Crystal Structures of Calcium IV and V under High Pressure

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High-pressure phases IV and V of calcium discovered in 2005 have the highest superconducting transition temperature of 25 K among all the elements; however, their crystal structures have not been determined. From the x-ray powder diffraction data, both Ca IV and V have been found to form unique and complex structures with a coordination number of 7. They were confirmed to be identical to the theoretical models that were recently predicted [Ishikawa *et al.*, Phys. Rev. B **77** 020101(R) (2008)].

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The physical properties of alkaline-earth metals, e.g., Ca, Sr, and Ba under high pressure have been studied experimentally as well as theoretically from the viewpoint of *s*-*d* electron transfer [1]. Recent structural experiments have revealed that a "host-guest" structure is popular in a high-pressure phase even for simple elements such as the alkaline-earth metals of Sr [2] and Ba [3], and other elements of K [4], Rb [5,6], As [7], Sb [7,8], Bi [9], and Sc [10,11]. Successive structural transitions consisting of face centered cubic (fcc) → body centered cubic (bcc) → simple cubic (sc) are reported in compressed calcium at 20 and 32 GPa [12]. Our powder x-ray diffraction analysis of calcium under high pressure revealed that the sc phase is stable up to 109 GPa and that calcium transforms to the new high-pressure phases of Ca IV and Ca V above 113 and 139 GPa, respectively [13]. The crystal structures of Ca IV and Ca V could not be determined from the analysis; however, it was proved that Ca IV was not of the "host-guest" structure.

For alkaline-earth metals, the increment of the *d*-band occupation number of electrons under pressure may increase the superconducting critical temperature T_c [12]. The T_c of Ba increases with pressure and has a maximum in the Ba-IV phase, where the *s*-*d* electron transfer is considered to be completed [14]. The T_c of Ca was first confirmed at 2 K at 44 GPa [15] and found to increase linearly with elevating pressure up to 15 K at 150 GPa [16] and reached about 25 K at 161 GPa [17] which is the highest value of T_c among all the elements.

Ishikawa *et al.* have predicted the crystal structures of Ca IV and V by the first-principles metadynamics simulation method [18]. Their Ca-IV and -V models consisted of helical and zigzag chains, and their space groups were assigned to be tetragonal $P4_3$ and orthorhombic *Cmca*, respectively. Since the calculated x-ray diffraction patterns from their models are similar to the experimental data [13] as shown in the bottom profiles in Figs. 1 and 3, their models must be very close to the true structures.

We have continued the x-ray powder diffraction experiments to determine the true structures of Ca IV and V. Consequently, the transition pressures to Ca IV and to Ca V were redetermined to be 119 and 143 GPa, respectively. A diffraction pattern of a single phase with no gasket peak was obtained for each phase [19]. The purpose of this study is to determine the crystal structures of Ca IV and V by

