

Crystal structure searching by free energy surface trekking: application to carbon at 1 TPa

T Ishikawa¹, N Suzuki² and K Shimizu¹

¹ KYOKUGEN, Center for Quantum Science and Technology under Extreme Conditions, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

² Department of Pure and Applied Physics, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan

E-mail: ishikawa@cqst.osaka-u.ac.jp

Abstract. We have developed an *ab-initio* crystal structure searching method, free energy surface trekking (FEST). This method consists of an ascent-run and a descent-run. First, the system is forced to climb up a free energy surface following by the inversion of the restoring forces acting on the simulation cell (ascent-run). Then, the system climbs down the surface toward neighboring local minima according to the release from the constraint of the inversion immediately after the system crosses the ridges of the surface (descent-run). We have applied the FEST simulations to carbon at terapascal pressures and obtained a BC8-like structure with a tetragonal $I4_1$ in addition to the earlier-predicted BC8, R8, and simple cubic structures. This structure is mechanically stable in the pressure range of at least 0.5-3.5 TPa, and has a potential to survive as a metastable structure in carbon at terapascal pressures.

1. Introduction

Explorations of stable crystal structures and their transformation pathways are crucial for the understanding on physical properties of materials under high-pressure. To obtain the informations, we need to explore the Gibbs free energy surface at given pressures and temperatures, and molecular dynamics (MD) simulations have been employed as one of useful methods for the purpose. However, the free energy surface consists of many activation barriers, and there exist many cases that the system is trapped in a local minimum and fails to escape from it within realistic simulation time. In order to overcome this problem, many theoretical researchers have suggested improved MD simulations: metadynamics [1, 2], simulated annealing [3, 4], basin hopping [5], minima hopping [6], and evolutionary metadynamics [7]. These methods have been classified as neighborhood methods and enable us to find stable structures existing around the starting structure for the simulations. On the other hand, global methods, which are typified by genetic algorithm [8–11], evolutionary algorithm [12], random searching [13, 14], and particle swarm optimization [15], are effective for the findings of the global minimum of the free energy surface at a given pressure.

In this study, we have developed an *ab-initio* crystal structure searching technique classified into the neighborhood method, which we refer to as the free energy surface trekking (FEST). This method consists of an ascent-run and a descent-run. First, slight distortions are given to a starting crystal structure for the simulation. At this time, the system receives restoring forces toward the starting local minimum. In the FEST simulation, the inversion of the restoring forces



are employed. The system is forced to climb up the energy surface following by the inverted restoring forces until the system crosses the ridges of the energy surface (ascent-run). Then, the inverted restoring forces are switched to the original driving forces, and the system climbs down toward neighboring local minima (descent-run). As a result, stable structures separated by activation barriers from the starting structure are quickly obtained by the trekking from the ascent-run through the descent-run.

We have applied the FEST simulations to carbon at terapascal pressures, where the cubic diamond (CD) structure with the highest hardness of all materials has been expected to become energetically unstable. In *ab-initio* calculations, many candidates of post-CD phases and its metastable phases have been proposed. The CD phase has been predicted to exist up to around 1 TPa and to transform into a body-centered cubic structure with eight atoms per cell (BC8). Clark *et al.* have proposed a trigonal structure of $R\bar{3}m$ (R8) as the post-CD phase [16]. By further compression, the BC8 phase exhibits the transition into the simple cubic (SC) phase at 2.9 TPa [17–20]. *Ab-initio* molecular dynamics (MD) studies by Scandolo *et al.* clarified that the CD structure survives in a metastable state at approximately 3 TPa and transforms into a metastable metallic sixfold coordinated structure (SC4) with a space group of $P4_332$ [21]. Sun *et al.* studied the structural phase transitions of carbon under terapascal pressure using *ab-initio* metadynamics simulations, and found a cubic $P4_132$ structure, the simple cubic structure, a monoclinic $P2/c$ structure, and an orthorhombic $Pccn$ structure [22].

This paper is organized as follows. In section 2, the details of the FEST simulation and the computational methods are presented. In section 3, a BC8-like structure obtained by the simulation and its trekking path from CD are shown. The summary is drawn in section 4.

