

CHEMICAL THERMODYNAMICS  
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# Ab Initio Molecular Dynamics Simulation of Pressure-Induced Phase Transition in MgS<sup>1</sup>

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**Abstract**—Pressure-induced phase transition in MgS is studied using a constant pressure ab initio molecular dynamics method, and a solid evidence of existence of its high-pressure phase is provided. As predicted by total energy calculations, MgS undergoes a structural phase transformation from the rocksalt structure to a CsCl-type structure under hydrostatic pressure. The transformation mechanism is characterized, and two intermediate phases having  $P4/nmm$  and  $P2_1/m$  symmetries for the rocksalt-to-CsCl-type phase transformation of MgS are proposed, which is different from the previously proposed mechanisms. We also study this phase transition using the total energy calculations. Our predicted transition parameters and bulk properties are in good agreement with the earlier first principle simulations.

**Keywords:** ab initio molecular dynamics, phase transition, high-pressure effects in solids, semiconductors

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## 1. INTRODUCTION

The magnesium chalcogenides, MgSe, MgS, and MgTe, which are wide band gap semiconductors have attracted much attention in recent years because of the increasing demand for a wide range of semiconductors for various electrical and optical devices. They have a wide range of applications in opto-electronics [1] and luminescent devices [2]. Therefore, these binary compounds have been extensively studied experimentally and theoretically [3–17]. The magnesium chalcogenides can crystallize in the rocksalt (RS), zincblende (ZB), and wurtzite (WZ) structures, but their ground state and high pressure structures are still remaining puzzle.

Experiments suggested that the MgS at its ground state under ambient conditions belongs to RS structural type [3]. The MgS crystals with ZB structure were also prepared by epitaxial growth over GaAs substrate [4–6]. Additionally, the WZ state of MgS was also synthesized after annealing of their evaporated thin films by electron bombardment [7]. The theoretical calculations based on density functional theory (DFT) carefully analyzed these three structures and suggested that the RS state is energetically more favorable than the other phases but the relative energy differences between phases are very small.

The MgS phase with NaCl structure was found to be stable up to 54 GPa [3]. To our knowledge, no

phase transformations were observed experimentally in MgS so far. The theoretical calculations based on DFT, on the other hand, suggested a possible pressure-induced phase transformation from the RS state to the cesium chloride (CsCl) type structure at 200–255 GPa [8, 11]. These theoretical simulations are based on the energy-volume calculations and the thermodynamic criterion of Gibbs free energies, and have to rely on educated guesses on the possible structures and offer no clue as to dynamics. Perhaps, the CsCl-type phase is the best candidate for the high pressure phase of MgS because the materials having RS structure at ambient conditions often transform into the eightfold coordinated CsCl-type structure upon the application of pressure. Yet there are some exceptional cases. Perhaps the best example is the behavior of MgSe; Ruoff et al. [18] have studied MgSe using both energy dispersive X-ray diffraction (EDXD) at pressures up to 202 GPa and first principles calculations with a local density approximation and ultrasoft pseudopotentials up to 500 GPa. The authors found that MgSe undergoes a continuous phase transformation from the RS-type to FeSi-type beginning at around  $99 \pm 8$  GPa and approaching sevenfold coordination at 202 GPa. On the other hand, theoretical investigation suggests the transition to FeSi-type begins at 58 GPa, and the transformation to the CsCl structure with orthorhombic distortion occurs at 429 GPa. The observation of FeSi-type phase, particularly, in a magnesium chalcogenide MgSe, implies that it is also a

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strong candidate for high pressure phase of MgS. In addition, the hexagonal NiAs-type and the orthorhombic *Pnma* phases are also a possible structures, because BaO converts to the hexagonal NiAs-type phase [19] and PbTe transforms into an orthorhombic *Pnma* structure [20] at high pressures.

Which path does MgS follow at high pressure? The answer of this question remains unsolved for decades. The aim of this study is to solve this problem using ab initio molecular dynamics (MD) simulations. Our findings indicate that MgS does indeed transform into a CsCl-type phase. The simulations also allow us to characterize the mechanism of the RS-to-CsCl phase transformation and suggest that it proceeds via two intermediate phases with *P4/nmm* and *P21/m* symmetries. The transformation mechanism observed for MgS appears to differ from the previously proposed mechanisms.

