



# Orthorhombic intermediate phases for the wurtzite-to-rocksalt phase transformation of CdSe: An *ab initio* constant pressure study

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## ABSTRACT

Pressure-induced phase transition of CdSe is studied using constant pressure *ab initio* molecular dynamic simulations. A phase transition from the wurtzite structure to a rocksalt structure is successfully observed through the simulations. Based on the constant pressure simulation's results, we propose a transformation mechanism having two orthorhombic intermediate phases within  $Cmc2_1$  and  $Cmcm$  symmetries.

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## 1. Introduction

The pressure-induced phase transformations from the fourfold to sixfold coordinated structure in binary semiconducting compounds are a fundamental topic in condensed matter physics. Of particular interest are wurtzite (WZ)-type materials. The WZ-to-rocksalt (RS) phase transition has been studied extensively for decades and considerable information concerning this phase change has been obtained. Yet a clear atomic level picture of this phase transition could not be obtained in static high pressure experiments. In the past few years, much effort has been devoted to determine the transition mechanism of the WZ-to-RS phase transition because an understanding of its mechanism is very important for technological applications and controlling transition process. Recently, the direct observation of the transition pathway became possible experimentally using picosecond time-resolved electronic spectroscopy in shock wave experiments [1] or by monitoring the shape changes of nanocrystals [2].

The WZ-to-RS phase transformation, in particular the transformation mechanism of this simple phase transformation, has been studied extensively [1–15] and so far several mechanisms having different intermediate phases have been proposed. Some conclusions presented in these studies, however, have been challenged by other studies [6,10–12].

At ambient conditions, CdSe crystallizes in the WZ structure. The metastable zinc-blende phase can be grown using molecular

beam epitaxy. As seen in most WZ materials, CdSe transforms into a RS structure with the application of pressure [16–20]. This phase transformation was successfully reproduced in molecular dynamics (MD) simulations [3] in which multiple transformation mechanisms (including hexagonal pathway in which a WZ structure is first compressed along the *c*-axis, resulting into a fivefold coordinated hexagonal intermediate state with space group  $P6_3/mmc$  and then a RS phase form through the opening of the hexagonal angle) with almost the same energy barrier were proposed. The phase transformation of CdSe was also reproduced at a transition pressure, close to the experimental value, using metadynamics technique with an empirical potential and it was suggested that the phase transition takes place with the characters of hexagonal mechanism [9].

In principle, *ab initio* techniques produce more accurate results and hence they are ideally suited to eliminate limitations or doubts observed in empirical potentials. Here we use, for the first time, a constant pressure *ab initio* MD technique to study the pressure-induced phase transition in CdSe and propose that this simple phase transformation proceeds via two orthorhombic intermediate phases, different from the previously proposed mechanisms.

## 2. Method

We used the first-principles pseudopotential method within density functional theory and the generalized gradient approximation of Perdew–Burke and Ernzerhof for the exchange–correlation energy [21]. The calculation was carried out with the *ab initio* program SIESTA [22] using a linear combination of atomic orbitals as the basis set, and norm-conservative Troullier–Martins

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pseudopotentials [23]. A split-valence double- $\xi$  plus polarized basis set was employed. A uniform mesh with a plane wave cut-off of 350 Ry was used to represent the electron density, the local part of the pseudopotentials, and the Hartree and the exchange–correlation potential. The simulation cell consists of 72 atoms with periodic boundary conditions. We used  $\Gamma$ -point sampling for the Brillouin zone integration. The system was first equilibrated at zero pressure, and then pressure was gradually increased by an increment of 3.0 GPa. For each value of the applied pressure, the structure was allowed to relax and find its equilibrium volume and lowest-energy by optimizing its lattice vectors and atomic positions together until the stress tolerance was less than 0.5 GPa and the maximum atomic force was smaller than  $0.01 \text{ eV \AA}^{-1}$ . For minimization of geometries, a variable-cell shape conjugate-gradient method under a constant pressure was used. For the energy volume calculations, we considered the primitive cell for CdSe phases. The Brillouin zone integration was performed with automatically generated  $10 \times 10 \times 10$  k-point mesh for the phases following the convention of Monkhorst and Pack [24]. In order to determine symmetry of the high pressure phases formed in the simulations, we used the KPLLOT program [25] that provides detailed information about space group, cell parameters and atomic position of a given structure. For the symmetry analysis we used  $0.2 \text{ \AA}$ ,  $4^\circ$ , and  $0.7 \text{ \AA}$  tolerances for bond lengths, bond angles and interplanar spacing, respectively.

