Ca-VII: A Chain Ordered Host-Guest Structure of Calcium above 210 GPa

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The recently discovered high pressure phase VII of calcium [M. Sakata *et al.*, Phys. Rev. B **83**, 220512(R) (2011)] has the highest superconducting transition temperature (T_c) of 29 K among all the elements. Understanding the cause for such a high T_c state is necessary to clarify its crystal structure. The structure of this phase was determined by an x-ray powder diffraction experiment and a density functional theory calculation and was not found to be the usual host-guest type but consisted of a 2×2 supercell in the tetragonal ab plane with a commensurate host-guest ratio of $4/3$ along the c axis containing 128 atoms.

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A total of 53 kinds of elements have been known to show superconductivity at ambient or high pressure [1]. The superconductivity transition temperature (T_c) increases by pressure in some of these elements. Among them, Li, Ca, Y, and Sc have high T_c near 20 K, and their highest T_cs are observed under a high pressure condition. The highest T_c of alkali earth elements Sr and Ba [2] occurs when they have a complex host-guest type structure. The relation between the crystal structure and T_c is very interesting. Six crystalline phases of calcium Ca-I (fcc), Ca-II (bcc), Ca-III (simple cubic, sc), Ca-IV ($P4_12_12$), Ca-V (*Cmca*), and Ca-VI (*Pnma*) have been found to exist at room temperature under high pressure at ambient, 20, 32 [3], 119, 143 [4–7], and 158 GPa [8], respectively. Superconductivity for Ca was first reported at about 44 GPa and 2 K [9]. The T_c of Ca has been predicted to increase with the occupancy of d electrons [10] and would continue to occur with successive phase transitions. The T_c of Ca-IV and Ca-V increased with pressure and reached 25 K at 161 GPa [11,12] and exceeded the previous record of 20 K of Li at 48 GPa [13], 17.2 K of V at 120 GPa [14], and 19.5 K of Y at 115 GPa [15]. Aftabuzzaman *et al.* calculated the T_c of Ca-VI as 24.7 K with the *Pnma* model at 172 GPa, which is close to the experimental T_c of 25 K [16]. Some theoretical studies have shown the phonon instability of the sc structure for Ca-III by first-principle calculations [17–20]. Furthermore, the $I4_1/amd$ model was claimed to stabilize at a lower temperature than that of the sc model [21–23]. These results have led to an increase in the interest towards Ca-III. Many groups have recently performed high-pressure low-temperature experiments and calculations at around 50 GPa [8,24–28] and have been able to confirm the existence of two new phases, the *Cmmm* and the $I4_1/amd$ structures.

Some models such as *Cmcm* [19] and $I4/mcm(00\gamma)$ $\gamma = 4/3$ (called $I4/mcm$-32 by Oganov) host-guest structures [23,29,30] have been predicted as the next high pressure phase. Oganov *et al.* has also predicted other host-guest structures of $C2/m$-32 and $C2/c$-32 which have guest chains with different heights [23].

Sakata *et al.* performed an x-ray powder diffraction experiment quite recently and discovered a new phase (Ca-VII) at around 210 GPa [31]. They measured the electrical resistance at low temperature and found that Ca-VII has the highest T_c among all the elements at 29 K and 216 GPa. Its crystal structure is thought to be a host-guest type, although it has not been confirmed yet. The aim of this study is to solve the fascinating structure of Ca-VII using the synchrotron x-ray diffraction data and the density functional theory (DFT) calculation and then to compare it to a typical host-guest structure to understand the relation of the crystal structure and its highest T_c.

Diffraction patterns for Ca-VII from Ref. [31] were used in this work. The experimental conditions were as follows: beveled diamond anvils with a 100-μm inner diameter, a 300-μm outer diameter, and an 8° beveled angle for high pressure generation. A rhenium gasket with a 40-μm diameter and a 15-μm thickness was used as a sample chamber. A pressure transmitting media was not used. A powder x-ray diffraction experiment was carried out at SPring-8 BL10XU. The beams were monochromatized to a wavelength of 0.41231 Å and collimated to a 10-μm diameter. A powder diffraction pattern was detected by an imaging plate detector with a typical exposure time of 10 min, and the sample-detector distance was 296.16 mm. Two-dimensional Debye-Scherrer rings were obtained and converted to one-dimensional 2θ-intensity patterns by the software PIP [32].

The peak indexing and the Rietveld analysis were performed with the software Materials Studio (MS) X-Cell [33] and the MS Reflex of Accelrys, Inc. The DFT calculations for structural optimizations and enthalpies were carried out using the program MS CASTEP of Accelrys, Inc. [34] We employed the GGA (generalized gradient approximation)-PBEsol (Perdew-Burke-Ernzerhof for solids) exchange-correlation functional [35] and ultrasoft pseudopotentials [36] with the energy cutoff of 380 eV. The Monkhorst-Pack grid separation [37] was set to approximately 0.03 $Å^{-1}$.

