

High pressure phase transitions for CdSe

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Abstract. The structure and pressure-induced phase transitions for CdSe are investigated using first-principles calculations. The pressure-induced phase transition sequence $WZ/ZB \rightarrow Rs \rightarrow Cmcm \rightarrow CsCl$ for CdSe is drawn reasonably for the first time, the corresponding transition pressures are 3.8, 29 and 107 GPa, respectively and the intermediate states between the *Cmcm* structure and the *CsCl* structure should exist.

Keywords. Semiconductor; high pressure; phase transition.

1. Introduction

CdSe has become quite interesting and important because of its major applications in solar cells and other optoelectronic devices due to its optimum bandgap (~ 1.9 eV), high absorption coefficient and n-type of conductivity. CdSe, along with some additive in it, forms an important class of semiconductor materials, which finds applications in low cost devices such as LEDs, solar panels, photodetectors, lasers, gas sensors, thin film transistors, etc. (Ramaiah *et al* 2001; Hankare *et al* 2004). So, it is not surprising that a great deal of fundamental studies in experiments have been done on CdSe bulk crystals (Hodes *et al* 1987; He *et al* 2008), nanocrystals (Asami *et al* 2003; Chahboun *et al* 2009), especially on CdSe thin films (Bhuse 2005; Chen *et al* 2008; Mohamed *et al* 2011) in recent years; while in theory, most authors mainly focused on the studies of bulk crystals because of the limitations of calculations. These theoretical researches involved in the crystal structure, electronic band structure, dielectric function and vibrational properties of CdSe at zero temperature and zero pressure (Huang and Ching 1993; Xu and Ching 1993; Ouendadji *et al* 2011), the pressure dependences of bandgap and elastic constants (Deligoz *et al* 2006; Zhuravlev 2007; Sarasamak 2010) as well as the pressure-induced phase transitions (Payne *et al* 1992; Zakharov *et al* 1995; Cote *et al* 1997; Benkhetou *et al* 2004). However, some problems about the high pressure phase transitions of CdSe need to be further clarified. In experiments, the pressure-induced phase transition sequence $WZ/ZB \rightarrow Rs \rightarrow Cmcm$ for CdSe was

observed at around 3 (Milman *et al* 2000) and 27 GPa (Perdew *et al* 1996), respectively. In theory, Zakharov *et al* (1995) predicted firstly a high pressure phase transition from *Rs* to *CsCl*-type at about 95 GPa using *ab initio* pseudopotential method within the local-density approximation. The transition sequence under pressure $WZ/ZB \rightarrow Rs \rightarrow Cmcm$ for CdSe has also been successfully simulated using the similar method in 1997 (Cote *et al* 1997), the corresponding transition pressures are 2.5 and 29 G, respectively. Later in 2004, Benkhetou *et al* (2004) again investigated the high pressure phase transitions of CdSe using the full-potential linear muffin-tin-orbital method (FP-LMTO), they obtained the pressure-induced phase transition sequence $WZ/ZB \rightarrow Rs \rightarrow CsCl \rightarrow Cmcm$ and the corresponding transition pressures were about 3, 15, 21 GPa, respectively. It is noted that the results from Zakharov *et al* (1995) and Benkhetou *et al* (2004) have very large difference, while the high pressure *CsCl* phase is not observed until now (Benkhetou *et al* 2004). Thus, further theoretical and experimental works are desired.

In the present work, the crystal structure, as well as the pressure-induced structural phase transitions of CdSe were investigated using first-principles calculations. The organization of this communication is as follows. In §2, we give the computational details. The results and detailed discussions are presented in §3. A short conclusion is drawn in §4.