2. Methods

2.1. Details of free energy surface trekking

The flowchart of the FEST simulation is shown in figure 1. Since the purpose of FEST is to simulate a phase transition at given pressure (P) and temperature (T), the surface of the Gibbs free energy, $\mathcal{G}(\mathbf{h}) = \mathcal{F}(\mathbf{h}) + PV$, is explored as a function of a cell matrix $\mathbf{h} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$, where \mathbf{a} , \mathbf{b} and \mathbf{c} are lattice vectors of the simulation cell and $\mathcal{F}(\mathbf{h})$ is the Helmholtz free energy of the system at fixed box with volume V . In order to freeze cell-rotations, we use a symmetric matrix for \mathbf{h} , *i.e.*, $h_{ij} = h_{ji}$. First, the simulation cell is slightly distorted from the equilibrated one: $\mathbf{h} = \mathbf{h}_0 + \epsilon$, where \mathbf{h}_0 is the cell matrix of the starting structure for the simulation and ϵ a distortion matrix. Next, atomic positions in the cell are equilibrated by a few hundred or thousand MD-runs with the cell fixed, and an averaged stress tensor, \mathbf{p} , is obtained. At this time, the cell receives a restoring force, \mathbf{F} , defined as a set of derivatives of $\mathcal{G}(\mathbf{h})$ with respect to the six parameters of \mathbf{h} : $F_{ij} = -\partial\mathcal{G}/\partial h_{ij} = V\{[(\mathbf{p} - P\mathbf{I})\mathbf{h}^{-1}]_{ij} + [(\mathbf{p} - P\mathbf{I})\mathbf{h}^{-1}]_{ji}\}(1 - \delta_{ij}/2)$, where \mathbf{I} and δ_{ij} are the unit tensor and the Kronecker delta, respectively [2, 23]. In the ascent-run, the inversion of \mathbf{F} is employed for the update of the simulation cell. The update is called a meta-step in this paper. The simulation cell is updated along the steepest-ascent direction by $h_{ij}^{t+1} = h_{ij}^t - (\delta h_{ij})F_{ij}^t/|F_{ij}^t|$, where t is the number of the meta-steps and δh_{ij} a stepping parameter, and then the cell is modified to maintain constant volume by isotropic expansion or compression. Here, $J_{ij} = (h_{ij}^t - h_{ij}^{t-1})(h_{ij}^{t+1} - h_{ij}^t)/|(h_{ij}^t - h_{ij}^{t-1})(h_{ij}^{t+1} - h_{ij}^t)|$ helps one judge whether or not the system crosses the ridges of the energy surface. If at least one of 6 elements in \mathbf{J} changes from 1 to -1, then the inverted restoring force is flipped to the original driving force, and the descent-run starts. In the descent-run, the simulation cell is updated according to $h_{ij}^{t+1} = h_{ij}^t + (\delta h_{ij})F_{ij}^t/|F_{ij}^t|$ with the system released from the constant-volume constraint.

There is a difference between the metadynamics and FEST in the driving force acting on the system. In the metadynamics, the driving force is defined as the sum of the restoring force toward a local minimum on the energy surface and a biasing force derived from the Gaussian