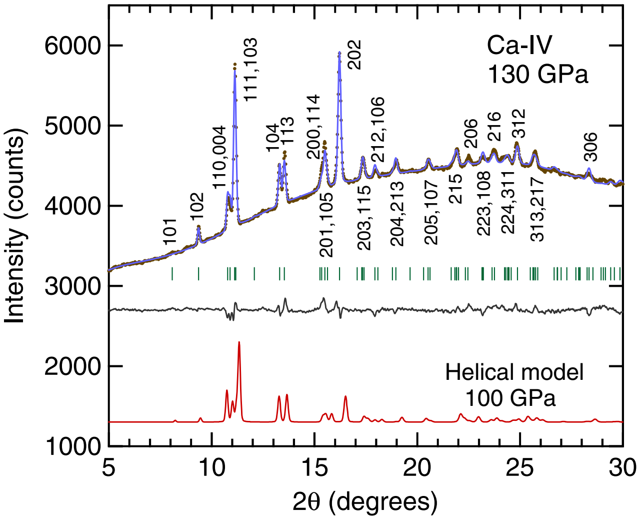

FIG. 1 (color online). The observed diffraction pattern of calcium phase IV at 130 GPa (dots) and the calculated profile (curve) after the Rietveld refinement. The x-ray wavelength was 0.42640 Å. The tick marks show the calculated peak positions for the proposed $P4_12_12$ structure. The differences between the observed and calculated profiles are shown below the tick marks. The preferred orientation direction and the R_0 value for the March-Dollase function were converged to (0.575, 0.106, 0.811) and 0.416, respectively. The final fit resulted in the reliability factors of $R_{wp} = 0.66\%$, $R_p = 0.45\%$, and R_{wp} (without background) = 15.26%. The bottom profile displays the diffraction pattern calculated from Ishikawa's helical chain structure [18].

analyzing our diffraction data and to compare them to Ishikawa's models.

Since the experimental condition is described in Ref. [19], minimal information is given here. The beveled diamond anvils were used for pressure generation up to 158 GPa. No pressure transmitting medium was applied. The powder x-ray diffraction experiments were carried out using a synchrotron radiation source on the BL-13A station at the Photon Factory, KEK, Japan. Powder diffraction patterns of the calcium samples were collected by an angle-dispersive method with an imaging plate detector. A one-dimensional powder pattern was obtained by averaging the diffraction intensities along the ring [20].

Structure analyses were carried out using the diffraction patterns at 130 and 154 GPa consisting of a single phase of Ca IV and V, respectively. The peak intensity at $2\theta = 16.2°$ in the Ca-IV pattern is relatively stronger than that in the previous pattern [13]. The peak at $2\theta = 16.7°$ in the Ca-V pattern is also stronger than that in the previous data. These stronger peaks would originate from the preferred orientation effect induced by the ultra high pressure. We performed a structure analysis with a normal procedure of an indexing, a space group determination, and a Rietveld refinement without using Ishikawa's model, since there is no guarantee that their space group is correct.

The Ca-IV pattern shown in Fig. 1 was indexed with 16 peaks by the software X-CELL [21] of Accelrys, Inc. The most probable candidate for the unit cell is a tetragonal lattice of $a = 3.202$ Å, $c = 8.981$ Å with a cell volume of $V = 92.1$ Å^3. Since the atomic volume V_1 at 130 GPa was estimated to be from 11.4 to 11.8 Å^3 by extrapolating the Ca-III data, this cell could be considered to contain 8 atoms. The following 23 space group numbers were allowed for this tetragonal cell from the extinction rule: 75–78, 81, 83–86, 89–96, 99, 111, 113, 115, 123, 129. A Rietveld analysis was performed with the software MATERIALS STUDIO REFLEX of Accelrys, Inc. A structure model with the space group $P4_1$ and its enantiomorph $P4_3$ could fit the diffraction intensities. By raising the symmetry, the space groups $P4_12_12$ or $P4_32_12$ could finally be obtained without worsening the fit. Other candidates with higher space group numbers could not build the preferable structure. A reliability factor of the fit with the $P4_12_12$ model and no preferred orientation correction was $R_{wp} = 1.61\%$. The main misfit was found at the peak at $2\theta = 16.2°$ which was indexed as 202. This misfit could not be improved by changing the atomic coordinates or by breaking the tetragonal symmetry. After employing a preferred orientation correction of the March-Dollase type, the misfit was eliminated, and the R_{wp} was greatly reduced to 0.66%. Thus, the structural parameters were determined to be $a = 3.209 \pm 0.001$ Å, $c = 8.976 \pm 0.001$ Å, $V = 92.42$ Å^3, and the Ca atom at the $8b$ Wyckoff position of $(0.527 \pm 0.001, 0.175 \pm 0.001, 0.096 \pm 0.001)$ as displayed in Fig. 2. When the space group $P4_32_12$ is used, the atomic coordinate of (0.175, 0.527, 0.096) produces the enantiomorph structure of Fig. 2. This structure also becomes a solution which has exactly the same Rietveld fit and R_{wp}.

