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# Structural and elastic properties of MgS via first-principle calculations

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## Abstract

The structural B1–B2 (B1 is the NaCl phase and B2 is the CsCl phase) phase transition of MgS and the elastic properties of the B1 and B2 phases of MgS are investigated by ab initio plane-wave pseudopotential density functional theory method. The dependences of the elastic constants $c_{ij}$, the aggregate elastic modulus $B_S$, $G$, and the Debye temperature $\Theta_D$ on pressure are successfully discussed. From the usual condition of equal enthalpies, we find that the structure B1–B2 phase transition of MgS occurs at 255.5 GPa. Moreover, the dependences of the aggregate elastic modulus and the Debye temperature on the pressure $P$ have been investigated for the first time.
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## 1. Introduction

First-principle calculations have been very successful in predicting the phase stability, metallization transitions and high-pressure equations of state of a number of alkali metal halides and alkaline earth chalcogeniedes [1–7]. In recent years, Mg chalcogenides have attracted both scientific and technological interest. There are several reasons for studying these semiconductors. Due to their large band gaps and low dielectric constants, they can be used in blue- and ultraviolet-wavelength optics and high-temperature electronics [8–11]. Moreover, these semiconductors are also a potentially very good choice for protective coatings for their hardness, high melting point, high thermal conductivity, and large bulk modulus.

Up to now, for MgS, some theoretical calculations [12–22] and experimental measurements [23,24] have yielded some information on aspects of the structural properties and the electronic properties. The elastic properties have also attracted the subject of considerable attention [25–31]. For example, pressure-induced structural phase transition of MgS and CaS are investigated by using a three-body potential approach [12], they predict the B1–B2 phase transition for MgS at 158 GPa. Chen et al. [13] researched the phase transition is below 200.3 GPa. Lee and Chang [15] found that Mg-based compounds have higher ionicity and favor the rock-salt phase at zero pressure using self-consistent ab initio pseudopotential calculations to study the structural properties of Mg- and Zn-based binary compounds. Duman et al. [16] and Drief et al. [17] studied structural, electronic, elastic and optical properties of MgS, MgSe, MgTe using first-principles. Froyen et al. [18] described how hydrostatic pressure versus volume data relate to epitaxial structural energies. Kalpana et al. [19] investigated the electronic band structures of MgS and MgSe using the tight binding linear muffin tin orbital method. Sahraoui et al. [20] studied the structural and elastic properties in the B3 and B1 phases. O'Brien et al. [21] calculated the molecular orbital and crystal field of the optical transition in Ce doped alkaline earth sulfide (MgS, CaS, SrS, and BaS) phosphors. The structural and

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electronic properties of the binary semiconductor compounds ZnS, ZnSe, MgS, and MgSe in the cubic structure are calculated using the self-consistent scalar-relativistic full potential linear-augmented plane-wave method within the local density approximation [22].

## 2. Theoretical methods

In this work, we investigate the transition phase, elastic and thermodynamic properties of the MgS by using the plane-wave pseudopotential density functional theory method through the Cambridge serial Total Energy Package (CASTEP) program [32,33], which allows us to obtain all thermodynamics quantities from the calculated energy–volume points. We have successfully obtained the lattice constant, the bulk modulus and the pressure derivatives of bulk modulus of the B1 and B2 phases for MgS at zero pressure. In addition, the elastic constants, shear modulus and bulk modulus of the B1 and B2 phases of MgS are investigated. In the electronic structure calculations, we here use the non-local ultrasoft pseudopotential introduced by Vanderbilt [34], together with the Perdew–Wang (1991) version (PW91) of the generalized gradient approximation (GGA) exchange-correlation function [35], a plane wave basis set with energy cut-off 500.0 eV is applied. Pseudo atomic calculations are performed for Mg $2s^22p^63s^2$ and S $3s^23p^4$. For the Brillouin-zone sampling, we use the $10\times10\times10$ Monkhorst–Pack mesh, where the self-consistent convergence of the total energy is at 10–6 eV/atom. All the total energy electronic structure calculations are implemented through the CASTEP code.

For both the B1 and B2 structures of MgS, a series of different values of lattice constants are set to calculate the total energy $E$ and the corresponding primitive cell volumes $V$. Then, a least-square fits of these energy–volume ($E$–$V$) data are made to the Brich–Murnaghan's equation of state (B–M EOS) [36]. The calculated energies as a function of the primitive cell volume for MgS are shown in Fig. 1, together with the information concerning the static equation of state and the phase stability data. The obtained equilibrium lattice constants, bulk modulus and its pressure derivatives are listed in Table 1.