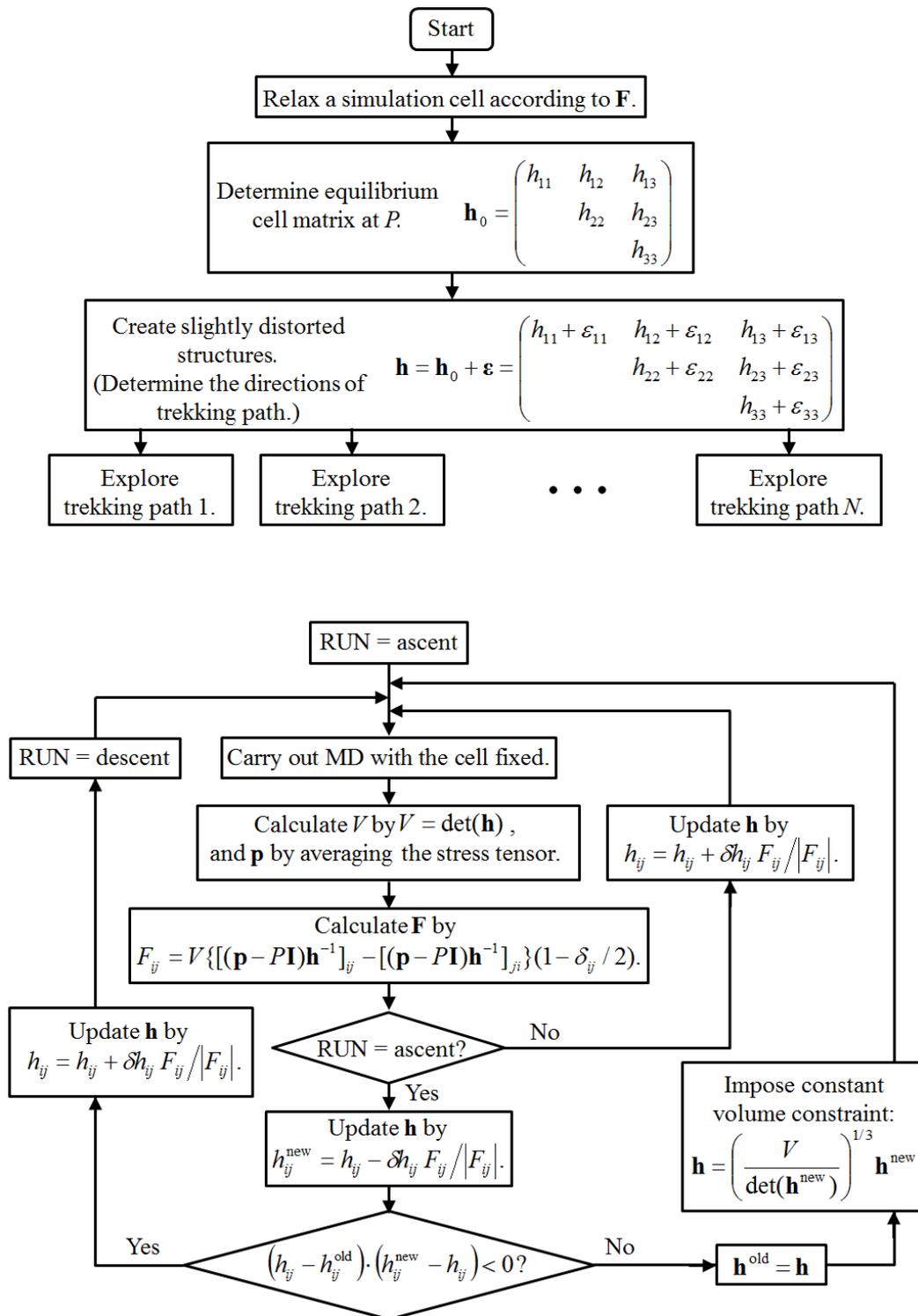


Figure 1. Flowchart of the free energy surface trekking.

potential [2]. On the other hand, in FEST, the driving force is defined as the inversion of the restoring force. These two methods are compatible with each other because one can easily switch the simulation by changing the driving force only.