The structure analysis was performed on the pattern shown in Fig. 1 taken from Ref. [31] at 241 GPa. Tetragonal candidates with combinations of $a = 3.90$, 5.51, 7.80 Å and $c = 3.85$, 7.40, 11.60 Å were obtained by indexing the 14 strong peaks from this pattern. However, none of these candidates were found to be appropriate since they could not fit the observed pattern. On the other hand, a theoretically predicted model corresponding to that of the $I4/mcm$-32 model [23,29,30] with $a = 5.51$ Å and $c = 9.18$ Å fit the observed pattern almost perfectly. First, the Rietveld analysis was performed on the $I4/mcm$-32 model, and the intensities of the main peaks were found to fit the ones in the observed pattern. The results of the refinement and its structure are shown in Figs. 1(a)–1(c). The lattice constants were converged to $a = 5.511$ Å and $c = 9.181$ Å. As shown in the left inset in (a), the calculated but unobserved peaks appearing at 10.2° and 12.0° which are indicated by the cross symbols (×) as well as the small observed peaks at 10.6°, 11.3°, 12.1°, 13.0°, and 15.0° which are indicated by the arrows (↑) failed to be fitted. We also tried to fit these peaks with the $I4/mcm(00\gamma)$ model by adjusting the incommensurability γ with the program Jana2006 [38] but were unable to fit them (see Fig. S2 in the Supplemental Material [39]). Thus, we can conclude that Ca-VII basically has the host-guest type structure but requires some modifications.

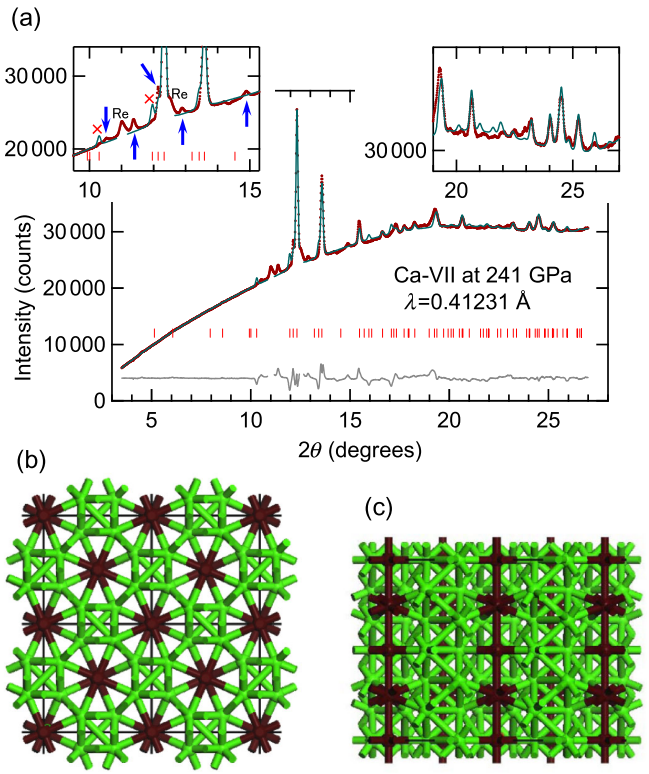

FIG. 1 (color online). (a) Diffraction pattern and Rietveld analysis with the $I4/mcm$-32 model for Ca-VII at 241 GPa. The closed circles show the experimental values. The dark green solid lines show the calculated diffraction pattern. The labels "Re" denote the diffraction peaks from the rhenium gasket. The reliability factors are $R_{wp} = 1.63\%$, $R_p = 1.03\%$, and R_{wp} (without background) $= 24.32\%$. Its structure for $2 \times 2 \times 1$ cells are drawn in (b) ab and (c) ac planes. The Ca atoms forming the host and guest structure are shown in green and brown, respectively. The crystallographic information file (CIF) for this model and the Rietveld analysis result as a four-dimensional composite crystal are provided in the Supplemental Material [39].

Second, we tried to fit the pattern with the monoclinic $C2/m$-32 and $C2/c$-32 models predicted by Oganov *et al.* [23]. The main peaks could be fitted with these models as well as some other host-guest models; however, the models could not fit the small observed peaks despite the adjustments of the lattice constants. Thus, there are still some unresolved problems that are related to the guest structure.