### 3. Results

In order to determine the nature of the phase transition of CdSe in the dynamical simulation, we first plot its pressure–volume curve in Fig. 1. Accordingly, the volume monotonically decreases with increasing pressure and the WZ state is still preserved to 9 GPa. As the pressure is increased from 9 to 12 GPa, the structural phase transition begins and is accompanied by a sharp volume drop, which is a characteristic of a first-order phase transition. Owing to the transformation, the WZ structure converts into a RS structure in excellent agreement with experiments. However, the predicted transition pressure is noticeably larger than the experimental result of about 2–3 GPa [16–20]. This result is anticipated because the simulation conditions such as loading rate, the limited box size, the lack of defects in the simulated structure and the use of periodic boundary conditions are significantly different from the experimental ones. Experimentally, phase transformations proceed via nucleation of a new phase, which often start on the surface or on structural defects. The periodic boundary conditions eliminate surfaces and lead to an additional coupling of the ions in the simulation box. The lack of any defects in the simulated structure also

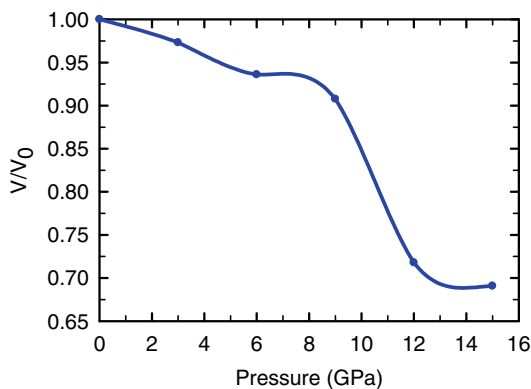


Fig. 1. Pressure–volume curve of the WZ CdSe as a function of pressure.

suppresses nucleation and growing. These tend to favor a phase change, in which the whole system undergoes the phase transformation as a collective movement of all ions. As a result, systems have to cross a significant energy barrier to transform from one phase to another one. Additionally the absence of thermal motion (relaxation of the structure at constant pressure) in our simulations shifts the transitions to a higher pressure. On the other hand, the thermodynamic theorem does not take into account the possible existence of such an activation barrier separating the two structural phases and the thermal motion. Therefore, as a next step, we consider the energy–volume calculations to study the stability of the WZ and RS phases. We fit their energy–volume data to the third-order Birch–Murnaghan equation of state and they are shown in Fig. 2. In order to determine the transition pressure at  $T = 0 \text{ K}$ , we calculate the enthalpy,  $H = E + PV$ , where  $P = -dE/dV$  is obtained by direct differentiation of the calculated the energy–volume curves. The stable structure at a given pressure is the state for which the enthalpy has its lowest value and the transition pressure is calculated at which the enthalpies for the two phases are equal. Fig. 3 shows the enthalpy curves of both WZ and RS phases. We obtain a transition pressure of about 1.8 GPa, which is comparable with the experimental result of about 2.0–3.0 GPa [16–20].

In the simulations, we can easily track the transformation mechanism of this phase change by simply analyzing the modification of the simulation cell vectors and the motion of the atomic coordinates. Fig. 4 shows the modification of the simulation cell lengths and angles at 12.0 GPa as a function of minimization step. The simulation cell vectors **A**, **B**, and **C** are the  $[100]$ ,  $[\bar{1}10]$  and  $[001]$  directions, respectively. The magnitude of these vectors is plotted in figure. We observe a simultaneous compression along the  $c$ -direction and shear deformation on the  $a$ – $b$  planes in the structure during the phase transformation. The hexagonal angle between **A** and **B** lattice vectors gradually changes from  $120^\circ$  about  $90^\circ$ . This mechanism is similar to the hexagonal and tetragonal paths proposed or observed for WZ materials; in the hexagonal path a WZ structure is first compressed along the  $c$ -axis, resulting in a fivefold coordinated hexagonal intermediate state with space group  $P6_3/mmc$  and then a RS phase forms through the opening of the hexagonal angle whereas in the tetragonal pathway, the hexagonal angle first opens up and the atoms move horizontally to the center of the square and then a decreasing in the  $a/c$  ratio results in a RS state. Note that the hexagonal and tetragonal mechanisms proceed in two steps while the transition observed in the present study occurs in one step.

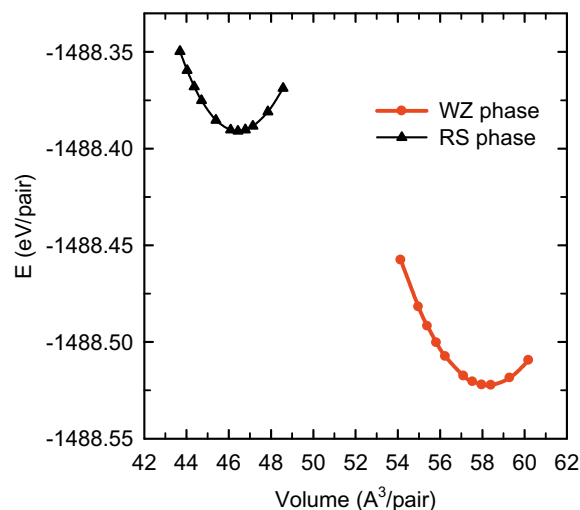


Fig. 2. Energy–volume relations.