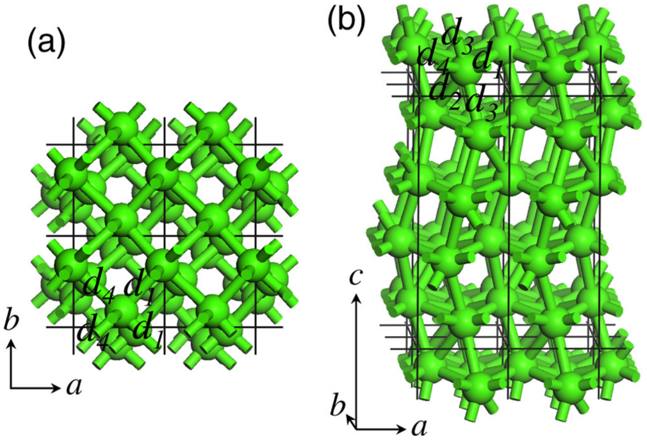

FIG. 2 (color online). Crystal structure of calcium phase IV at 130 GPa in (a) the ab and (b) the ac planes for $2 \times 2 \times 1$ unit cells. The interatomic distances of less than 2.5 Å are shown by the sticks. Labels d_1 to d_4 on the sticks represent the 1st to 4th nearest distances.

The Ca-V pattern at 154 GPa shown in Fig. 3 was indexed with 17 peaks. The probable candidates for the unit cell are a tetragonal lattice of $a = 4.314$ Å, $c = 4.495$ Å and an orthorhombic one of $a = 4.316$ Å, $b = 4.494$ Å, $c = 4.307$ Å. These cells must contain 8 atoms judging from the V of Ca IV. No structural model with any

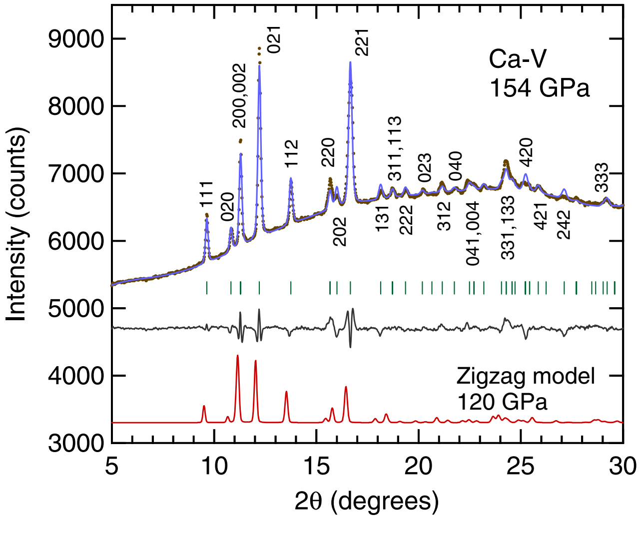

FIG. 3 (color online). Rietveld refinement of calcium phase V at 154 GPa. The x-ray wavelength was 0.42505 Å. The tick marks show the calculated peak positions for the proposed $Cmca$ structure. The preferred orientation direction and the R_0 value for the March-Dollase function converged to (0.467, 0.774, 0.427) and 0.458, respectively. The final fit produced the reliability factors of $R_{wp} = 0.73\%$, $R_p = 0.44\%$, and R_{wp} (without background) = 17.89%. The bottom profile displays the diffraction pattern calculated from Ishikawa's zigzag chain structure [18].

tetragonal space group could fit the diffraction intensities. The following 41 space group numbers were allowed for the orthorhombic cell from the extinction rule: 16–21, 25–36, 38–41, 47, 49–65, 67. The best space group was found to be *Cmca* which had the highest symmetry with the smallest number of atomic parameters without worsening the fit. A reliability factor of the fit without any preferred orientation correction was $R_{wp} = 1.79\%$. After employing a preferred orientation correction of the March-Dollase type, the R_{wp} was greatly reduced to 0.73%. The structural parameters were finally determined to be $a = 4.319 \pm 0.001$ Å, $b = 4.505 \pm 0.001$ Å, $c = 4.315 \pm 0.001$ Å, $V = 83.96$ Å^3, and the Ca atom at the $8f$ Wyckoff position of $(0, 0.158 \pm 0.001, 0.197 \pm 0.001)$ as displayed in Fig. 4.