2. Theoretical methods

2.1 Total energy electronic structure calculations

We calculated the electronic structures of CdSe using the plane-wave pseudopotential density functional theory

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method through the Cambridge Serial Total Energy Package (CASTEP) (Payne *et al* 1992; Milman *et al* 2000), together with the generalized gradient approximation (GGA-PBE) (Perdew *et al* 1996) for the exchange–correlation function. The Kohn–Sham equation was solved by means of the ultrasoft pseudopotentials introduced by Vanderbilt (1990). Pseudo-atomic calculations were performed for Cd $4d^{10}5s^2$ and Se $4s^24p^4$. Integration over the Brillouin-zone (BZ) was executed using $20 \times 20 \times 18$ and $20 \times 20 \times 20$ Monkhorst–Pack grids for hexagonal (WZ) and cubic (ZB) CdSe, respectively. The cutoff energy in the calculations was 500 eV. The convergence of the total energies within 10^{-6} eV/atom was ensured with these parameters. A full optimization of the unit cell structure for each target external pressure was performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique (Pfrommer *et al* 1997), which can let one obtain the structural parameters, energies and enthalpies for one crystal at different hydrostatic pressures. The drawn $E(V)$ data were fitted to the Birch–Murnaghan equation of states (Birch 1947) under the quasi-harmonic Debye model (Blanco *et al* 2004). The equilibrium Gibbs free energy and bulk modulus and the first pressure derivative of bulk modulus at different pressures and temperatures were extracted.

3. Results and discussion

3.1 Ground state structure and thermal equation of state

In the cubic zinc-blende (ZB) and hexagonal wurzite (WZ) phases, the calculated zero-pressure equilibrium lattice constants, equilibrium cell volume V_0 , bulk modulus B_0 and its pressure derivative B'_0 together with the available experimental (Madelung *et al* 1982; Bonello and Fernandez 1993) and theoretical data (Rabani 2002; Deligoz *et al* 2006; Zhuravlev 2007) are summarized in table 1. It is seen that the obtained equilibrium lattice constants and cell volumes with CASTEP code (GGA-PBE) are a little bigger than the experimental data so that the drawn bulk modulus are underestimated. This may be due to the fact that GGA calculations usually overestimate the structural parameters (Zaoui and Elhaj Hassan 2001).

The thermal EOS is a measurement of the relationship among pressure, volume, and temperature (P – V – T). The inclusion of temperature makes it more important than P – V EOS . In figure 1, we illustrate the normalized cell volume dependence on pressure for the ZB structural CdSe from 0 to 10 GPa at 0 K, 300, 500 and 800 K. The temperature effect is considered through the quasi-harmonic Debye model (Blanco *et al* 2004). Unfortunately, there are no available experimental or theoretical data for the comparison. It is noted that the normalized cell volume V/V_0 decreases with increasing pressure at a given temperature, and is not sensitive to temperature especially at low pressure. At a given pressure, the normalized cell volume V/V_0 of the ZB structural CdSe also decreases with increasing temperature, which means it is easier to compress CdSe at high temperature. In fact, the ZB or WZ structural CdSe transforms to RS structure (NaCl structure) around 3 GPa in experiment (Yu and Gielisse 1971); whether the ZB or WZ structural CdSe will transform to other structure with increasing temperature is unknown. In principle, one could obtain the phase diagram of one crystal material combining first-principle calculations and the quasi-harmonic Debye model since Gibbs free energy, at different pressures and temperatures for the different structural phases, could be extracted from the calculated E – V data points. However, there are almost no reports about the successful examples for our best knowledge. This is the serious limitation of the quasi-harmonic Debye model, although the model has been applied successfully to the investigations of the thermodynamics properties of many materials (Bouhemadou *et al* 2011; Sun *et al* 2011).