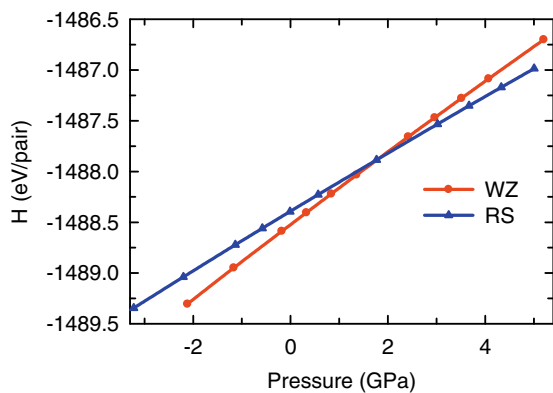


Fig. 3. Enthalpy curves of the WZ and RS phase of CdSe.

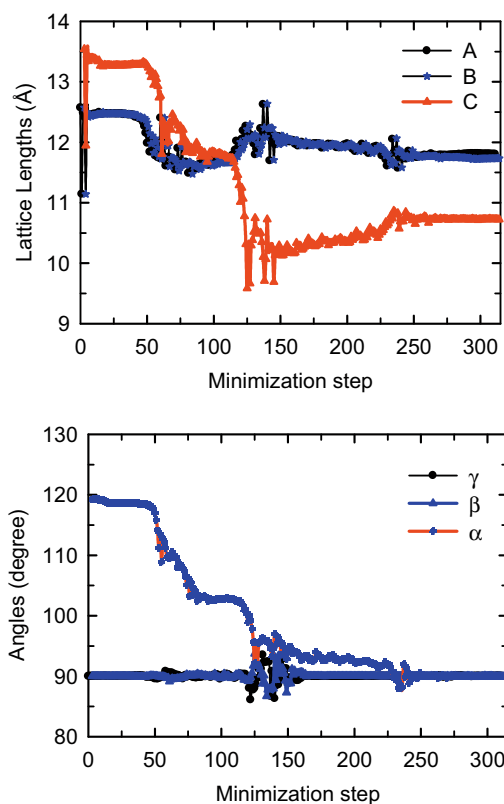


Fig. 4. Change the simulation cell lengths and angles as a function of minimization step at 12 GPa.

In order to determine the intermediate phases formed in our simulation we carefully analyze the structure each minimization step using the KPLOT program. At 12 minimization step, we determine an orthorhombic structure having  $Cmc2_1$  symmetry. The lattice constant of this phase are  $a = 4.51 \text{ \AA}$ ,  $b = 6.92 \text{ \AA}$ ,  $c = 6.39 \text{ \AA}$ . At

**Table 1**  
The atomic fractional coordinates and the lattice parameters of the intermediate phases formed at 12 GPa.

Structure	$a$ (Å)	$b$ (Å)	$c$ (Å)	$x$	$y$	$z$
$Cmc2_1$	4.51	6.92	6.39	Cd: 0.0	0.6506	0.9891
				Se: 0.0	0.7059	0.5924
$Cmcm$	5.53	5.62	5.32	Cd: 0.0	0.7991	0.25
				Se: 0.0	0.2889	0.25

later minimization step, another orthorhombic intermediate phase within  $Cmcm$  symmetry is identified, whose lattice parameters are  $a = 5.51 \text{ \AA}$ ,  $b = 5.62 \text{ \AA}$  and  $c = 5.30 \text{ \AA}$ . At 250 minimization step, a RS structure forms. The lattice parameters and atomic positions of these intermediate phases are given in Table 1. The evolution of the WZ-to-RS phase transformation presented in Fig. 5.