## 2. METHOD

All calculations were performed using the SIESTA code [21], which is based on the first principles pseudopotential method within DFT. For the Kohn-Sham Hamiltonian, the generalized-gradient approximation (GGA) for the exchange correlation functional of Perdew-Burke and Ernzerhof [22] was chosen with norm-conserving pseudopotentials of Troullier-Martin type [23]. A double-zeta plus polarization numerical basis set was selected together with a real-space mesh cutoff corresponding to upper energy cutoff of 150.0 Ry. The simulation cell consists of 64 atoms with periodic boundary conditions. We used  $\Gamma$ -point sampling for the Brillouin zone integration, which is reasonable for a simulation cell with 64-atoms. The molecular dynamics (MD) simulations were performed using the NPH (constant number of atoms, constant pressure, and constant enthalpy) ensemble. The reason for choosing this ensemble is to remove the thermal fluctuation, which facilitates easier examination of the structure during the phase transformation. In the present work, our density functional calculations are essentially performed at zero temperature. The possible phase transitions and structural stability of this compound can be better established with the calculated total energy and enthalpy curves at ground state (at  $T = 0$  K), so entropic contributions can be neglected. Gibbs free energy is defined as:  $G = E_{\text{tot}} + PV - TS$ . Therefore, the enthalpy values,  $H = E_{\text{tot}} + PV$ , including the pressure-volume effects are calculated.

Pressure was applied by the Parrinello and Rahman method [24]. The system was first equilibrated at zero pressure, and then pressure was gradually increased with an increment of 100.0 GPa. The equilibration period is 1000 time steps with a time step of 1 fs. We also used the power quenching technique during the MD simulations. In this technique, each velocity

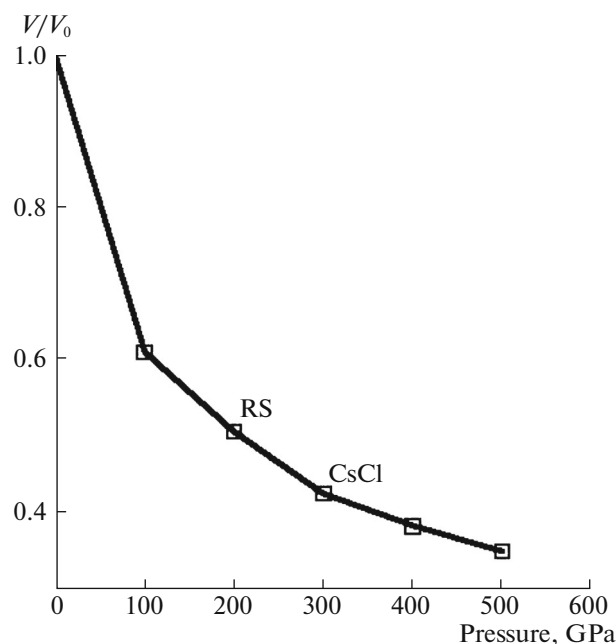
component is quenched individually. At each time step, if the force and velocity components have opposite signs, the velocity component is set equal to zero. All atoms or supercell velocities (for cell shape optimizations) are then allowed to accelerate at the next time step. For the energy volume calculations, we considered the primitive cell of both RS and CsCl-type phases. The Brillouin zone integration was performed with automatically generated  $10 \times 10 \times 10$  k-point mesh for both phases following the convention of Monkhorst and Pack [25].

In order to determine the intermediate state during the phase transformation, we used the KPLOT program [26] that provides detailed information about space group, cell parameters and atomic position of a given structure. For the symmetry analysis we used 0.2 Å, 4°, and 0.7 Å tolerances for bond lengths, bond angles and interplanar spacing, respectively.

## 3. RESULTS

In order to determine the thermodynamic nature of pressure-induced phase transition of MgS, we first plot the pressure-volume relation (Fig. 1). As can be seen from the figure, MgS is dramatically compressed. The volume change is about 50% at 200 GPa, but at this pressure the RS structure is still preserved. As the applied pressure is increased from 200.0 GPa to 300.0 GPa, the structural phase transition begins as indicated by a dramatic change in the simulation cell vectors. This phase transformation is accompanied by a small volume drop, implying a first order phase transformation. Owing to this phase transformation, the RS crystal transforms into a CsCl-type structure as shown in Fig. 2. This result is particularly important because it provides first solid evidence about the high pressure phase of MgS.