Third, we tried to expand the cell size of the $I4/mcm$-32 model in the ab plane and created two tetragonal supercells with dimensions of $\sqrt{2} \times \sqrt{2} \times 1$ ($a = 7.794$ Å, $c = 9.181$ Å, $Z = 64$) and $2 \times 2 \times 1$ ($a = 11.022$ Å, $c = 9.181$ Å, $Z = 128$). The former model could neither explain the small observed peaks nor improve the Rietveld fit. However, these peaks could be fitted successfully in the latter model by optimizing the z coordinates of the guest chains. The converged structure has two kinds of z coordinates, which will be explained later. Since this model, which is assumed to be commensurate (host:guest = 4:3), could fit all the peak positions perfectly, the host-guest ratio might be truly commensurate. The incommensurability γ fitted by the Jana2006 [38] converged to 1.333 and could also be regarded as 4/3 (see Fig. S3 in the Supplemental Material [39]). This supercell can be assigned to the three-dimensional space group $P4_2/ncm$. The model containing 128 atoms will be called $P4_2/ncm$-128. The final Rietveld fit with this model is shown in Fig. 2(a). The Miller indexes for the 5 observed peaks marked with arrows were 104, 214, 440 + 304, 324, 434 + 504, respectively. Among them, only the 440 is the common host and guest peak and the rest are the guest only peaks. Since there is no additional unindexed peak in the observed pattern, a larger unit cell is not necessary. The index of 104 indicates that the size of the $2 \times 2 \times 1$ tetragonal cell could not be reduced any further. Its atomic coordinates for all 12 sites are refined as shown in the left

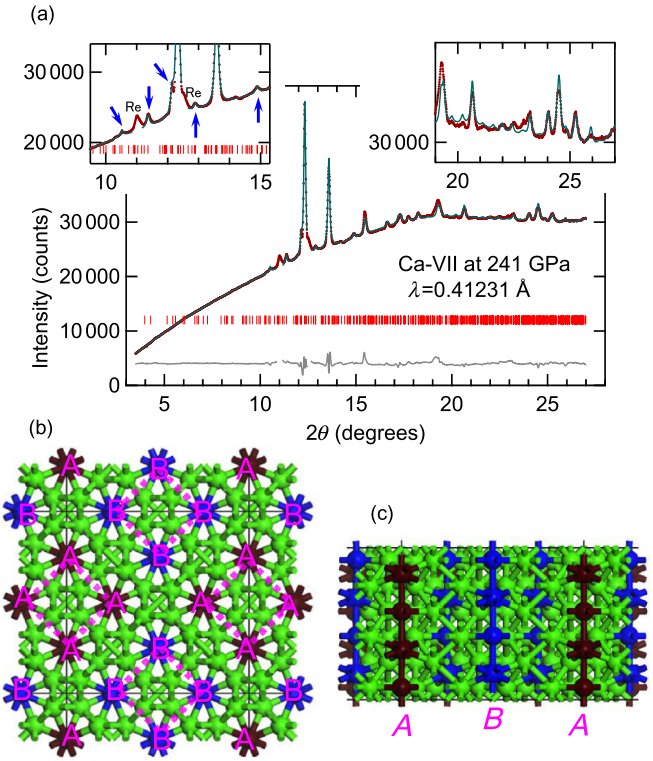

FIG. 2 (color online). (a) Rietveld fit with the proposed $P4_2/ncm$-128 model for Ca-VII. The preferred orientation direction and the R_0 value for the March-Dollase function were converged to (0.732, 0.682, 0.005) and 0.834, respectively. The final fit resulted in reliability factors of $R_{\mathrm{wp}} = 0.95\%$, $R_p = 0.68\%$, and R_{wp} (without background) $= 13.93\%$. Its structure is drawn in the (b) ab and (c) ac planes. The labels A and B show the two different types of heights of the guest atom. The CIF for this model and the Rietveld analysis result as a four-dimensional composite crystal are provided in the Supplemental Material [39].

column of Table S1 in the Supplemental Material [39]. They were also optimized by the DFT calculation and have values that are close to the ones in the right column. The DFT optimized structure is shown in Figs. 2(b) and 2(c). The calculated stress and its anisotropy ratio became $\sigma_{xx} = \sigma_{yy} = 212.8$ GPa, $\sigma_{zz} = 211.4$ GPa, and $\sigma_{xx}/\sigma_{zz} = 1.006$. These values match the experimental pressure of 241 GPa quite well.

Figure 3 shows the pressure evolution of the volume per atom for calcium which decreased to 22% from Ca-I to Ca-VII. The atomic distances were expected to shrink on the average by 60% by taking the cubic root. The transition from Ca-VI to Ca-VII was found to be of a first order judging from the coexistence of these phases. The volume discontinuity was estimated to be approximately 2% by the following formula: $(V_{\mathrm{VI}} - V_{\mathrm{VII}})/[(V_{\mathrm{VI}} + V_{\mathrm{VII}})/2]$, where V_{VI} is the volume per atom at 207 GPa and V_{VII} is that at 212 GPa.

