Determining the structure of compressed calcium in phase V by the \textit{ab-initio} molecular dynamics simulation

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Abstract. We searched for the structure of calcium in phase V by a metadynamics based on the first-principles calculation, and found a new structure, where the positions of the calcium atoms in the unit cell have a zigzag pattern. Calculating the x-ray diffraction pattern of the new structure and comparing it with the experimental patterns of Ca-IV and Ca-V, we conclude that the new zigzag structure is a candidate of the structure of Ca-V.

1. Introduction
High-pressure studies have revealed that many elements have low symmetrical and complex structures under pressure. Amazingly, some of the complex structures appear above 100GPa. The complex structures are reviewed by McMahon and Nelmes and classified into four categories: incommensurate composite structures, incommensurately modulated structures, modulated layer structures, and other complex structures [1]. Group 2 element Ba is the first element found to have the incommensurate composite structure in high pressure. The structure of Ba in phase III is hexagonal close-packed structure and it transforms to a host-guest structure Ba-IV\textsubscript{a} at 12.6 GPa which has the incommensurate composite structure [2] [3]. Ba-IV\textsubscript{a} transforms to hcp (Ba-V) again via other three Ba-IV-type structures (Ba-IV\textsubscript{b}, Ba-IV\textsubscript{c} and Ba-IV\textsubscript{d}) at 45 GPa. Another group 2 element Sr also has complex structures and the $\beta$-tin structure taking the helical distortion appears at 35 GPa (Sr-IV) [4]. On further compression, Sr-IV transforms to the incommensurate composite structure (Sr-V) [5].

Calcium, which is the group 2 element similar to Ba and Sr, also has complex structures in high pressures. Calcium has the fcc structure at ambient pressure. The fcc structure transforms to bcc at 20 GPa and then it has the transition to a simple cubic (sc) structure at 32 GPa [6]. The sc structure is rare in compressed elements and it is also observed in P above 10 GPa (P-III) [7]
and As above 25 GPa (As-II) [8]. In P the sc structure transforms to a complex structure at 107 GPa (P-IV). This structure has not been identified but it is theoretically predicted to be an incommensurately modulated structure [9]. In As sc transforms to a monoclinic incommensurate composite structure at 46 GPa (As-III) [10].

In 2005 Yabuuchi et al. observed that the sc structure of Ca-III transforms to Ca-IV at 113 GPa and further to Ca-V at 139 GPa [11]. The structures of Ca-IV and Ca-V are complex structures. In these phases calcium shows the high superconducting transition temperature. In 1996 Okada et al. measured an electrical resistance up to 150 GPa and found that $T_c$ linearly increased and reached about 15 K at 150 GPa. The transition temperature $T_c$ shows a tendency of further increase above the pressure [12]. In 2006 Yabuuchi et al. observed that the transition temperature $T_c$ dramatically increased in the Ca-III phase and it reached to 20 K above 100 GPa. On further compression, $T_c$ was increasing in Ca-IV and Ca-V and exceeded 25 K at 161 GPa [13]. In elements the highest $T_c$ had been found in lithium and it had been 20 K and calcium updates the highest record. Thus, in order to clarify the origin of the interesting behavior on the superconductivity of calcium, it is crucial to determine the structures of Ca-IV and Ca-V. Very recently we theoretically determined these structures by an ab-initio metadynamics simulation: Ca-IV has a tetragonal lattice with a helical modulation and Ca-V a orthorhombic one with a zigzag modulation [14].

In this work, we focused on the zigzag structure of Ca-V. We compared the x-ray diffraction pattern of the structure obtained by the metadynamics simulation with that obtained by a conventional molecular dynamics (MD) simulation. We compared the enthalpies among sc, the hexagonal close-packed (hcp) structure and the zigzag structure. We also investigated the atomic volume and the electronic states.

2. Computational details

To explore the structures of calcium in Ca-IV and Ca-V, we performed the ab-initio MD and metadynamics simulations. For the simulation, we used density functional theory in a generalized gradient approximation (GGA) and an ultrasoft pseudopotential, where we employed the expression by Perdew and Wang for the exchange-correlation energy functional [15]. Using the full-potential augmented plane-wave + local orbitals method as embodied in the WIEN2k code [16], we checked a localization of electrons of the calcium atom. 2p level is 330.97 eV below the Fermi level and it is deep in energy. But 3s level lies 43.33 eV and the charge is not completely confined inside an atomic sphere. Thus, for the pseudopotential used in this study, we regard 10 electrons, 3s, 3p and 4s, as the valence electrons. We performed the k-space integration using $8 \times 8 \times 8$ mesh points in the first Brillouin zone and set the energy cut-off of the plane wave basis at 24 Ry.

