PHYSICAL REVIEW B **72**, 073208 (2005)

Ab initio simulation of the rhombohedral–to–simple-cubic transition in arsenic

Murat Durandurdu
Department of Physics, University of Texas at El Paso, El Paso, Texas 79968, USA

(Received 10 December 2004; revised manuscript received 9 May 2005; published 19 August 2005)

The pressure-induced phase transition of arsenic is investigated using an *ab initio* constant-pressure relaxation technique. A transition from the rhombohedral structure to a simple cubic structure is successfully reproduced through the simulation. The transition is found to be accompanied by a volume reduction of 3.2%.

DOI: 10.1103/PhysRevB.72.073208 PACS number(s): 64.70.Kb

I. INTRODUCTION

Arsenic (As), one of the group-V elements, crystallizes in a low-symmetry rhombohedral $A7$ structure that can be derived from a simple cubic (sc) structure by a rhombohedral shear distortion along the [111] direction and an internal displacement of (111) planes toward each other in pairs along the [111] (Ref. 1). The distortion from sc is large enough that the resulting structure is layer like with three nearest (intralayer) and three next (interlayer) neighbors. The lowering symmetry from sc to $A7$ yields a strong decrease of the electronic states near the Fermi level, and hence the distortion-induced metal-to-semimetal transition is observed.

The behavior of the group-V elements and the group-IV-VI binary compounds under pressure are a subject of experimental and theoretical interest. Since the $A7$ structure can be derived from sc or NaCl by distortion, one might expect to see a gradual decrease of the distortion and finally the formation of sc structure in the group-V elements or the NaCl-type structure in the group-IV-VI binary compounds with the application of pressure. Indeed, a sc structure was observed in Sb at 7 GPa (Ref. 2) and P at 11 GPa (Refs. 3 and 4), but to our knowledge not in Bi (Ref. 5). Furthermore, the sc phase of both Sb and P was found to be superconducting. Experiments showed that As also transformed into a sc phase at high pressures.[1,6] However, the transformation mechanisms and pressures reported in these experiments are not consistent with each other. Earlier energy-disperse x-ray diffraction investigations[6] found that the transition occurred around 35 GPa and was associated with a slight volume drop of about 5%. Beister *et al.*,[1] on the other hand, observed the transition near 25 GPa without any volume discontinuity even though the lattice parameters exhibited an abrupt change during the transformation. Greene *et al.*[7] studied the behavior of As up to 122 GPa and found that the sc phase of As transformed into As(III). Upon further increase of pressure, As(III) converted to bcc. A metastable tetragonal phase was recovered during the quenching from 15 GPa.[8]

The stability of the $A7$ and sc structures and the pressure-induced phase transition of As also have been investigated using first-principles simulations.[9–11] The theoretical investigations reported contradictory results as well. At the present, therefore, several issues regarding the pressure-induced phase transition of As remain unclear. In this work, we perform a constant-pressure *ab initio* method to study the nature of the transformation mechanism in As. Such an investigation is also important for understanding the behavior of the other group-V elements and the group-IV-VI binary compounds at high pressure.

II. METHOD

A local-orbital first-principles quantum molecular dynamic (MD) method of Sankey and Niklewski[12] is applied to investigate the pressure-induced phase transition in As. This method employs the density functional theory within the local density approximation (LDA) and the Harris functional with hard norm-conserving pseudopotentials. The simulation cell contains 250 atoms with periodic boundary conditions. Pressure is increased with an increment of 5 GPa up to 30 GPa, after which an increment of 2.5 GPa is carried out. At each applied pressure, the system is fully relaxed until a maximum force smaller than 0.01 eV/Å. The structural minimization is performed with a conjugate-gradient technique. All the calculations use solely the Γ point to sample the Brillouin zone, which is reasonable for cells with 250 atoms.

Our previous calculations reveal that this Hamiltonian with the Parrinnelo-Rahman technique[13] is very successful in reproducing high-pressure phases of various amorphous and crystalline materials.[14–18] In the simulations, however, heterogeneous nucleation is suppressed because of the finite-size system with periodic boundary conditions, and thus large hysteric effects are observed. Consequently simulation

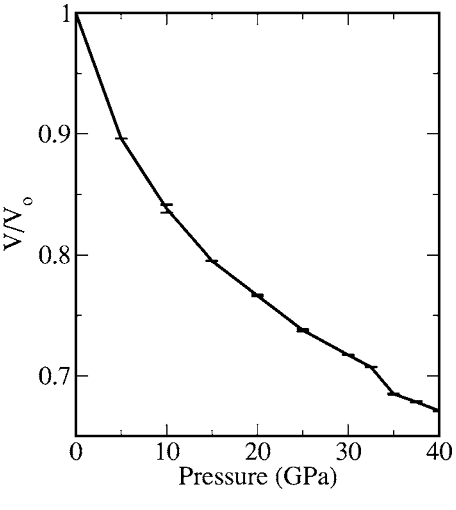

FIG. 1. Pressure-volume curve of As.