To check the energy stability of the experimentally obtained structures of Ca-IV and -V, DFT calculations were performed by the software CASTEP [22] of Accelrys, Inc. The lattice parameters were set to the experimental values. The atomic positions were optimized to minimize the total energy. We employed the Wu-Cohen GGA [23] and used an ultrasoft pseudopotential [24]. The atomic positions after the optimization for Ca IV and V converged to (0.5145, 0.1840, 0.0949) and (0, 0.1596, 0.1893), respectively. The shifts from the experimental values were small enough to maintain the structures and could not be identified in Figs. 2 and 4. Thus, the experimental structures and the energetically optimized ones were confirmed to be an excellent match.

By analyzing a coexisting diffraction pattern of Ca III and IV obtained at 123 GPa, the atomic volume V_1 was determined to be 12.29 and 11.81 Å^3, respectively. The volume reduction for the III–IV transition was 4.0%, which is a relatively large value. By analyzing a coexisting pattern of Ca IV and V at 152 GPa, the V_1 was determined to be 10.64 and 10.59 Å^3, respectively. The volume reduction for the IV–V transition was 0.4%.

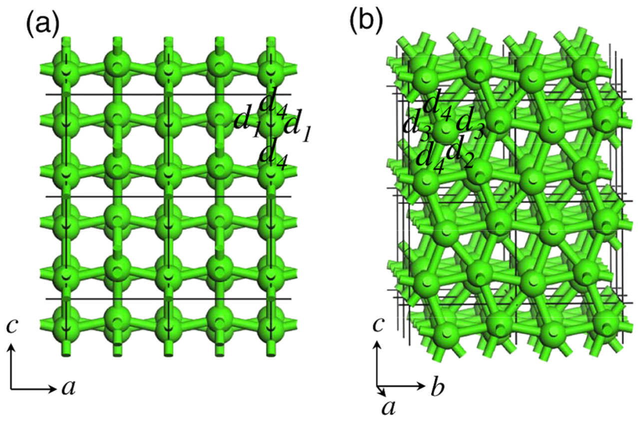

FIG. 4 (color online). Crystal structure of calcium phase V at 154 GPa in (a) the *ac* and (b) the *bc* planes for $2 \times 2 \times 2$ unit cells. The interatomic distances of less than 2.5 Å are shown by the sticks. Labels d_1 to d_4 on the sticks represent the 1st to 4th nearest distances.

Figure 5 shows the interatomic distances at various pressures for the previous Ca I, II, and III, and the present Ca-IV and -V data. There are no distances located between 2.5 and 2.8 Å for both Ca IV and V. The nearest-neighbor distances d_1, d_2, d_3, and d_4 located from 2.2 to 2.5 Å can be bound to the first group, since they are all close to the first nearest distance of Ca III. A total of 7 distances are included in the first group, corresponding to the distances shown on the sticks in Figs. 2 and 4. The nearest-neighbors d_5, d_6, and d_7 located from 2.8 to 3.3 Å can be bound to the second group, since they are close to the second nearest distance of Ca III. A total of 5 distances are included in the second group. For the Ca-IV structure at 130 GPa, there are twofold $d_1 = 2.216$ Å, single $d_2 = 2.341$ Å, twofold $d_3 = 2.384$ Å, and twofold $d_4 = 2.451$ Å in the first group. For the Ca-V structure at 154 GPa, there are twofold $d_1 = 2.208$ Å, single $d_2 = 2.216$ Å, twofold $d_3 = 2.299$ Å, and twofold $d_4 = 2.311$ Å in the first group.