There has been increasing interest to understand the RS-to-CsCl phase transformation at the atomistic level. Several mechanisms have been proposed for this simple phase transformation. The first mechanism is known as Buerger mechanism [27] and is based on compression of the primitive cell of the RS structure along its threefold axis and hence a gradual increase of the rhombohedral angle of the intermediate  $R\bar{3}m$  state from 60° to 90°. The second one was proposed by Watanabe, Tokonami and Motimoto (WTM) [28] and is based on shifts of adjacent (001) planes of RS leading to an intermediate orthorhombic *Pmnm* symmetry. The third mechanism was recently proposed by Stokes and Hatch [29] on the basis of group theory, and relies upon a *P2<sub>1</sub>/m* monoclinic intermediate state. Indeed, the authors propose twelve pathways but *P2<sub>1</sub>/m* has the lowest activation barrier than the other intermediate phases. The fourth one was introduced by Tolédano et al [30]; it consists of two consecutive displacement mechanisms, coupled to tensile and shear



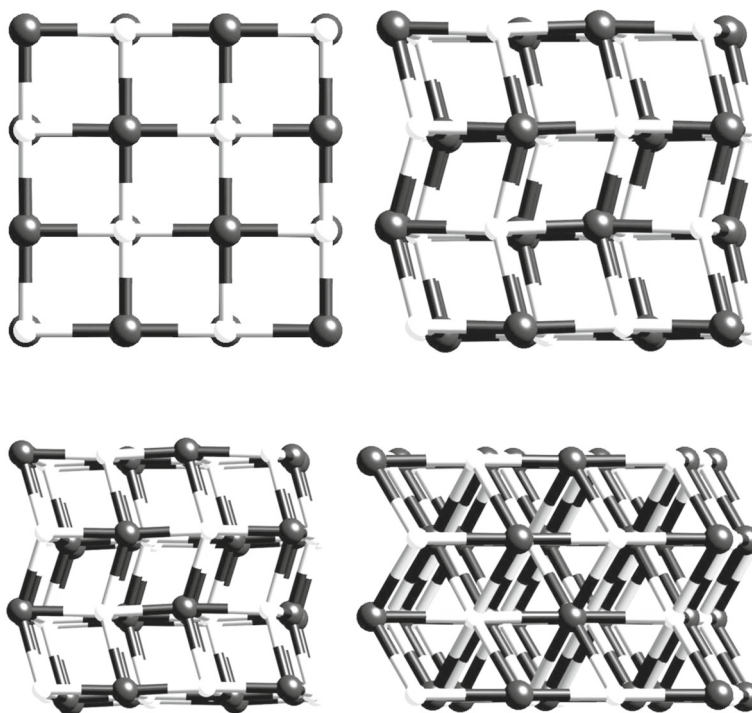
**Fig. 1.** The pressure-volume curve from the constant-pressure *ab initio* simulation.

strain. This mechanism gives rise to two intermediate orthorhombic structures with B16 and B33.

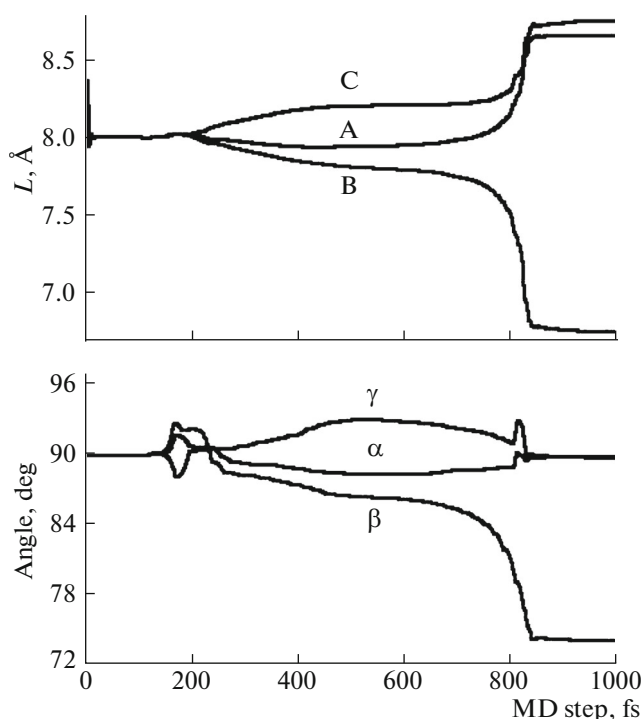
In the simulations, we can easily track the transformation mechanism of this phase change by simply

analyzing the modification of the simulation cell vectors and the motion of the atomic coordinates. The simulation cell lengths and angles as a function of the MD time step at 300 GPa are presented in Fig. 3. The simulation box has initially a cubic cell whose lattice vectors, A, B, and C are along the [001], [010], and [001] directions, respectively. The magnitude of these vectors is plotted in the figure. As clearly seen from the figure, the system undergoes dramatic rearrangements around 200 MD step: |C| barely increases while |B| decreases slightly because of small changes in the simulation cell angles. The structure is compressed along [010] direction while it is expanded along the other directions around 800 MD step. The angle between A and C vectors varies from  $90^\circ$  to about  $74^\circ$ , demonstrating that the pressure-induced phase transformation of MgS is associated with shear deformations.