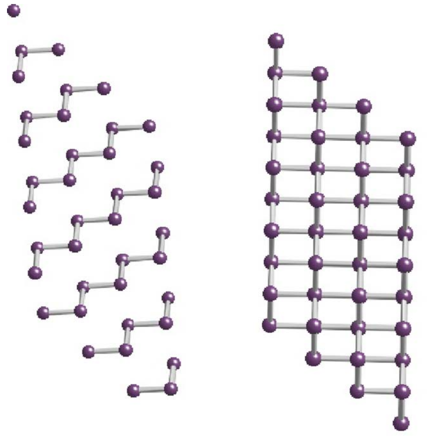
(a) A7 **(b) Simple Cubic**

FIG. 2. (Color online) (a) The rhombohedral *A*7 structure at 0 GPa. (b) The simple cubic structure obtained at 35 GPa. For clarity, a small portion of the simulation cell is shown.

boxes must be superpressurized in order to achieve structural phase transitions, and hence transition pressures and volumes predicted in simulations generally differ from experiments. This behavior is analogous to isobaric superheating in MD simulations. Nevertheless, the technique provides substantial information regarding the transformation mechanisms of materials under pressure.

III. RESULTS AND DISCUSSION

In order to better understand the transformation mechanism of As, we first show its pressure-volume curve in Fig. 1. Accordingly, the volume decreases gradually and a small volume drop occurs at 35 GPa, indicating a structural phase transition in As. At this pressure, the *A*7 structure transforms into a sc structure with an increase of coordination from threefold to sixfold (see Fig. 2). The volume reduction due to the structural transformation is found to be about 3.2%, which is comparable with the experimental value of about 5%.[6] This finding suggests that the pressure-induced phase transition in As is associated with a small volume drop as found in the earlier experiment.[6]

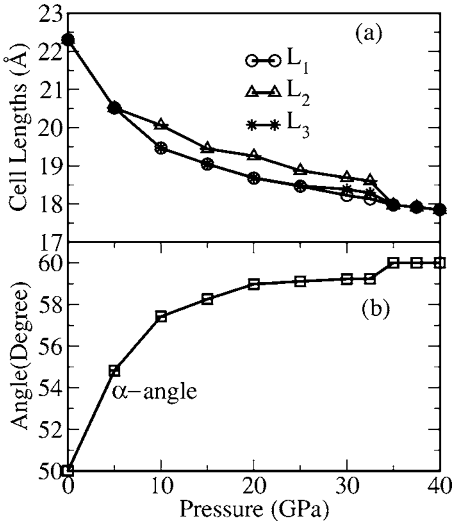

FIG. 3. The pressure-induced changes in (a) the simulation cell lengths and (b) the rhombohedral angle α.

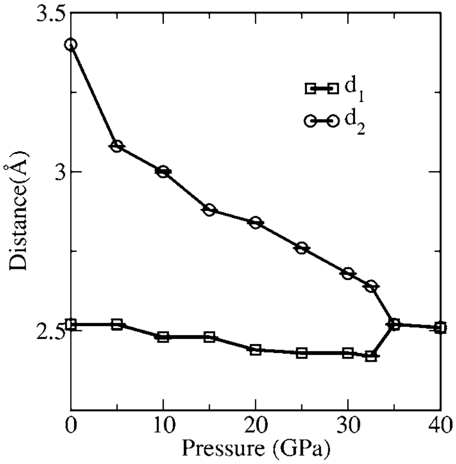

FIG. 4. The first- (d_1) and second- (d_2) nearest-neighbor distances as a function of pressure.

The pressure dependence of the simulation cell lengths and angles might provide additional information regarding the nature of the structural transition of As. Figure 3(a) shows the simulation cell lengths as a function of the applied pressure. We find that the *A*7 structure is anisotropically compressed as reported in experiments.[1,6] Such a behavior is commonly seen in layerlike structures and is due to the weak interlayer and strong intralayer bonding. Owing to the phase transition, all cell lengths are decreased. This observation is in contrast to Ref. 1 in which one of the lattice parameters is found to be elongated and the transition proceeds without any volume discontinuity. This finding demonstrates that the compressibility of the system during the transformation achieved in the simulation is clearly different from Ref. 1.

Figure 3(b) shows the change of rhombohedral angle α with pressure. The angle α at zero pressure deviates slightly from the experimentally accepted value. With the application of pressure, the angle tends to increase gradually and accom-

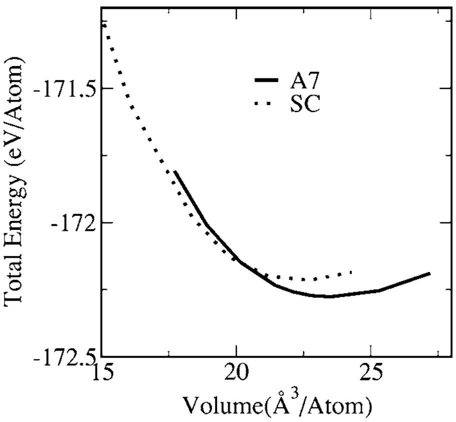

FIG. 5. Total energy and volume of the *A*7 and simple cubic phases of As.

TABLE I. Structural parameters of crystalline As. Equilibrium volume V_0, bulk modulus K, and pressure derivative of the bulk modulus, K'.