Figure 4 shows the pressure dependence of the interatomic distances for calcium. The distances for Ca-VII

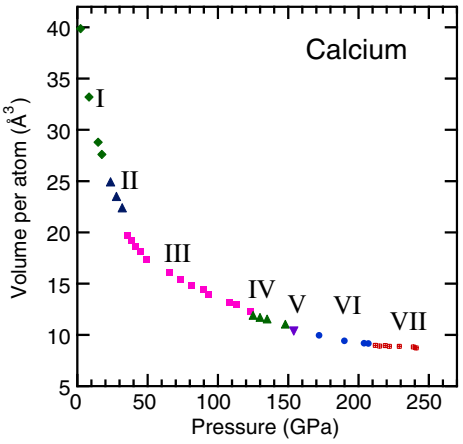

FIG. 3 (color online). Pressure dependence of the atomic volume for calcium. Data points for Ca-VII were obtained by the Rietveld analysis with the $P4_2/ncm$-128 model. Numerical values for Ca-VII are given in Table S2 in the Supplemental Material [39].

from 2.10 to 2.35 Å were interpreted as the first nearest region and are shown by the bottom arrow in Fig. 4. The distances above 2.5 Å were treated as the second nearest region (upper arrow in Fig. 4). However, the second nearest distance of 2.7 Å for Ca-VI shrank abruptly to 2.5 Å in Ca-VII; therefore, the clear gap between the 1st and 2nd distances disappeared. On the average, Ca-VII seems to have a 9 coordinated structure, which is 1 value larger than that of Ca-VI.

There are two kinds of guest chains labeled A and B in Figs. 2(b) and 2(c) which can be distinguished by their z coordinates in Ca-VII. Square patterns with a 45° slope were obtained by connecting the four parts labeled A and the four parts labeled B with dashed lines. A previously known host-guest structure including a monoclinic type [40] contained two guest chains of the corner chain and the

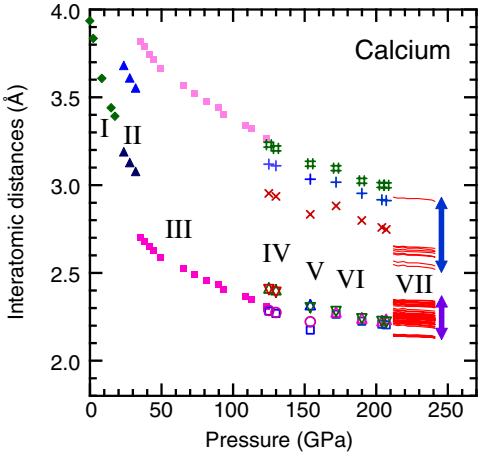

FIG. 4 (color online). Pressure change of the interatomic distances for calcium. Ca-VII data include numerous distances; therefore, its data points are marked with thin lines.

center chain in the unit cell. However, Ca-VII shows a unique ordering of 8 chains. Thus, we can say that the formation of this pattern is the origin of the 2×2 supercell.

To check the stability of the $P4_2/ncm$-128 model, its enthalpy of $-125\,653.704$ eV per 128 atoms or $-314\,13.426$ eV per 32 atoms was compared to that of the previous $I4/mcm$-32 model which was calculated to be $-314\,13.355$ eV per 32 atoms and was found to be 71 meV smaller. However, it would be very difficult to predict the $P4_2/ncm$-128 model only by a theoretical calculation since the difference of enthalpy from that of the $I4/mcm$-32 model is too small and the number of atoms of 128 is too large for the *ab initio* structure prediction. Our phonon calculation for the $P4_2/ncm$-128 model has confirmed that there is no imaginary frequency.

Loa *et al.* reported another new host-guest structure for barium (Ba-IVc) at 19 GPa quite recently [41]. Surprisingly, this structure has a 3×4 supercell in the ab plane and also has a guest chain ordering with an s-shaped pattern. The expansion in the ab plane due to the chain ordering resembles the phenomenon of Ca-VII. Their model was determined by a single crystal x-ray diffraction experiment, while only a powder x-ray diffraction technique would allow us to obtain the crystal structure of Ca-VII under very high pressure conditions exceeding 200 GPa.

Andersson [42] commented that the T_c for Ca-VII should be 21 K from Fig. 4 in Ref. [31]. However, we obtained the same T_c of 29 K in our recent T_c measurement up to 250 GPa. This result is described in the Supplemental Material [39]. Thus, our present work stimulates theoretical investigations so that the T_c for Ca-VII may be calculated using this exotic $P4_2/ncm$-128 model. The calculations using the $I4/mcm$-32 model containing only 16 atoms in its primitive cell are also considered to be quite practical. An extensive x-ray diffraction study at the beginning of the superconducting state at around 250 GPa and 20 K is necessary in the future to determine whether Ca-VII remains stable or a new phase appears.

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