Since the interatomic distances of Ca IV and V are split in this way, it is difficult to explain their bonding natures. Therefore, we would like to call them a 7 (= 2 + 1 + 2 + 2) coordinated structure by summing the 4 kinds of distances in the first group. A previously known structure with a 7 coordination number in an element is α-gallium with the space group *Cmca* existing at ambient pressure and temperature [25]. This shows $1 + 2 + 2 + 2 = 7$ nearest neighbors of which the 1st nearest distance ($d_1 = 2.482$ Å)

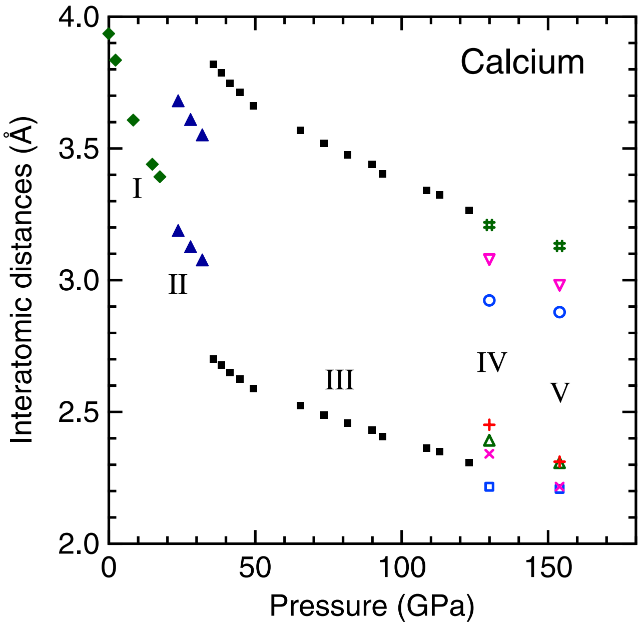

FIG. 5 (color online). Dependence of the interatomic distances on pressure for calcium phases I, II, III, IV, and V. Filled diamonds (◆) indicate the 1st nearest-neighbor distance for Ca I. Filled triangles (▲) and squares (■) represent the 1st and the 2nd nearest-neighbor distances for Ca II and Ca III, respectively. The distances up to the 7th nearest neighbor for Ca IV and Ca V are shown by the following symbols: d_1: □, d_2: ×, d_3: △, d_4: +, d_5: ○, d_6: ▽, d_7: #.

is clearly shorter than the 2nd one ($d_2 = 2.691$ Å, $d_2/d_1 = 1.084$); therefore, a Ga_2 dimer can be recognized in the structure. We investigated the possibility of forming a Ca_2 dimer in Ca V. When we changed the atomic coordinate to (0, 0.1518, 0.1801), a single distance of d_2 was shortened to 2.070 Å and a twofold d_1 was elongated to 2.242 Å, forming a clear Ca_2 dimer ($d_1/d_2 = 1.083$). The DFT calculation with this model produced 35 meV higher free energy per atom than that of the experimental model. This value is large enough to deny the possibility of the Ca_2 model. Lithium is predicted to form a Li_2 dimer with the space group *Cmca* above 98 GPa [26], and its intramolecular distance looks much shorter than the 2nd neighbor. If we assume such configuration in Ca V, the free energy became 5 eV higher per atom. Ca V does not seem to have a bonding nature for forming a dimer. Thus, we conclude that both Ca IV and V have structures which have never been seen in other alkaline-earth metals or in other elements.

The differences between our experimental and Ishikawa's models can now be discussed. Ishikawa's Ca-IV model contains 2 different atomic sites in the space group $P4_3$. Each site of the atom forms a helical chain along the c-axis. From their structural parameters, we calculated the intrachain distance between the same atomic site to be 2.41 Å and found it to correspond to the d_3 of our model. When we measured the distances between atoms at a different atomic site, we were able to find 3 kinds of shorter distances of 2.24, 2.27, and 2.33 Å which corresponded to our d_1, d_2, and d_4. Finally, we found that their Ca-IV model could be fully converted to $P4_32_12$ with only 1 atomic site [27]. For Ca V, the space group of Ishikawa's model was reported to be *Cmca*, the same as our experimental result. They called their Ca-V model a "zigzag chain" structure. However, we found that their intrachain distance along the c-axis was not the first nearest distance but the 4th one and corresponded to the d_4 of our model. By comparing only the atomic positions, Ishikawa's models of both Ca IV and V matched ours well. They have focused on the 1-dimensional chain and discussed an incommensurately modulated structure as found in P-IV [28]. Unfortunately, neither Ca IV nor V was found to have such a character judging from the present experimental result. By excluding the interpretation of the bonding nature, their metadynamics simulation was found to have predicted correct structures as well as the P-IV case [29].