In order to determine the intermediate phase formed during the phase transformation we carefully analyze the structure at each MD step using the KPLOT program. The RS symmetry is maintained up to 200 time steps, and then a tetragonal phase with  $P4/nmm$  symmetry is formed. The lattice parameters of this phase are  $a = b = 3.94 \text{ \AA}$  and  $c = 4.09 \text{ \AA}$ . At later time step, the tetragonal phase transforms into a monoclinic one with  $P2_1/m$  symmetry with lattice parameters  $a = 4.01 \text{ \AA}$ ,  $b = 3.90 \text{ \AA}$ ,  $c = 3.97 \text{ \AA}$ , and the monoclinic angle of  $92^\circ$ . We are unable to clearly determine the symmetry of the structure between 550 and 640 fs (the symmetry is determined as  $P1$  in this time range), but at later time steps (640–830 fs) we



**Fig. 2.** Evolution of the CsCl phase.



**Fig. 3.** Change of the simulation cell lengths and angles as a function of MD time step at 300 GPa. The A, B, and C simulation cell vectors are along the [001], [010], and [001] directions, respectively. The angle between A and B, A and C, and B and C are represented by  $\alpha$ ,  $\beta$ ,  $\gamma$  angles, respectively.

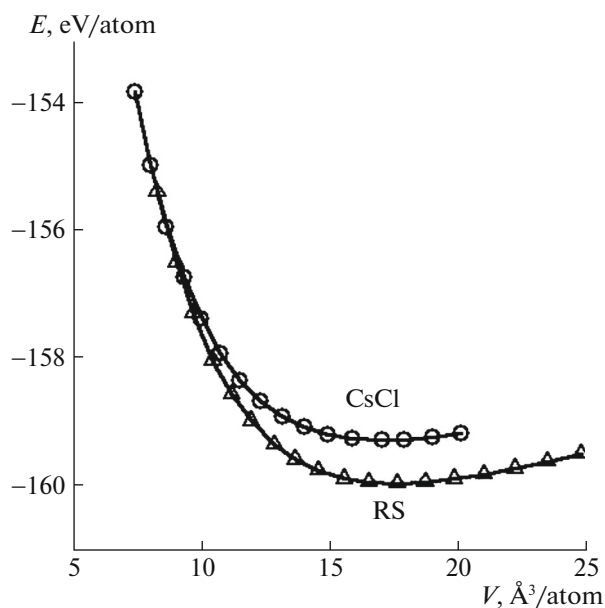
observe the monoclinic state again. The monoclinic angle gradually increases and reaches a value of  $100^\circ$ . At 827 fs, a CsCl-type structure ( $a = 2.49 \text{ \AA}$ ) is formed. The lattice parameters and atomic position of the phases observed at 300 GPa is presented in Table 1. The evaluation of the CsCl-type structure is shown in Fig. 2.

Based on the symmetry analysis, we propose that the RS-to-CsCl phase transition is associated with two intermediate phases, tetragonal and monoclinic. This mechanism, however, has not been observed or suggested in any studies before. A  $P2_1/m$  monoclinic intermediate state was proposed in groups theory analysis, but the tetragonal phase has not been considered or observed before. We need to underline that the formation of the tetragonal intermediate phase might be due to some limitations of the simulation. The first limitation is the use of rather small size of the supercell, which may artificially favor such a transformation mechanism. The second limitation is the loading conditions, in which rapid changes in pressure might result to instabilities, probably changing the statistical weight of the different transformation mechanism. We should also note here that using the same simulation technique, the size of the simulation box and loading condition, we observed the Buerger mechanism in CdO [31]. These dissimilar observations under similar conditions suggest that the RS-to-CsCl phase change might be dependent on the nature of the material. Based on only two different observations we cannot, however, explain which properties of the materials with RS structure lead to a specific transformation mechanism. Therefore, further studies are certainly needed to explain the physical origin of distinct transformation mechanism observed or proposed for the RS-to-CsCl phase transformations.

