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To cite this article: M. Özduran and M. Durandurdu 2008 *EPL* **84** 56001

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# An *ab initio* constant-pressure study of pressure-induced phase transition of MgSe

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received 11 September 2008; accepted 23 October 2008

published online 2 December 2008

PACS 64.70.K- – Solid-solid transitions

PACS 62.50.-p – High-pressure effects in solids and liquids

**Abstract** – We study the pressure-induced phase transition of MgSe using a constant-pressure *ab initio* technique and find that the rocksalt-structured MgSe transforms into a FeSi-type structure. Furthermore, we find that this phase transformation is based on a cubic intermediate state with space group of  $F\bar{4}3m$ . The rocksalt-to-FeSi-type phase transition is also studied using total-energy calculations. Our transition pressure and bulk properties are in good agreement with the available experimental and theoretical results.

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**Introduction.** – The materials that crystallize in the sixfold-coordinated rocksalt structure (B1) at ambient conditions, often transform into the eightfold-coordinated CsCl structure (B2) with the application of pressure. There are some exceptional cases, for example, BaO converts to the hexagonal NiAs phase [1] and PbTe transforms into an orthorhombic *Pnma* structure [2]. An interesting phase transformation occurs in MgSe; Ruoff *et al.* [3] have studied MgSe using energy dispersive X-ray diffraction (EDXD) 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 rocksalt to FeSi (B28) beginning at around  $99 \pm 8$  GPa and approaching sevenfold coordination at 202 GPa. On the other hand, theoretical investigation suggests the B28 transition begins at 58 GPa and it transforms to an orthorhombic distortion of the B2 structure at 429 GPa. This B1-B28-type phase transformation in MgSe has not been verified in any other experiment yet.

The FeSe-type structure is a modulated deformation of the rocksalt (RS) structure and hence one might think that this transformation is an artifact of non-hydrostatic conditions because at high pressures, the pressure-transmitting medium solidifies resulting in strong nonhydrostatic effects. Even at low-pressure regime, pressure in the diamond anvil cell is not exactly hydrostatic. One of the difficulties with experiments is the knowledge of

the actual state of pressure. This condition is more easily assessed and controlled in simulations. Therefore reliable simulations are very appealing to potentially reveal structural states that very sensitively depend on the precise nature of the applied stress.

The limited information about the high-pressure phase of MgSe stimulates us to explore the behavior of this material under perfect hydrostatic compression using an *ab initio* constant-pressure technique. Our results confirm that MgSe does indeed transform into a FeSi (B28)-type structure. The observation of this phase change through molecular-dynamics simulation will eliminate any doubts about the high-pressure phase of MgSe. Furthermore, we find that the B1-B28 phase change of MgSe is due to a cubic intermediate state with the space group of  $F\bar{4}3m$ . We also study this phase change from the energy-volume calculations and compared our results with available experiments and theoretical calculations based on the density functional theory.

**Computational method.** – All calculations were performed using the SIESTA code [4], which is based on the first-principles pseudopotential method within the density functional theory. For the Kohn-Sham Hamiltonian, the generalized-gradient approximation (GGA) for the exchange correlation functional of Perdew, Burke and Ernzerhof [5] was chosen with norm-conserving pseudopotentials of Troullier-Martins type [6]. A double-zeta plus polarization numerical basis set was selected together with a real-space mesh cutoff corresponding to upper

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energy cutoff 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 since the energy difference between the 64-atoms simulation cell with only  $\Gamma$ -point and the 8-atoms unitcell with 256  $k$ -points (see below) is less than about 0.03 eV/atom. 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. Pressure was applied via the method of Parrinello and Rahman [7]. The equilibration period is 1000 time step 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 sign, 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 unit cell of both RS and FeSi-type phases. The Brillouin zone integration was performed with automatically generated  $8 \times 8 \times 8$   $k$ -point mesh for both phases following the convention of Monkhorst and Pack [8].

In order to determine the intermediate state during the phase transformation, we used the KPLOT program [9] that supplies 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.

**Results and discussion.** – We equilibrate the RS phase of MgSe at 100 GPa for 1000 fs and find no indication of phase transformation. Then we increase the applied pressure to 200 GPa and let the system equilibrate for 1000 fs. At this pressure, the simulation cell vectors (see below) undergo noticeable changes, indicating a phase transition in MgSe. The structural analysis using the KPLOT program indicates that the RS structure transforms into a FeSi-type structure as shown in fig. 1. This observation is particularly important because it provides the first solid evidence about the high-pressure phase of MgSe.