To calculate the elastic constants under hydrostatic pressure $P$, we use the strains to be non-volume conserving because this method is consistent with our calculated elastic constants using the stress–strain coefficients, which are appropriate for the calculation of the elastic wave velocities. The elastic constants, $c_{ijkl}$, with respect to the finite strain variables is defined as

$$c_{ijkl} = \left(\frac{\partial \sigma_{ij} x}{\partial e_{kl}}\right)_X, \tag{1}$$

where $\sigma_{ij}$ and $e_{kl}$ are the applied stress and Eulerian strain tensors, $X$ and $x$ are the coordinates before and after the deformation [37–39]. For the isotropic stress, we have

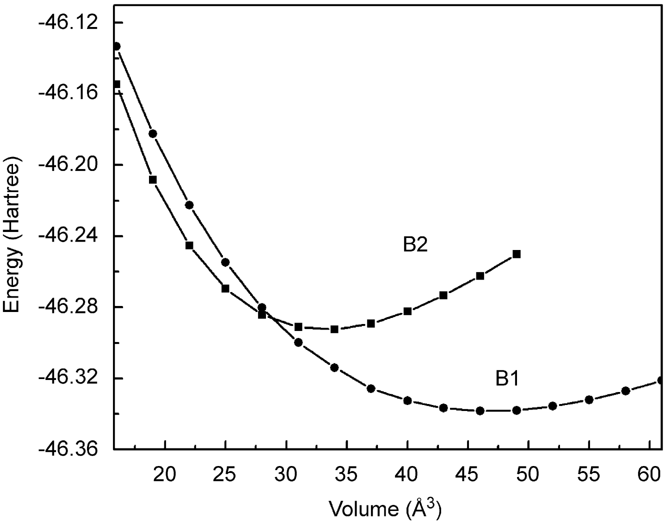

Fig. 1. Energy as a function of primitive cell volume for MgS.

$$c_{ijkl} = C_{ijkl} + \frac{P}{2}(2\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}), \tag{2}$$

$$C_{ijkl} = \left(\frac{1}{V(x)}\frac{\partial^2 Ex}{\partial e_{ij}\partial e_{kl}}\right)_X, \tag{3}$$

where $C_{ijkl}$ denotes the second-order derivatives with respect to the infinitesimal strain (Eulerian) [35–40]. The fourth rank tensor $c$ has generally 21 independent components. However, this number is greatly reduced when taking into account the symmetry of the crystal. In the cubic crystals, MgS, there are only three independent elastic constants, i.e. $c_{11}$, $c_{12}$ and $c_{44}$. In our calculations, for all strains, $\delta = \pm 0.0006$, $\pm 0.00018$, $\pm 0.003$ are taken into calculation of the total energies $E$ for the strained crystal structure. The calculated $E$–$\delta$ points are then fitted to second-order polynomials $E(V,\delta)$. In Fig. 2, we show the $E$–$\delta$ curve of the B1-phase MgS at 255.5 GPa.

Note that under hydrostatic compression, in order to compare with experimental results, the elastic constants $C_{ij}$ must be transformed into the observable elastic constants $c_{ij}$ defined with respect to the finite strain variables. $C_{ij}$ is transformed into $c_{ij}$ in the case of hydrostatic pressure $P$ as follows [39,40]:

$$c_{11} = C_{11}, \quad c_{12} = C_{12} + P, \quad c_{44} = C_{44} - \frac{P}{2}. \tag{4}$$

The adiabatic bulk $B_S$ and the shear modulus $G$ can be defined by the following equations [37,41]:

$$B_S = \frac{c_{11} + 2c_{12}}{3}, \quad G = \frac{1}{2}\left[\frac{(c_{11} - c_{12}) + 3c_{44}}{5} + \frac{5c_{44}(c_{11} - c_{12})}{4c_{44} + 3(c_{11} - c_{12})}\right]. \tag{5}$$

Calculated elastic constants $c_{ij}$, the adiabatic bulk $B_S$ and the shear modulus $G$ of the B1 and B2 phases MgS are also presented in Table 1 at zero pressure and zero temperature.