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Crystal structures, elastic, and lattice dynamical properties of BeB_2, NaB_2, and CaB_2 from the first principles

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ABSTRACT

Based on density functional theory, we have studied the structural stability, elastic, mechanical, and lattice dynamical properties of BeB_2, NaB_2, and CaB_2 compounds in AlB_2, OsB_2, and ReB_2 structures, respectively. Generalized gradient approximation has been used for modeling exchange-correlation effects. Our calculations indicate that ReB_2, AlB_2, and OsB_2 structures are energetically the most stable for BeB_2, NaB_2, and CaB_2 compounds, respectively. The results show that these structures are both mechanically and dynamically stable. The bulk modulus, elastic constants, shear modulus, Young's modulus, Poisson's ratio, Debye temperature, sound velocities, and anisotropic factors are also calculated and discussed. Furthermore, the phonon dispersion curves and corresponding phonon density of states are presented. Our structural and some other results are in agreement with the available experimental and theoretical data.

1. Introduction

The discovery of superconductivity in MgB_2 at $T_c=39$ K [1] has revived new interest in finding superconductivity in other diborides. The superconductivity in MgB_2 has been associated with medium to strong electron–phonon coupling, high density of electronic states of the two dimensional $\sigma(p_{x,y})$ boron bands at the Fermi level and the presence of $p_{x,y}$ hole states at the Γ point in the Brillouin zone [2]. However, superconductivity is observed [3–5] in only some of them, and various studies are currently directed to shed light on other properties of diborides, including their elastic, mechanical, and thermodynamical properties [5–9].

BeB_2, NaB_2, and CaB_2 have the same structure (AlB_2-type) as MgB_2. In the past, some detailed works have been carried out [10–23] on the structural, elastic, and electronic properties of these compounds. Tupitsyn et al. [10] have reported the average experimental lattice constants of BeB_2. The structural and thermodynamic properties of BeB_2 compound have been studied by Wang et al. [11]. Profeta et al. [12] have investigated the electronic and dynamical properties of superconducting BeB_2. Islam et al. [13] have performed a density functional study on the elastic constants of this compound. The electronic and structural properties have been reported by Satta et al. [14]. Medvedeva et al. [15] have explained the absence of medium-T_c superconductivity for BeB_2. Ravindran et al. [16] have studied the ground state and electronic properties BeB_2 and CaB_2 compounds. Okatov et al. [17] have investigated the electronic properties of CaB_2. The superconductivity and lattice dynamical properties have been studied by Choi et al. [18]. Oguchi [19] has reported the systematic trend in lattice constants and the heat of formation for BeB_2, NaB_2, and CaB_2. Shein and Ivanovskii [20] have investigated the structural and elastic properties using the full-potential linearized augmented plane-wave (FP-LAPW) method with the generalized gradient approximation (GGA) for these compounds. Recently, Benhelal et al. [21] have studied the structural, electronic, and bonding properties of BeB_2 and CaB_2 using the full-potential linearized augmented plane-wave (FP-LAPW) method. Singh [22] has presented the results of fully relaxed, full-potential electronic structure calculations for the BeB_2 and NaB_2, using density-functional-based methods. The cohesive and thermal properties of BeB_2, using the Rigid Ion Model, have been investigated by Kaur et al. [23].

But until now – to our best knowledge – no systematic research on the structural stability, elastic, mechanical, and vibrational properties of BeB_2, CaB_2, and NaB_2 compounds in AlB_2, ReB_2, and OsB_2 structures, respectively, has been reported. Therefore, we have aimed to provide some additional information to the existing data on the physical properties of these compounds using the ab initio total energy calculations. Especially, we focus our attention on the mechanical and lattice dynamical behaviors, which are the important bulk properties of solids. The method of calculation is given in Section 2; the results are

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discussed in Section 3. Finally, the summary and conclusion are given in Section 4.

2. Method of calculation

In the present paper, all calculations have been carried out using the Vienna ab initio simulation package (VASP) [24–27] based on the density functional theory (DFT). The electron–ion interaction was considered in the form of the projector-augmented-wave (PAW) method with plane wave up to energy of 450 eV [27,28]. This cut-off was found to be adequate for studying the structural, elastic, and lattice dynamical properties. For the exchange and correlation terms in the electron–electron interaction, Perdew–Burke–Ernzerhof (PBE) type functional [29] was used within the generalized gradient approximation (GGA). For k-space summation the $17\times17\times13$ gamma-centered for AlB_2 and ReB_2-type and $9\times17\times11$ for OsB_2-type structure Monkhorst and Pack [30] grid of k-points have been used.

3. Results and discussion

3.1. Structural properties

We have fully relaxed the cell volume and the ionic positions of atoms in reciprocal coordinates, which are supported by VASP code [24–27] for all considered compounds. In all calculations, we have used these relaxed parameters. The calculated energy–volume values for the different values of lattice parameters (at constant b/a and c/a) are fitted by means of Murnaghan's equation of state (eos) [31] and are given in Fig. 1.