In simulations, we can easily track the transformation mechanism of phase changes by simply analyzing the modification of the simulation cell and the motion of the atomic coordinates. In fig. 2 we plot the simulation cell lengths and angles as a function of the MD time step. As clearly seen from the figure, the system undergoes dramatic rearrangements between 300 and 600 fs. A small change in the simulation cell angles indicates that the pressure-induced phase transformation of MgSe is associated with small shear deformations.

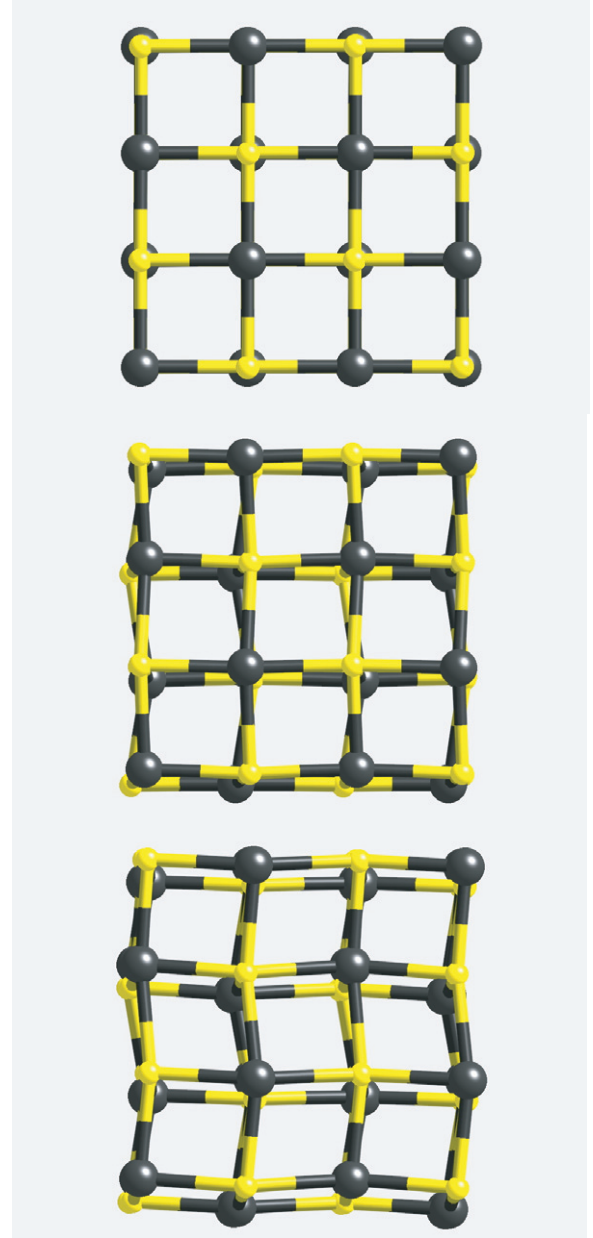


Fig. 1: Evaluation of the FeSi-type structure at 200 GPa. The RS structure (top), intermediate cubic structure  $F\bar{4}3m$  (middle) and FeSi-type structure (bottom).

In order to see whether this simple phase change has any metastable phase, we carefully analyze the structure each MD step. MgSe preserves its symmetry until 400 fs and then it forms a cubic intermediate phase. This intermediate phase has  $F\bar{4}3m$  symmetry and is characterized by the lattice parameters  $a = b = c = 4.3579$  Å. At 560 MD step, the FeSi-like phase forms, whose lattice constants are  $a = b = c = 4.3531$  Å.

The simulation conditions such as finite-size of simulation cell, lack of any defect in simulated structures, the degree of hydrostatic conditions and the fast application pressure are quite different from those of experiments.

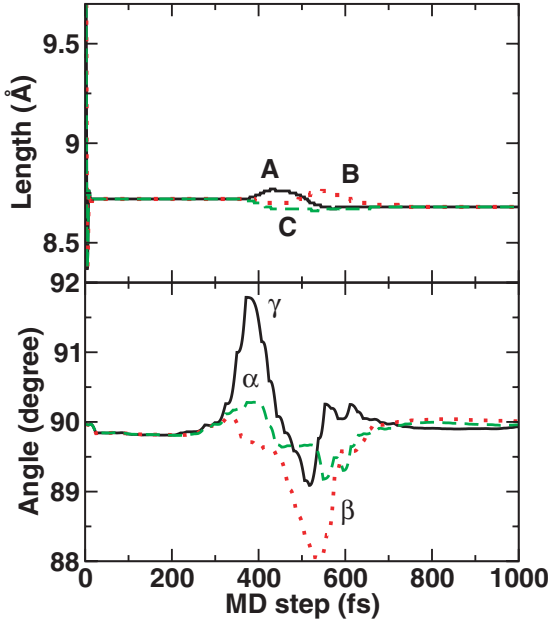


Fig. 2: The change of the simulation cell lengths and angles as a function of the MD step at 200.0 GPa.