3.2 High pressure phase transition

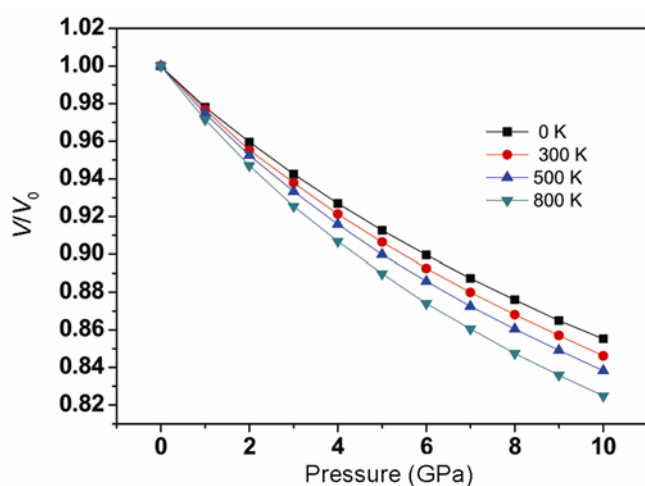
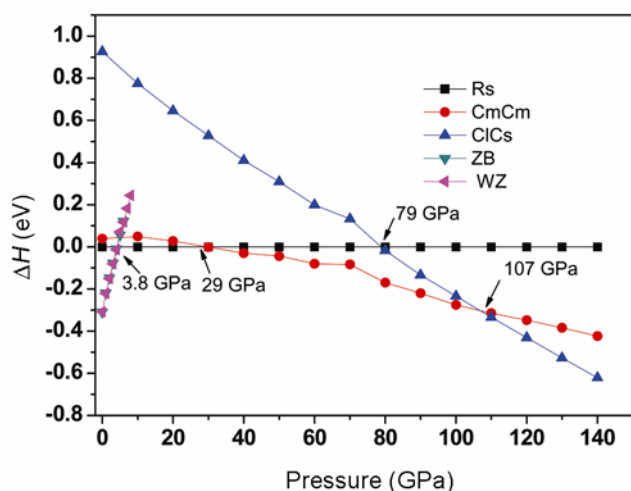
From the drawn Gibbs free energy with the help of the quasi-harmonic Debye model, it is difficult to calculate and discuss the phase transition of one crystal material. This is pointed out in §3.1. So the investigations for the high pressure phase transitions of CdSe were carried out using Broyden–Fletcher–Goldfarb–Shanno (BFGS) minimization technique (Pfrommer *et al* 1997) implemented in CASTEP code.

Table 1. Lattice constants a and c (Å), primitive cell volume V_0 (Å³), bulk modulus B_0 and its pressure derivative B'_0 for ZB and WZ structural CdSe at 0 GPa and 0 K.

Structure			V_0	a	c	B	B'
ZB	Theory	Present	59.87	4.391		43.9	4.839
		Benkhettou <i>et al</i> (2004)	56.08	4.292		59.2	4.67
		Deligoz <i>et al</i> (2006)	55.36	4.277		65.12	4.2
	Experiment	Madelung <i>et al</i> (1982)	56.10	4.297		53	
WZ	Theory	Present	119.85	4.391	7.175	44.2	4.803
		Zhuravlev (2007)		4.3	7.02	53.6	4.57
		Rabani (2002)		4.34	7.02	45.6	
	Experiment	Bonello and Fernandez (1993)	112.5	4.298	7.01	53.4	

Table 2. Transition pressure P_t (GPa) and the corresponding volume collapses at 0 K for CdSe.

Structural transitions	Transition pressure P_t			Volume collapses (%)		
	Theory		Experiment	Theory		
	Present	Others		Present	Others	Experiment
WZ/ZB \rightarrow Rs	3.8	3.5 (Benkhetou <i>et al</i> 2004), 2.5 (Cote <i>et al</i> 1997)	3 (Yu and Gielisse, 1971)	19.6	19.8 (Cote <i>et al</i> 1997)	
Rs \rightarrow <i>Cmcm</i>	29	20 (Benkhetou <i>et al</i> 2004), 29 (Cote <i>et al</i> 1997)	27 (McMahon and Nelmes 1996)	1.4	1.7 (Cote <i>et al</i> 1997)	
<i>Cmcm</i> \rightarrow CsCl	107			3.6		
Rs \rightarrow CsCl	79	95 (Zakharov <i>et al</i> 1995) 15 (Benkhetou <i>et al</i> 2004)		5.6		

**Figure 1.** Thermal equations of state of ZB structural CdSe at $T = 0, 300, 500$ and 800 K.**Figure 2.** Enthalpy as a function of pressure for WZ, ZB, Rs, *Cmcm*, CsCl structures taking Rs structure as reference for CdSe at 0 GPa and 0 K.