It can be clearly seen that the ReB_2, AlB_2, and OsB_2 structures are the most stable structures for BeB_2, NaB_2, and CaB_2 compounds, respectively. The calculated bulk modulus, and its pressure derivative have also been estimated based on the same Murnaghan's eos, and the results are given in Table 1 along with the experimental and theoretical values. It is seen that the present lattice parameters for BeB_2 and NaB_2 compounds in AlB_2 structure are in good agreement with the experimental and theoretical values of Refs. [10,15,22]. But the same parameters for CaB_2 in AlB_2 structure are overestimated by 1–2% with regard to those evaluated by the other theoretical values [15,16,19–22]. The present value of bulk moduli is lower (about 11%) than those of the other theoretical results [16,21]. In the present case, the largest value of bulk modulus (195.8 GPa) is obtained for BeB_2 in ReB_2 structure. Unfortunately, there are no theoretical or experimental results for these compounds in OsB_2 and ReB_2 structures for comparing with the present work.

The cohesive energy is known as a measure of the strength of the forces, which binds atoms together in the solid state. In this context, the cohesive energy of compounds in considered structures is calculated. The cohesive energies (E_{coh}) of given structures are defined as

$$E_{coh}^{XB_2}=E_{total}^{XB_2}-[E_{atom}^{X}+2E_{atom}^{B}] \quad (1)$$

where $E_{total}^{XB_2}$ is the total energy (in formul unit) of the compound at equilibrium lattice constant and E_{atom}^{X} and E_{atom}^{B} are the isolated atomic energies of the pure constituents. Also, from the total energy of the compound and the constituent elemental solids (B: α-B, 166, R-3m; Be: A3, 194, $P6_3/mmc$; Ca: A1, 225, Fm-3m; Na: A2, 229, Im-3m), one can find the formation energy using the relation

$$\Delta H_f^{XB_2}=E_{total}^{XB_2}-[E_{solid}^{X}+2E_{solid}^{B}] \quad (2)$$

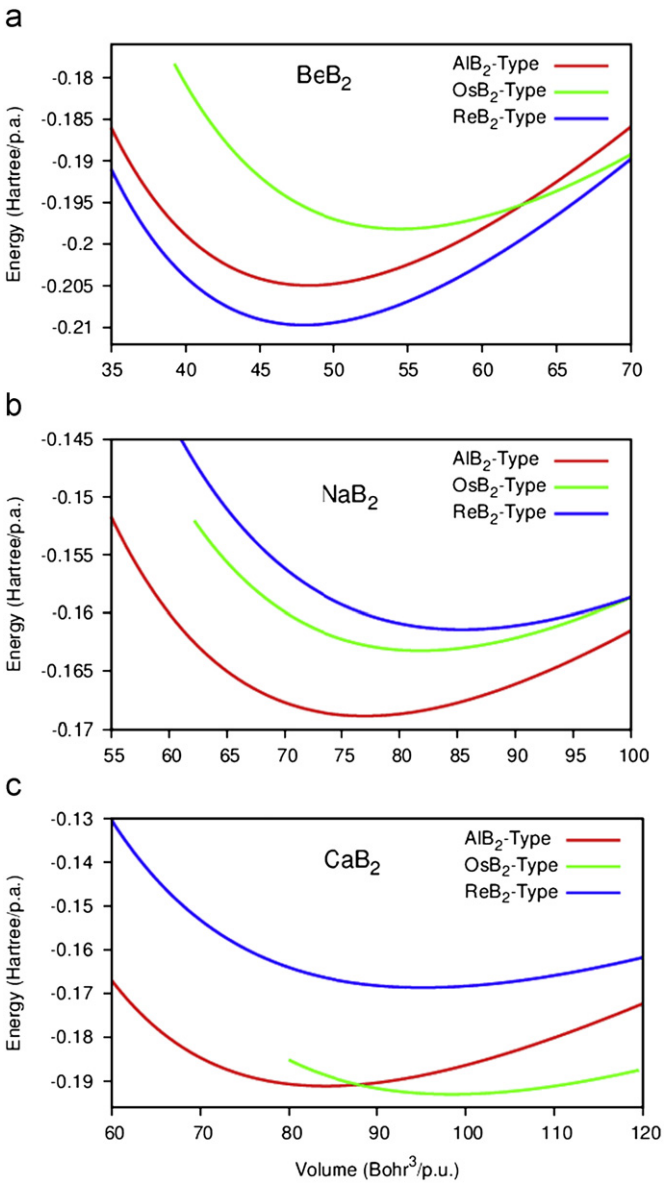

Fig. 1. Energy versus volume curves for (a) BeB_2, (b) NaB_2, and (c) CaB_2.

The calculated cohesive and formation energies are listed in Table 1 and they are consistent with the energy–volume curves in Fig. 1.

3.2. Elastic properties

The elastic constants of solids provide a link between mechanical and dynamical behavior of crystals, and give important information concerning the nature of the forces operating in solids. In particular, they provide information on the stability and stiffness of materials, and their ab initio calculations require precise methods. Since the forces and the elastic constants are functions of the first-order and second-order derivatives of the potentials, their calculation will provide a further check on the accuracy of the calculation of forces in solids.

The calculated elastic tensor for rigid ions has been determined by performing six finite distortions of the lattice and deriving the elastic constants from the strain–stress relationship [32], and the findings are given in Table 2 with the available theoretical values [13,20] for considered structures. Clearly, the calculated elastic constants satisfy the Born stability criteria for