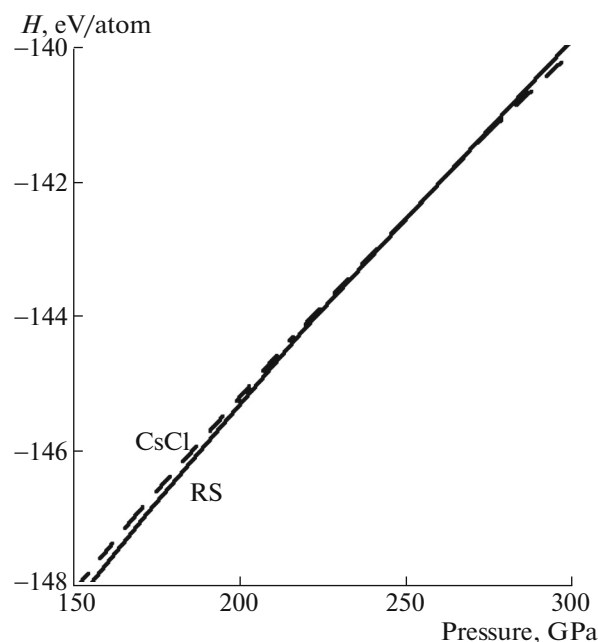
In order to obtain more information about this phase transformation and validate the parameters used in the simulations, as a next step we consider the energy-volume calculations. The computed total energy volume relations are fitted the third-order Birch-Murnaghan equation of states and shown in Fig. 4. From the energy-volume data we calculate the static enthalpy,  $H = E_{\text{tot}} + PV$  (where  $P = -dE_{\text{tot}}/dV$ ) is obtained by direct differentiation of the calculated

**Table 1.** The atomic fractional coordinates and the lattice parameters of the phases formed at 300.0 GPa

Structure	$a$ (Å)	$b$ (Å)	$c$ (Å)	$x$	$y$	$z$
RS $Fm\bar{3}m$	4.01	4.01	4.01	Mg: 0.000	0.000	0.000
				S: 0.500	0.500	0.500
Tetragonal $P4/nmm$	3.94	3.94	4.09	Mg: 0.750	0.250	0.500
				Mg: 0.250	0.200	0.871
				S: 0.750	0.250	0.000
				S: 0.250	0.250	0.382
Monoclinic $P2_1/m$	4.01	3.90	3.97	Mg: 0.008	0.250	0.786
				Mg: 0.636	0.250	0.306
				S: 0.506	0.250	0.793
				S: 0.125	0.250	0.287
CsCl $Pm\bar{3}m$	2.49	2.49	2.49	Mg: 0.000	0.000	0.000
				S: 0.500	0.500	0.500



**Fig. 4.** The computed energies of the RS and CsCl phases as a function of volume.



**Fig. 5.** The calculated enthalpy of the RS and CsCl structures as a function of pressure.

energy volume curves) because at zero temperature the thermodynamically stable phase has the lowest enthalpy. The crossing of two enthalpy curves indicates a pressure-induced phase transition between these two phases. Figure 5 shows the enthalpy changes as a function of pressure. The RS-CsCl phase transition in our calculations occurs around 251 GPa, which is in good agreement with previous *ab initio* predictions of 200–255.5 GPa [8, 11]. A summary of the predicted transition parameters and bulk properties, along with available experimental and theoretical data,

is tabulated in Table 2. Overall, we can find a reasonable agreement between the present study and previous experimental and theoretical investigations.

## CONCLUSIONS

*Ab initio* calculations were performed using constant pressure method to study the pressure-induced phase transition in MgS. A phase transformation from the RS structure to a CsCl-type phase is confirmed for the first time through *ab initio* MD simulations. Furthermore, we successfully characterize the transformation mechanism and propose that this phase transformation proceeds via two intermediate phases: tetragonal and monoclinic. This mechanism differs from the previously suggested mechanisms. The transition parameters and bulk properties predicted in the present work from the energy-volume calculations are in excellent agreement with the earlier density functional theory calculations. The observation of CsCl-type phase formation in MgS at high pressure is particularly important because it might provide an evidence about the high pressure phase of MgO that is of great interest to geophysicists as it is one of the likely components of the lower mantle.

**Table 2.** Equilibrium lattice parameters, the transition pressure, the bulk modulus and its pressure derivative

Structure	$a$ (Å)	$B_0$ (GPa)	$B'_0$	$P_t$ (GPa)	Refs.
RS	5.257	94.5	3.76	251	This study
	5.2277	71.33	3.85	255.5	8
	5.16	80	3.70	—	9
	5.22	76.36	3.66	—	10
	5.234	72.64	4.779	200.25	11
	5.18	81.0	4.15	—	12
	5.147	82.8	3.98	—	13
	5.244	85.1	3.077	—	14
	5.135	77.7	3.5	—	15
	5.13	82.0	—	—	16
CsCl	3.23	93.1	3.68	—	This study
	3.2729	72.45	5.615	—	8
	3.278	70.27	4.05	—	10

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