First we performed a conventional constant-pressure MD at 120 GPa to find an initial local minimum on the Gibbs free energy surface, and then explored other local minima around the initial one by the metadynamics [17] which is a method to fill the potential wells with a Gaussian potential. In the method, we treated 6 independent variables of a cell matrix $\mathbf{h} = (\vec{a}, \vec{b}, \vec{c})$ as reaction coordinates. We updated the simulation cell by the steepest-descent method with a stepping parameter $\delta h$: $\mathbf{h}_{ij}^{t+1} = \mathbf{h}_{ij}^{t} + \delta h \mathbf{F}_{ij}^{t} / |\mathbf{F}_{ij}^{t}|$ where $t$ is the number of the update of $\mathbf{h}$ and $\mathbf{F}$ is a driving force for the update. If we defined the Gibbs potential and the Gaussian potential as $G_o(\mathbf{h}^t)$ and $G_g(\mathbf{h}^t) = \sum_{h<t} \prod_{h<i,j} W \exp(-[h^t - h^{t'}]_{ij}^2/2\delta h^2),$ respectively, then the driving force $\mathbf{F}^t$ is the sum of $\mathbf{F}_o = -\partial G_o(\mathbf{h}^t)/\partial h_{ij}$ and $\mathbf{F}_g = -\partial G_g(\mathbf{h}^t)/\partial h_{ij}$. We defined an update of the cell as a meta-step and ran 100 MD steps for the atoms between each meta-step. For the MD with fixed cell we used the PWscf code [18].
3. Simulated results
We started the conventional constant-pressure MD from the sc structure. At 120 GPa the sc structure was unstable and it easily transformed to other structure. The volume of the obtained structure decreased about 4.5%. The unit cell is an orthorhombic, $a = 3.05\, \text{Å}$, $b/a = 1.08$, $c/a = 1.44\, \text{Å}$, and it consists of 4 atoms which locate at $(-0.08, 0, -0.08)$, $(0.08, 0.42, 0.42, 0.5, 0.08)$ and $(0.58, 0.5, 0.58)$. Comparing the x-ray diffraction pattern of the structure with the experimental ones, we found that the orthorhombic structure was neither the structure of Ca-IV nor that of Ca-V (Fig. 2).

Then, we explored other local minima by the metadynamics. We started the simulation from the orthorhombic unit cell obtained by the above conventional constant-pressure MD and set the Gaussian parameters $W$ and $\delta h$ to 10 mRy and 20 mÅ, respectively. Cell parameters $\gamma$, $a$ and $b$ began to change around 270 meta-steps and then we switched the Gaussian potential off by setting $W = 0$ mRy to confirm whether the system had escaped from the initial potential well. As a result the orthorhombic structure transformed to a new structure having a monoclinic distortion. The angle $\gamma$ increased from 90° to approximately 92° and $a$ and $b$ were equal to each other. When we switched the Gaussian potential off before 270 meta-steps, the structure returned to the initial orthorhombic structure.

We found that the primitive unit cell of the new monoclinic lattice has the dimensions of $a = 3.16\, \text{Å}$, $b/a = 1.00$, $c/a = 1.39$, $\gamma = 92.66^\circ$ at 120 GPa and consists of four atoms. The atomic positions are Ca(1)=($-0.10, 0.10, -0.06$), Ca(2)=($0.10, -0.10, 0.44$), Ca(1')=($0.40, 0.60, 0.06$) and Ca(2')=($0.60, 0.40, 0.56$). It can be viewed as the lattice consisting of two zigzag chains. Calcium atoms on each chain are shown by red or blue colors in Fig. 1. This structure can be redefined as an orthorhombic lattice by the choice of the double sized unit cell. The space group of the zigzag structure is $Cmca (D_{3h}^{18})$, which is orthorhombic, with atoms occupying 8f sites. The 8f sites parameters can be defined as $(y, z)=(1/4 + d_1, -1/4 + e_1)$ with $d_1 = -0.10$ and $e_1 = 0.06$, after shifting origin.