The intersections of the enthalpy-pressure curves of different structures in figure 2 show the transition pressures from one structure to the other structure and the stable ranges of the different structures. It is seen that the enthalpies of the WZ and ZB structural CdSe are almost same in the pressure range from 0 to 6 GPa. This corresponds to the fact that CdSe can crystallize in the WZ or ZB structure at ambient conditions. At about 3.8 GPa, the WZ/ZB structure transforms to the Rs structure. With continuous increasing pressure, the Rs structure transforms to the *Cmcm* structure at about 29 GPa. At the pressure, the optimized structural parameters for the *Cmcm* structure are: Cd: $4c$ 0, 0.691, 0.25; Se: $4c$: 0, 0.198, 0.25 with $a = 5.245$, $b = 5.328$ and $c = 5.135$ Å. The *Cmcm* structure is stable in the pressure range from 29 to 107 GPa. After 107 GPa, the CsCl structure is more stable than the *Cmcm* structure. These transition pressures as well as the corresponding changes of volume collapses at transition points are listed in table 2 together with the available experimental and other theoretical data. It is seen that the present theoretical transition pressures from the WZ/ZB structure to the Rs structure and from the Rs structure to the *Cmcm* structure are overestimated by about 0.8 and 2 GPa respectively, in contrast to the experimental data (Yu and Gielisse 1971; McMahon and Nelmes 1996). The deviations may originate in the above mentioned GGA calculations. From the deviations, it can be speculated that the drawn transition pressures from the RS structure to the CsCl structure or from the *Cmcm* structure to the CsCl structure also should be overestimated. The transition pressure from the *Cmcm* structure to the CsCl structure may be lower than 100 GPa. The overestimated transition pressures and the above overestimated lattice constants show the limitations of the theoretical techniques used in this work. However, the theoretical transition pressure from the RS structure to the CsCl structure is lower than the theoretical result obtained by Zakharov *et al* (1995). So, the present theoretical predictions may be more reasonable than those of

Zakharov *et al* (1995). Combining with the above contrast between the theory and the experiments, the deviations should be in an appropriate range. In addition, the following several points need to be emphasized: (i) the present theoretical transition pressure from RS to CsCl is near to the result of Zakharov *et al* (1995), while Benkhetou *et al* (2004) underestimated the transition pressure, further obtaining the unreasonable phase transition sequence and the inappropriate stable ranges of phases (Benkhetou *et al* 2004); (ii) the *Cmcm* structure is the intermediate state from Rs to CsCl, and a reasonable pressure-induced phase transition sequence $WZ/ZB \rightarrow Rs \rightarrow Cmcm \rightarrow CsCl$ is drawn. In an experiment, Nelmes and McMahon (1998) carried out an ADX study of CdSe up to 85 GPa and found the evidence of a further transition from the *Cmcm* structure to a distorted-*Cmcm* structure at 36 GPa. This distorted-*Cmcm* structure has so far remained unsolved despite considerable experimental efforts, while the present stable range (29–107 GPa) for the *Cmcm* structure is much larger than the observed stable range (27–36 GPa). So, there should be certain intermediate states between the *Cmcm* structure and the CsCl structure and (iii) the change of volume collapse at the transition from Rs to *Cmcm* is very small and the structural transition might belong to the second-order phase transition, while other transitions should attribute to the first-order phase transitions.

4. Conclusions

In the short communication, the pressure-induced phase transition sequence $WZ/ZB \rightarrow Rs \rightarrow Cmcm \rightarrow CsCl$ for CdSe was drawn reasonably for the first time. The corresponding transition pressures are 3.8, 29 and 107 GPa, respectively. The transition *Cmcm* \rightarrow CsCl was predicted appropriately. Combining with the experimental data, it was speculated that there should be the intermediate states between the *Cmcm* structure and the CsCl structure. This may provide a reference for the future experimental and theoretical studies.

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