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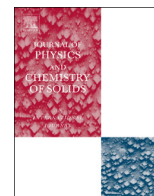
First-principle study of phase stability, electronic structure and thermodynamic properties of cadmium sulfide under high pressure

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ABSTRACT

By employing first principle and a quasi-harmonic Debye model, we study the phase stability, phase transition, electronic structure and thermodynamic properties of cadmium sulfide (CdS). The results indicate that CdS is a typical ionic crystal and that the zinc-blende phase in CdS is thermodynamically unstable. Moreover, the heat capacity of the wurtzite and rocksalt phases of CdS decreases with pressure and increases with temperature, obeying the rule of the Debye T^3 law at low temperature and the Dulong–Petit limit at high temperature.

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1. Introduction

With the rapid development of optoelectronic devices, wide band-gap semiconductors have received considerable attention for their phase stability and thermodynamic properties. Cadmium chalcogenides are considered prospective new optoelectronic device materials [1–3], including cadmium sulfide (CdS), cadmium selenide and cadmium telluride. CdS has been widely used in optical and chemical cells and energy storage devices [4–8] for its unique physical properties. Many experiments on CdS have focused on the material's optical, electrical and catalytic properties. However, there are hardly any reports on the phase stability and thermodynamic properties of CdS.

There are three crystal structures in CdS: wurtzite structure (WZ), zinc-blende structure (ZB), and rocksalt structure (RS). The WZ structure exists under normal pressure and temperature with a band gap of 2.42 eV [9–11]. The ZB and RS phases exhibit different elastic constants and thermal expansion coefficients. For the application of CdS in optoelectronic devices, it is essential to clarify the properties of these three phases under different pressures and temperatures. There are only two reported phase transitions. One is from single ZB to the RS phase and another is from WZ to the RS phase, which have been proved experimentally [10,12–15]. In this work, first principle and a quasi-harmonic

Debye modelare employed to reveal the phase stability and electronic structure of CdS under different pressures and temperatures. Moreover, the thermodynamic and elastic properties of CdS are determined.

Calculated results indicate that in the ground state the most stable state is WZ, and at high pressure, the most stable state is RS. The ZB phase is thermodynamically unstable. These results are notably useful for the application of optoelectronic devices fabricated using CdS.

2. Theoretical method

In this work, the phase stability and electronic and thermodynamic properties of CdS are described by the density functional theory (DFT) and a quasi-harmonic Debye model (GIBBS code [16,17]). All DFT calculations performed in our study are based on the CASTEP code [18–22]. To obtain an optimum exchange correlation function, LDA-CA-PZ [23], GGA-PBE [24], GGA-RPBE [25], GGA-WC [26], GGA-PW91 [27] and GGA-PBESOL [28] are tested. The lattice constants (a_0 and c_0) and bulk modulus (B_0) of CdS in the ground state are obtained from these six exchange-correlation functions. The calculated results, together with results reported in other experimental and theoretical studies [10,15, 29–35], are listed in Table 1. It can be observed that data calculated by the LDA-CA-PZ function are in agreement with the experimental data. Thus, in DFT calculations, the LDA-CA-PZ function is used. Moreover, an ultra-soft pseudo-potential [29] is employed to calculate the total energy and elastic constant. The parameters

Table 1
Lattice constant a_0 and bulk modulus B_0 of the ZB, RS and WZ structures in the ground state.

Methods	ZB		RS		WZ			
	a_0 (Å)	B_0 (GPa)	a_0 (Å)	B_0 (GPa)	$a_0 = b_0$	c_0	c/a	B_0 (GPa)
Present work								
LDA	5.783	66.011	5.362	90.144	4.099	6.660	1.625	66.881
PBE	5.958	52.433	5.519	70.851	4.226	6.859	1.623	52.326
RPBE	6.024	46.894	5.575	65.611	4.272	6.935	1.624	46.467
PW91	5.956	53.077	5.517	72.025	4.223	6.854	1.623	53.444
WC	5.873	58.502	5.438	74.838	4.167	6.752	1.621	58.844
PBESOL	5.868	59.052	5.432	84.057	4.163	6.752	1.622	59.131
Other work								
Expt	5.818[a]	64.4[b]	5.44[c]	86.7[c]	4.136[a]	6.714[a]	–	62[a]
LDA	–	–	5.358[d]	92.5[d]	4.12[e]	–	1.63[e]	–
Others	5.810[e]	69.44[f]	5.3527[g]	97.28[g]	4.18[h]	6.76[h]	1.62[h]	66.4[h]

[a] Ref. [42].
[b] Ref. [43].
[c] Ref. [44].
[d] Ref. [10].
[e] Ref. [45].
[f] Ref. [15].
[g] Ref. [29].
[h] Ref. [46].

used in the calculation are listed below. The plane wave basis cut-off energy of the three phases is 290 eV. Pseudo-atomic calculations are performed for S:$3s^2 3p^4$ and Cd: $4d^{10} 5s^2$. For the calculation of the Brillouin zone (BZ), we use $4 \times 4 \times 4$ Monkhorst–Pack meshes for ZB, $6 \times 6 \times 6$ meshes for RS and $7 \times 7 \times 4$ meshes for WZ. The self-consistent convergence of the total energy is 5×10^{-7} eV/atom. A norm-conserving pseudo-potential [30,31] is employed to determine the phonon dispersion. The cut-off energy of the WZ, RS and ZB phases is 400 eV, and the k-points are $6 \times 6 \times 6$, $7 \times 7 \times 7$ and $8 \times 8 \times 6$ for the ZB, RS and WZ structures, respectively. The self-consistent convergence of the phonon dispersion calculation is 5×10^{-7} eV/atom.