4. Comparison of the x-ray diffraction patterns
Figure 2 shows the comparison of the x-ray diffraction patterns of the crystal structures theoretically obtained with the experimental diffraction patterns. The first and second figures from the top are the diffraction patterns of Ca-V and Ca-IV, respectively [11]. In these patterns the diffraction peaks from the sample are indicated by arrows and $g$ represents reflections from a metal gasket. The third is the diffraction pattern of the structure obtained by the conventional constant-pressure MD, which is used as the initial structure for the metadynamics simulation. The bottom is the diffraction pattern of the structure obtained by the metadynamics simulation. At the transition from Ca-IV to Ca-V the most distinct change of the diffraction pattern is an

Figure 1. The zigzag structure obtained by the ab-initio metadynamics simulation. The left figure is a view along c axis and the right one a view along b axis. This structure has two zigzag chains in the unit cell and each chain is indicated by red or blue color. The number on the calcium atoms in the unit cell show their positions corresponding to those given in the text. In the right figure, $c_0$ is a lattice constant along c axis for an unmodulated structure.
appearance of the peak around $2\theta = 17^\circ$. Both of the structures obtained by the theoretical simulations have the peak and the Miller index is $(hkl) = (111)$. But for the initial structure the diffraction patterns around $2\theta = 20^\circ$ and $25^\circ$ agree with neither those of Ca-IV nor those of Ca-V. On the other hand the diffraction pattern of the final structure obtained by the metadynamics simulation shows good agreement with that of Ca-V.

5. Energy calculations of the zigzag structure of Ca-V
The structure of Ca-V has two types of distortion: (a) the displacement in the opposite direction along c axis between two zigzag chains which are identified by different colors and (b) the zigzag distortion along c axis (Fig.1). From the structure of Ca-V, we made three model structures, (i) a structure without the distortions (a) and (b), (ii) a structure with the distortion (a) only and (iii) a structure with the distortion (b) only, and compared the total energy of the structure of Ca-V with those of the model structures at the same volume determined at 100 GPa (Fig.3). If we treat the structure (i) as the reference for the comparison of the total energy, the total energies of the structure (ii) and the structure (iii) are $+1.55$ mRy/atom and $+1.78$ mRy/atom, respectively. However, the total energy of the structure of Ca-V, which has both the distortions (a) and (b), is lower than that of the structure (i) and the energy difference is $-8.97$ mRy/atom. Thus it is crucial for the stability of the candidate structure to take two distortions (a) and (b) simultaneously.

We compared the enthalpies among sc, the zigzag structure and hcp (Fig.4). The enthalpy of sc is the lowest of the three at 80 GPa. The enthalpy of the zigzag structure becomes lower than that of sc in the higher pressure region. The enthalpy difference between sc and the zigzag structure is 0.1 mRy/atom at 80 GPa. The hcp structure is a candidate structure of higher pressure phases of calcium [19], but the comparison of the enthalpies shows that hcp does not appear in the pressure range from 80 to 120 GPa. Atomic volume of the zigzag structure is smaller than that of sc and the volume decrease is 4.10% at 80 GPa. The volume decrease is attributed to the decrease of c/a due to the zigzag pattern along c axis.
Figure 3. Comparison of the total energies between the structure of Ca-V obtained by the ab-initio metadynamics simulation and three model structures ((i), (ii) and (iii)) at same volume determined at 100 GPa. The structure of Ca-V has two types of distortion, (a) the displacement in the opposite direction along c axis between two zigzag chains which are identified by different colors and (b) the zigzag distortion along c axis. The structure (i) is the structure without the distortions (a) and (b). The structure (ii) and the structure (iii) have the distortion (a) only and the distortion (b) only, respectively.

Figure 4. Comparison of the enthalpies among sc, hcp and the zigzag structure. The hcp structure has been one of the candidate structures of the higher pressure phases of calcium [19].

In the sc phase electrons of the s-character decreases and that of the d-character increases with compression. This s-d transfer advances more by the transformation from sc to Ca-V. Around the intersection of the enthalpy curve of sc with that of the Ca-V (80 GPa), the s-electrons and p-electrons decrease from 22.25 to 21.78 % and from 58.38 to 58.05 %, respectively, while the d-electrons increases from 19.38 to 20.17 %.

6. Summary
In this study, we showed the structures of calcium in phase V, which is obtained by the ab-initio metadynamics simulation. The structure of Ca-V is the complex structure with the zigzag pattern. This structure can not be obtained by the conventional MD only in our research. The x-ray diffraction pattern of the zigzag structure shows very good agreement with the experimental pattern of Ca-V. The validity of this prediction is also supported by the comparison of the enthalpies among sc, hcp and the zigzag structure. Since we have to impose a periodic boundary condition on a system for theoretical calculations, there remains a possibility that Ca-V has an incommensurate structure. But the good agreement of the diffraction pattern shows that the incommensurate structure should be very close to the predicted commensurate structure.
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