The structures of Ca IV and V determined in the present study would help to understand the mechanism that gives the highest T_c among all the elements. Calculations for the electronic and phonon structures are desirable, and additional x-ray diffraction and electrical resistance measurements above 200 GPa would be worthwhile since the T_c is still increasing with pressure and a further structural phase transition is expected to occur as well.

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[1] H. L. Skriver, Phys. Rev. Lett. **49**, 1768 (1982).
[2] M. I. McMahon *et al.*, Phys. Rev. B **61**, 3135 (2000).
[3] R. J. Nelmes, D. R. Allan, M. I. McMahon, and S. A. Belmonte, Phys. Rev. Lett. **83**, 4081 (1999).
[4] M. I. McMahon, R. J. Nelmes, U. Schwarz, and K. Syassen, Phys. Rev. B **74**, 140102(R) (2006).
[5] U. Schwarz *et al.*, Phys. Rev. Lett. **83**, 4085 (1999).
[6] M. I. McMahon, S. Rekhi, and R. J. Nelmes, Phys. Rev. Lett. **87**, 055501 (2001).
[7] O. Degtyareva, M. I. McMahon, and R. J. Nelmes, Phys. Rev. B **70**, 184119 (2004).
[8] U. Schwarz *et al.*, Phys. Rev. B **67**, 214101 (2003).
[9] M. I. McMahon, O. Degtyareva, and R. J. Nelmes, Phys. Rev. Lett. **85**, 4896 (2000).
[10] H. Fujihisa *et al.*, Phys. Rev. B **72**, 132103 (2005).
[11] M. I. McMahon *et al.*, Phys. Rev. B **73**, 134102 (2006).
[12] H. Olijnyk and W. B. Holzapfel, Phys. Lett. A **100**, 191 (1984).
[13] T. Yabuuchi, Y. Nakamoto, K. Shimizu, and T. Kikegawa, J. Phys. Soc. Jpn. **74**, 2391 (2005).
[14] K. J. Dunn and F. P. Bundy, Phys. Rev. B **25**, 194 (1982).
[15] K. J. Dunn and F. P. Bundy, Phys. Rev. B **24**, 1643 (1981).
[16] S. Okada *et al.*, J. Phys. Soc. Jpn. **65**, 1924 (1996).
[17] T. Yabuuchi, T. Matsuoka, Y. Nakamoto, and K. Shimizu, J. Phys. Soc. Jpn. **75**, 083703 (2006).
[18] T. Ishikawa *et al.*, Phys. Rev. B **77**, 020101(R) (2008).
[19] Y. Nakamoto *et al.*, J. Phys. Soc. Jpn. **76**, Suppl. A, 25 (2007).
[20] O. Shimomura *et al.*, Rev. Sci. Instrum. **63**, 967 (1992).
[21] M. A. Neumann, J. Appl. Crystallogr. **36**, 356 (2003).
[22] S. J. Clark *et al.*, Z. Kristallogr. **220**, 567 (2005).
[23] Z. Wu and R. E. Cohen, Phys. Rev. B **73**, 235116 (2006).
[24] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990).
[25] H. G. von Schnering, and R. Nesper, Acta Chem. Scand. **45**, 870 (1991).
[26] J. B. Neaton and N. W. Ashcroft, Nature (London) **400**, 141 (1999).
[27] We reported the space group modification to the authors of Ref. [18]. They corrected the space group to $P4_32_12$ in an erratum for their paper [18].
[28] H. Fujihisa *et al.*, Phys. Rev. Lett. **98**, 175501 (2007).
[29] T. Ishikawa, H. Nagara, K. Kusakabe, and N. Suzuki, Phys. Rev. Lett. **96**, 095502 (2006).