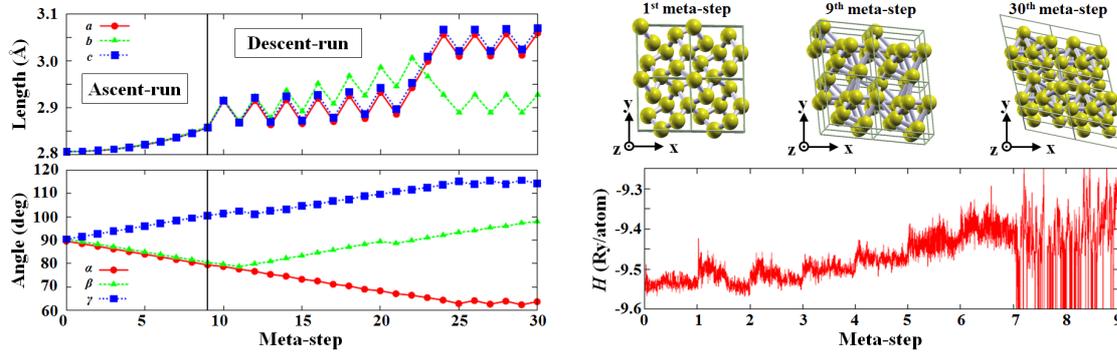


Figure 2. Evolution of the lattice parameters along the trekking path from the cubic diamond structure to the BC8-like structure. The right corner panel shows the evolution of the enthalpy up to the ninth meta-step, which corresponds to the ascent-run.

2.2. Computational details

We have combined our homemade FEST code with the Quantum ESPRESSO code [24]. Density functional theory was used in a generalized gradient approximation (GGA) with the expression by Perdew, Burke and Ernzerhof [25]. The Rabe-Rappe-Kaxiras-Joannopoulos ultrasoft pseudopotential [26] was employed. The primitive CD structure including 8 carbon atoms was used as the starting structure for the FEST simulations. The k -space integration over the Brillouin zone was performed on an $8 \times 8 \times 8$ grid, and the energy cutoff of the plane wave basis was set at 40 Ry. First, the system was equilibrated at given pressure and temperature for 50 meta-steps, and \mathbf{h}_0 was determined. Then, 64 starting directions for the ascent-run were created by the setting of each element in ϵ at either -0.05\AA or $+0.05\text{\AA}$. For the stepping parameter, δh_{11} , δh_{22} , and δh_{33} were set at 0.05\AA , and δh_{12} , δh_{13} , and δh_{23} at 0.03\AA . An MD-run of 1.0 ps (1000 MD-steps) was carried out at each meta-step, and \mathbf{p} was obtained by the average of the stress tensors for the last half of the MD steps. The pressure and temperature are set at 1.0 TPa and 7000 K, respectively.

3. Results

3.1. Trekking path from CD to BC8-like structure

In the FEST simulation at 1.0 TPa and 7000 K, a BC8-like structure was obtained through four trekking paths in addition to the earlier-predicted BC8, R8, and SC structures. The space group of the BC8-like structure is a tetragonal $I4_1$; the lattice parameters are $a = 3.5584\text{\AA}$ and $c/a = 0.9785$ at 1.0 TPa, and the atoms occupy two $8b$ sites with C1(0.3535, 0.1014, 0.2443) and C2(0.1014, 0.6465, 0.2557). Each atom is surrounded by four atoms: two atoms with a nearest neighbor distance of 1.26\AA , an atom with a second-nearest neighbor distance of 1.27\AA , and an atom with a third-nearest neighbor distance of 1.32\AA . The structural features are similar to those of BC8 and R8 [27]. Figure 2 shows a trekking path from CD to the BC8-like structure obtained through the FEST simulations. The evolution of the cell angles (α , β , and γ) shows that, in the ascent-run, the c axis changes from [001] toward [111] until α and β become 80° , and γ increases to 100° simultaneously with it. In the descent-run, the decreased β increases toward 100° , and α and β continue to decrease up to 65° and increase up to 115° , respectively. The cell lengths (a , b , and c) change from 2.8\AA and finally become as follows: $a = c = 3.3\text{\AA}$ and $b = 2.9\text{\AA}$.

The right corner panel in Fig. 2 shows the evolution of the enthalpy (H) in the ascent-run. In the current method, it is difficult to calculate the entropy S in $\mathcal{G} = H - TS$. Therefore, we