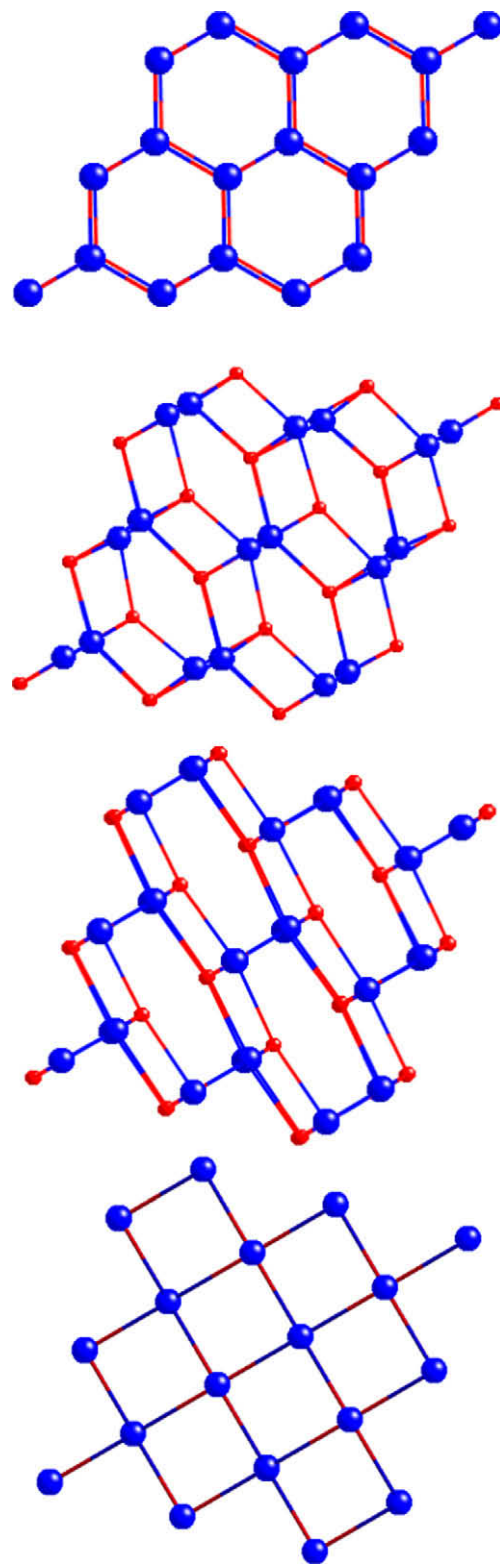


Fig. 5. At 12 GPa, evolution of the rocksalt structure.

#### 4. Discussion

The  $Cmc2_1$  and  $Cmcm$  orthorhombic intermediate phases observed in our simulation have not been observed in any previous MD simulations, to our knowledge. On the other hand, a  $Cmc2_1$  intermediate phase has been predicted in systematic group-theoretical analysis [15] and geometrical sphere packing methods [14]. However, our prediction does not agree with the previous MD simulations of CdSe based on empirical potentials and with the mechanism (a shearing of (1 1 0) layers) obtained using transition path sampling methods based on an empirical potential [26]. One might think that the discrepancy between the present and the classical MD simulations might be due to the limitation of empirical potentials, or some limitations such as finite size artifacts, loading conditions and overestimated transition pressure in our simulation. We need to underline here that using the same pressure controlling technique, the size of simulation cell and loading conditions, we were able to observe a first-order pressure-induced phase transformation into a RS state in WZ-BeO and AlN via the hexagonal intermediate state [8,13]. Additionally, we found that WZ-SiC (108 atoms) followed the same hexagonal pathway [5]. Furthermore, we studied the WZ-SiC and BeO under different loading conditions and found that the loading conditions have no influence on their mechanism. Therefore, we can say that the different mechanism observed in CdSe might not be associated with the size of simulation cell or loading conditions but the overestimated transition pressure. The critical pressure predicted in our simulation is considerably larger than ones observed in MD simulations. The different transition pressure might produce different pathways. Indeed, recent energy landscape calculations [12] suggest that the WZ-to-RS phase transformation mechanism for some WZ materials (but not all) is sensitive to the critical pressure and they might follow different pathways at low and high pressures. Consequently, the different mechanisms observed in CdSe might be due to overestimated transition pressure in our simulation. Nevertheless, the present simulation suggests, for the first time, a mechanism based on two orthorhombic intermediate phases for the WZ-to-RS phase transformation. In order to determine whether the transition mechanism obtained our simulation is related to the overestimated transition pressure or the mechanism observed in the MD simulations are associated with the empirical potentials, it is worth repeating the same type of simulation in CdSe using a DFT code with metadynamics technique [9] or path sampling methods [27].

#### 5. Conclusions

The stability of CdSe at high pressure is studied using a constant pressure *ab initio* technique. A first-order phase transformation

from the WZ structure to a RS structure successfully is reproduced in the simulations. Our finding suggests that the transformation proceeds via two orthorhombic intermediate phases having  $Cmc2_1$  and  $Cmcm$  symmetries. This mechanism is for first time observed in a constant pressure simulation and is consistent with group-theoretical analysis and geometrical sphere packing methods. Our finding provides different perspectives on the transformation mechanism of the WZ-to-RS phase change.

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