These conditions commonly lead to overestimated transition pressures in simulations relative to experiments. Therefore, the transition parameters predicted in MD simulations cannot be comparable with experimental data. On the other hand, the thermodynamic theorem often gives reliable information about phase transformations and hence as a next step, we consider the energy-volume calculations to study the stability of the RS and FeSi-type phases of MeSe. Both phases are equilibrated at several volumes. The computed total energies as a function of volume are given in fig. 3. Below a specific volume,  $V = 12.56 \text{ Å}^3/\text{atom}$ , corresponding to a pressure of about 97 GPa (this pressure is determined using two techniques: from the enthalpy calculation of the RS state at the same volume and from internal pressure given in the simulations), we were not able to observe a stable FeSi-type state in MgSe and instead the initial FeSi-type state transforms to a RS state after relaxation even in constant-pressure simulations. This tendency agrees with experiment and the previous calculations in which the internal parameters of the FeSi-type phase reaches to the values of the RS state at the transition pressure [3,10]. Above this volume the energies of both crystals overlap one another. This behavior is compatible with a continuous phase transition between these structures. The transition pressure, about 97 GPa, predicted in our simulations is in excellent agreement with the experimental result of  $99 \pm 8 \text{ GPa}$ . The corresponding transition volume is predicted to be about  $12.56 \text{ Å}^3/\text{atom}$ . This value is comparable with the plane-wave calculation result of about  $12.2 \text{ Å}^3/\text{atom}$  [10]. A small discrepancy between the present and previous works for the transition

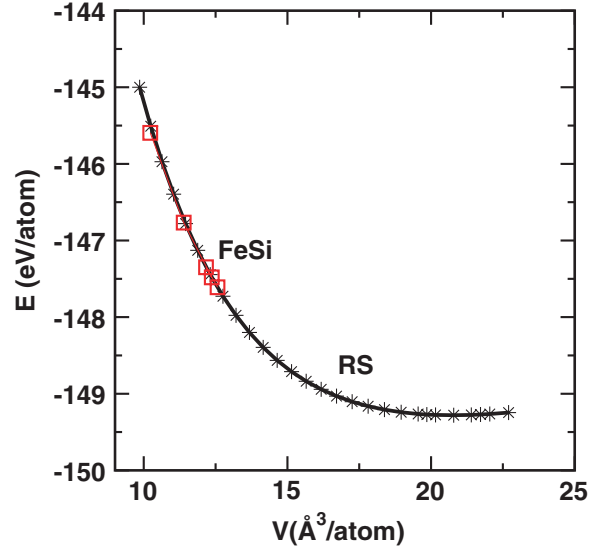


Fig. 3: Energy-volume relations.

volume is probably related to the predicted transition pressure (97 GPa and 111 GPa) in these simulations.

The equilibrium lattice parameter  $a$ , the zero-pressure bulk modulus phase ( $B_0$ ) and its pressure derivative ( $B'_0$ ) of the RS phase are determined by fitting the calculated energy-volume data to the third-order Birch-Murnaghan equation of state. Our calculated lattice constant is  $5.494 \text{ Å}$ , which is in good agreement with the experimental values of  $5.466(2) \text{ Å}$  [3] and the theoretical values of  $5.42\text{--}5.518 \text{ Å}$  [10–14].  $B_0$  and  $B'_0$  are predicted to be 75 GPa 3.94, respectively, which are again comparable with experimental (62.8 GPa, 4.1) [3] and theoretical (65.4–82.7 GPa and 3.75–4.2) values [10–14].

**Conclusions.** – We have carried out an *ab initio* constant-pressure technique to study the pressure-induced phase transition in MgSe. A phase transformation from the RS structure to a FeSi-type structure is successfully observed in our simulations. This observation validates the experiment and eliminates any doubt about the high-pressure behavior of MgSe. This transformation is found to be based on a cubic intermediate phase with space group  $F\bar{4}3m$ . The predicted transition pressure, transition parameters and bulk properties from the energy-volume calculations agree with experiments and the previous first-principles calculations.

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The visit of MD to Ahi Evran Üniversitesi was facilitated by the Scientific and Technical Research Council of Turkey (TÜBİTAK) BİDEB-2221. We are grateful to the SIESTA group for making their code publicly available. The calculations were partially run on Sacagawea, a 128 processor Beowulf cluster, in the University of Texas at El Paso.

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