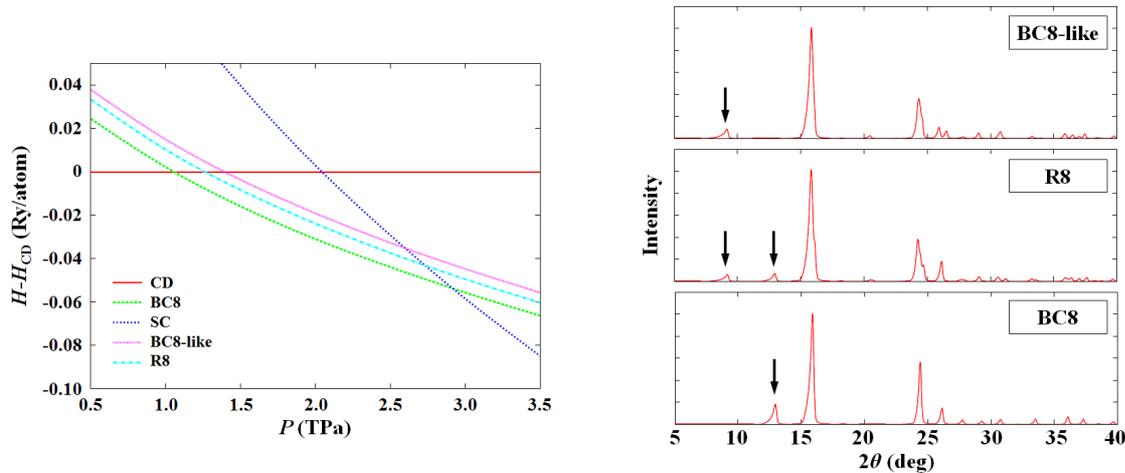


Figure 3. Enthalpies relative to CD for the BC8, BC8-like, R8, and SC structures. The right panels show simulated x-ray diffraction patterns for the BC8, R8, and BC8-like structures.

approximately estimated the height of the activation barrier from the evolution of H , *i.e.* the Gibbs free energy with $T = 0$. The height of the energy barrier can be roughly estimated from the increased quantity of H in the ascent-run. The H shows a significant fluctuation after the seventh meta-step owing to structural destabilization, but we determined the energy barrier to be approximately 0.15 Ry/atom. This is almost consistent with the energy barrier estimated in the transformation from CD into BC8 obtained through another trekking path of the FEST simulation.

3.2. Enthalpy comparison

Figure 3 exhibits the comparison of H among CD, BC8, R8, SC, and the BC8-like structure. The BC8 structure has the lowest H of all the structures in the pressure range of 1.0-2.9 TPa, which shows a good agreement with the earlier first-principles results. The H curves of R8 and the BC8-like structure reside nearly parallel to that of BC8 in higher enthalpy region over the entire pressure range, which result from the similarity of crystal structure among the three structures. The right panels show simulated x-ray diffraction patterns for the three structures, which are calculated by RIETAN-2000 [28]. The wavelength was set at 0.40 Å. The three structures are characterized by two small peaks at 9.0 and 12.5° indicated by arrows in the figures, but the patterns resemble each other in whole. For the R8 and BC8-like structures, the enthalpies relative to BC8 are within approximately 0.01 Ry/atom. However, as shown in 3.1, the height of the activation barriers required for the escape from CD is approximately 0.15 Ry/atom, which is 15 times as large as the difference of H among the three structures. In addition, the structures are mechanically stable in the entire pressure range of the figure. Therefore, the R8 and BC8-like structures may become metastable phases reached in the course of the phase transition from CD to BC8.

4. Summary

In this study, we have developed a crystal structure searching technique, which we refer to as the free energy surface trekking (FEST). This method is classified into the neighborhood methods and enables us to quickly find local minima of the Gibbs free energy surface, which neighbor the starting local minimum for the simulation. We have combined our FEST code with the Quantum ESPRESSO code and applied it to carbon at 1.0 TPa and 7000 K. As a result, the

structural transformations from CD to the BC8-like structure with a space group of $I4_1$ have been obtained through the FEST simulations in addition to the earlier-predicted BC8, R8, and SC structures. This structure resembles BC8 and R8, and the enthalpy differences among the three structures are within 0.01 Ry/atom from 0.5 to 3.5 TPa. The three structures are also mechanically stable in the pressure range. The height of the activation barriers from CD to BC8 or to the BC8-like structure is approximately 0.15 Ry/atom, which is approximately 15 times as large as the enthalpy differences. Therefore, the R8 and BC8-like structures have a potential to survive as metastable phases in the course of the phase transition from CD to BC8.

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