Phase	K (GPa)	K'	V_0 (a.u./atom)
$A7$	64.49[a]	3.99[a]	159.05[a]
	58[b]	3.3[b]	143.8[c]
	77[d]		147.1[d]
sc	74.15[a]	3.2[a]	151.61[a]
	87[d]		135.4[d]

[a] Present study.
[b] Reference 1 (experiment).
[c] Reference 19 (experiment).
[d] Reference 9 (theory).

panied by the transformation it reaches a value of 60°, similar to that found in experiment.[1]

The pressure-induced changes in the first- (d_1) and second- (d_2) nearest-neighbor distances illustrated in Fig. 4 give more insight into the transformation mechanism of As at the microscopic level. Accordingly, both distances gradually decrease as the $A7$ structure is compressed, but the decrease in the second-neighbor distance is more dramatic. This general trend is similar to what has been determined in experiment.[1] After the completion of the transition, d_1 is elongated by about 4% while d_2 is reduced by about 4.5%. The lattice constant of the sc structure at 35 GPa is calculated to be 2.52 Å, which is comparable to the experimental values of 2.465 Å (Ref. 1) and 2.55 Å (Ref. 6).

We find that the pressure dependence of the parameters obtained in the simulations shows a similar tendency as reported by Beister *et al.*[1] except the compressibility of the system during the transformation. This discrepancy, we believe, produces the different transformation mechanism and might be due to the finite size of the system and/or some approximations used in the simulation scheme. Therefore, further experimental and computational works are needed to clarify the nature of the phase transition in As.

Finally, we study stability of the $A7$ and sc structures using constant-volume calculations. Both phases are equilibrated at several volumes and fit to the third-order Birch-Murnaham equation of state. The energy-volume curve of the structures is given in Fig. 5. The relative energy difference between the $A7$ and sc structures is 0.061 eV/atom, which is in excellent agreement with the value of 0.06 eV/atom calculated within the LDA with pseudopotentials[11] and of ~0.07 eV obtained using a linearized augmented-plane-wave (LAPW) method.[9] The computed structural parameters of the $A7$ and simple cubic structures are listed in Table I. Our data appear to be comparable with experiments[1,19] and theoretical calculations[9] except that the equilibrium volume of both As phases is slightly overestimated.

IV. CONCLUSION

We have carried out an *ab initio* constant-pressure relaxation technique to probe the pressure-induced phase transition in As. The technique successfully reproduces the phase transition from the rhombohedral structure to a sc structure with a volume discontinuity of about 3.2%. Furthermore, the simulation provides substantial information regarding the transformation mechanism of As at the atomistic level, which is also helpful in understanding the phase transition in the group-V elements and the group-IV-VI binary compounds.

ACKNOWLEDGMENTS

The author is grateful to Professor D. A. Drabold for providing the FIREBALL96 MD code and Professor K. Hamed for reviewing the manuscript.

---

[1] H. J. Beister, K. Strössner, and K. Syassen, Phys. Rev. B **41**, 5535 (1990).
[2] T. N. Kolobyanina, S. S. Kabalkina, L. F. Verehchagin, and L. V. Fedina, Zh. Eksp. Teor. Fiz. **55**, 164 (1968) [Sov. Phys. JETP **28**, 88 (1969)].
[3] J. C. Jamieson, Science **139**, 1291 (1963).
[4] J. Wittig and B. T. Matthias, Science **160**, 994 (1968).
[5] K. Aoki, S. Fujiwara, and M. Kusakabe, J. Phys. Soc. Jpn. **51**, 3826 (1982).
[6] T. Kikegawa and H. Iwasaki, J. Phys. Soc. Jpn. **56**, 3417 (1987).
[7] R. G. Greene, H. Luo, and A. L. Ruoff, Phys. Rev. B **51**, 597 (1995).
[8] M. J. Duggin, J. Phys. Chem. Solids **33**, 1267 (1972).
[9] L. F. Mattheiss, D. R. Hamann, and W. Weber, Phys. Rev. B **34**, 2190 (1986).
[10] R. J. Needs, R. M. Martin, and O. H. Nielsen, Phys. Rev. B **33**, 3778 (1986).
[11] R. J. Needs, R. M. Martin, and O. H. Nielsen, Phys. Rev. B **35**, 9851 (1987).
[12] O. F. Sankey and D. J. Niklewski, Phys. Rev. B **40**, 3979 (1989).
[13] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196 (1980).
[14] M. Durandurdu and D. A. Drabold, Phys. Rev. B **64**, 014101 (2001).
[15] M. Durandurdu and D. A. Drabold, Phys. Rev. B **66**, 205204 (2002).
[16] M. Durandurdu and D. A. Drabold, Phys. Rev. B **66**, 041201(R) (2002).
[17] M. Durandurdu and D. A. Drabold, Phys. Rev. B **65**, 104208 (2001).
[18] M. Durandurdu and D. A. Drabold, Phys. Rev. B **66**, 045209 (2002).
[19] D. Schiferl and C. S. Barrett, J. Appl. Crystallogr. **2**, 30 (1969).