The total crystal energy vs. crystal cell volume is obtained by CASTEP and fitted by the three-order Brich–Murnaghan equation of state (BM-EOS) [32], which is the most important input datum of GIBBS [16,17]. The detailed calculation methods are discussed in Refs. [22,23]. The heat capacity (C_v) of CdS as a function of temperature and pressure is calculated by employing a quasi-harmonic Debye model.

The elastic constant of CdS is obtained by a numerical DFT calculation. The elastic constants are calculated by a Taylor expansion of elastic energy $E(V, \delta)$, where V is the cell volume with a small strain δ. $E(V, \delta)$ in a strained system is expressed as follows [33]:

$$E(V, \delta) = E(V_0, 0) + V_0 \left(\sum_i \tau_i \delta_i \xi_i + \frac{1}{2} \sum_{i,j} C_{ij} \delta_i \xi_i \delta_j \xi_j \right) \quad (1)$$

where $E(V_0, 0)$ is the energy of the unstrained system with equilibrium volume V_0, τ_i is an element of the stress tensor and ξ_i is a factor that reflects the Voigt index [33]. The detailed calculated methods employed to determine the elastic constants are discussed in Ref. [34].

In our work, the thermodynamic properties of CdS are predicted over a pressure range from 0 to 100 GPa and a temperature range from 0 to 2000 K, conditions under which DFT and the quasi-harmonic model are both valid [35–37].

3. Results and discussion

Fig. 1 shows the ZB, RS and WZ phases in CdS, together with possible phase transitions. It can be observed that in the WZ and ZB cells, one cadmium atom and the four nearest sulfur atoms form a tetrahedron. Each S atom of the WZ and ZB phases is shared by the four nearest tetrahedrons. However, in the RS phase, one Cd atom and the six nearest S atoms form an octahedron. The crystal space in the WZ and ZB phases is not fully occupied by S–Cd tetrahedrons, and the tetrahedral units of the WZ phase are arranged much more loosely than those of ZB. However, RS is filled by close-packed octahedrons without any interstice.

To determine the thermodynamic stability of these CdS phases, a series of geometrical optimizations are applied in our calculation. The relative enthalpies ΔH per molecule as a function of pressure are shown in Fig. 2(a) (here, $\Delta H_{RS} = H_{RS} - H_{RS}$, $\Delta H_{ZB} = H_{ZB} - H_{RS}$, $\Delta H_{WZ} = H_{WZ} - H_{RS}$.). The value of ΔH in the ZB phase is greater than that of WZ, which indicates that WZ is more stable than ZB under the same pressure. At pressures above 2.18 GPa, the relative enthalpy of RS is lower than that of WZ. This result implies that a phase transition from RS to WZ occurs at 2.18 GPa and that the ZB phase is not stable or non-existent. The phase transition point (2.18 GPa) from RS to WZ is in good agreement with the experimental result reported by Osugi et al. (2.25 GPa) [12]. Fig. 2(b) shows that there is a 20% volume collapse during the phase transition from WZ to RS. Thus, CdS in the RS structure is more compact than that in the WZ structure, which agrees with what is shown in Fig. 1.

Fig. 3(a)–(i) shows the phonon dispersion of the WZ, ZB and RS phases in CdS under different pressures. The imaginary phonon frequency in ZB implies dynamic instability. A softening tendency of the phonons can be observed in this figure. For the WZ and ZB phases, the phonon frequencies of both points H and L in BZ become soft with an increase in pressure. In addition, an imaginary frequency appears at pressures below 6 GPa, as shown in Fig. 3(a)–(f). This finding implies that the phase stability of WZ and ZB becomes weak at high pressures. However, there is no imaginary phonon frequency in the RS phase or distinct optical branch softening throughout the entire BZ phase, which indicates that RS is the dynamically stable phase under high pressures, as shown in Fig. 3(g)–(i).

Fig. 4 shows the elastic constants and mechanical stability of the ZB and RS phases under high pressures. For a cubic crystal, the mechanical stability criterion is [34]

$$\tilde{C}_{44} > 0, \tilde{C}_{11} - |\tilde{C}_{12}| > 0, \tilde{C}_{11} + 2\tilde{C}_{12} > 0 \quad (2)$$

where $\tilde{C}_{\alpha\alpha} = C_{\alpha\alpha} - P, \tilde{C}_{12} = C_{12} > 0$. $\tilde{C}_{44}$ and $\tilde{C}_{11} - |\tilde{C}_{12}|$ in the ZB phase clearly decreases with an increase in pressure, and