]. In this method, the unit cell is divided into non-overlapping spheres centered at atomic sites (muffin-tin (MT) spheres) of radius (R_{MT}) and an interstitial region. In the MT spheres, the Kohn–Sham wave functions are expanded as a linear combination of radial functions × spherical harmonics, and in the remaining space of the unit cell a plane wave basis set is chosen. The basis set inside each MT sphere split into core and valence subsets. The core states are treated within the spherical part of the potential only and are assumed to have spherically symmetric charge density totally confined inside the MT spheres. The valence part is treated within a potential expanded into spherical harmonics. The Dy ($6s^2$ $5p^6$ $5d^1$ $4f^9$) and Sb ($4d^{10}$ $5s^2$ $5p^3$) states are treated as valence electrons. We have used 9 as the value for the parameter $R_{\mathrm{MT}}K_{\max}$ which determines the matrix size, where $K_{\max}$ is the plane wave cut-off and R_{MT} is the MT radius. The valence wave functions inside MT spheres were expanded up to $l_{\max} = 10$, while the charge density was Fourier expanded up to $G_{\max} = 14\,(\mathrm{a.u.})^{-1}$. All calculations were spin polarized. For the exchange correlation potential, the LDA form was adopted [22]. To improve the description of Dy 4*f* electrons, we used the LSDA + U (on-site coulomb interaction) method [18]. In the LSDA + U-like methods, an orbital dependent potential is introduced for the chosen set of electron states, which in our case are 4*f* states of Dy. This additional potential has an atomic Hartree–Fock form but with screened Coulomb and exchange interaction parameters. The coulomb potential $U = 6.3$ eV and the exchange coupling $J = 0.1$ eV for the Dy 4*f* orbitals has been calculated in the super cell approximation using the method proposed by Madsen and Novak [23]. The fully localized limit version of the LSDA + U method has been employed. The spin–orbit coupling (SOC) was included on the basis of the second variational method by using a scalar relativistic wave functions [20]. A mesh of 4096 special k-points was taken in the irreducible wedge of the Brillouin zone. The iteration process was repeated until the calculated total energy of the material converged to less than 0.5 mRy/unit cell.

3. Results and discussion

3.1. Magnetic stability

To test the magnetic stability of the material at ambient conditions, we have performed the self-consistent calculations of total energy for non-magnetic (NM) and magnetic (M) states of DySb in B1 phase. For this purpose, the minimisation technique has been used to obtain the optimised values of the total energy at ambient and high pressure conditions. The optimised values of total energy thus computed in both NM and M states were fitted to the Murnaghan's equation of state [24] $V/V_0 = (1 + (B_0'/B_0)P)^{-1/B_0'}$ to obtain the pressure–volume relationship with B_0 $(= -V(\partial P/\partial V)_T)$ as the equilibrium bulk modulus $(= (\partial B_0/\partial P)_T)$ as its first-order pressure derivative and P $(= -\partial E/\partial V)$ as the pressure which is defined as the negative derivative of the total energy. From the calculations, it is clear that the energies in NM and M states do not intersect each other and the total energy remains lower in M phase, hence ferromagnetic (FM) state is stable at ambient as well as at high pressures. The equilibrium cell volume in the FM state at ambient pressure has been estimated as 386.66 a.u.^{3} which is very close to the experimental data (390.46 a.u.^{3}) [1].

Table 1
The values of lattice parameter (a in Å), bulk modulus (B_0 in GPa) and its pressure derivative (B_0') of DySb in B1 and B2 phases.

a	B_0	B_0'	References
B1 phase			
6.12	61.68	4.12	Present
6.14, 6.16	–	–	Expt. [1,2]
~6.16	64.49[a]	–	Others [7]
B2 phase			
3.69	66.51	3.74	Present

[a] Ref. [9].

3.2. Phase transition properties

To compute the phase transition properties of DySb, the total energy of the system has been computed self-consistently as a function of volume for B1 and B2 phases in FM state. The calculated results in B1 and B2 phases are plotted in Fig. 1. It is seen from this figure that it is stable in B1 phase at ambient conditions due to the fact that the energy in this phase is lower as compared to that in B2 phase. On further compression, beyond B1 → B2 transformation, the energy of B2 phase depresses more as compared to that of B1 phase showing first-order phase transition at high pressures which is consistent with experiments [1]. It is clear from this figure that convergence occurs at a value very close to the experimental lattice constant. The correct description of lattice constant confirms that the interactions considered in the present computation and the process of self-consistent field approach are capable of predicting correctly the minimum total energy of the compound in the parent (B1) phase. The calculated values of equilibrium lattice parameter, bulk modulus and its pressure derivative have been presented in Table 1 and compared with available experimental [1] and other theoretical [7] data.

The calculated value of equilibrium lattice constant deviates marginally by 0.3% from the measured value for DySb. This variation lies within the limits of DFT with LSDA. Under ambient conditions, it crystallizes in B1 phase with bulk modulus ($B_0 = 61.68$ GPa) which is smaller than the value ($B_0 = 66.51$ GPa) in the compressed B2 phase. The values of B_0 and its pressure derivative (B_0') are of academic interest at present due to non-availability of measured data.

To determine the phase transition pressure at $T = 0$ K (*i.e.*, ignoring the entropy of the crystal), Gibbs free (GF) energies ($G = E + PV$) of B1 and B2 phases have been calculated at different pressures. The pressure at which the two GF energies cross each other *i.e.*, ΔG $(= G_{\mathrm{B2}} - G_{\mathrm{B1}})$ becomes zero has been indicated as phase transition pressure (P_{T}). It is clear from Fig. 1 that at zero pressure, the B1 phase is a thermodynamically stable state and remains stable until the pressure reaches P_{T} (=22.2 GPa). At pressures above P_{T}, the B2 phase becomes stable with more minimum GF energy while the B1 phase becomes thermodynamically unstable with comparatively higher GF energy.

We have plotted the variation of reduced volume ($V(P)/V(0)$) with pressure (P) to get the equation of state/phase diagram in Fig. 2 for DySb along with the available experimental data. It is clear from this figure that the volume decreases smoothly up to