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Ca-VI: A high-pressure phase of calcium above 158 GPa

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Compressed calcium exhibits successive structural transitions: face-centered cubic (Ca-I)→body-centered cubic (Ca-II)→simple cubic (Ca-III)→$P4_12_12$ (Ca-IV)→$Cmca$ (Ca-V). We performed x-ray diffraction measurements of calcium at pressure up to 172 GPa at room temperature and noted a high-pressure phase "Ca-VI" above 158 GPa. The structure was determined to be an orthorhombic $Pnma$ by a Rietveld analysis and confirmed the structure with a density-functional theory calculation. The obtained structure matched to the ones predicted by Yao *et al.* [Phys. Rev. B **78**, 054506 (2008)] well. An orthorhombic model for Ca-III is briefly reported.

Among alkaline-earth metals, the physical properties of Ca, Sr, and Ba under high pressure have been studied experimentally as well as theoretically from the viewpoint of *s-d* electron transfer.[1] Structural experiments have revealed that a "host-guest" structure is formed in the high-pressure phase of Sr and Ba.[2,3] The superconducting transition temperature (T_c) of Ba increases with pressure and has a saddle point in the Ba-IV phase of the host-guest structure,[4] where the *s-d* electron transfer is considered to be completed.[3] In the case of Ca, the host-guest structure has not been found yet. The pressure dependence of T_c and the crystal structure in the high-pressure phase of Ca have been of interest.

Recently, the high-pressure phases of calcium were intensely examined experimentally and theoretically. At ambient pressure, Ca has a fcc structure. With increasing pressure, it undergoes successive phase transitions into a bcc phase at 20 GPa, then to a simple-cubic (sc) phase at 32 GPa.[5] We have previously reported that two more forms have been identified: the Ca-IV phase and the Ca-V phase above 113 GPa and 139 GPa, respectively,[6,7] as shown in Fig. 1. Later, their structures were also clarified; the space groups of Ca-IV and Ca-V are $P4_12_12$ and $Cmca$, respectively.[8] The superconducting transition of Ca was confirmed by Dunn and Bundy[9] at 2 K and 44 GPa. The T_c of Ca was found to increase linearly with pressure from 3 K at 85 GPa to 15 K at 150 GPa.[10] Furthermore, the increase in T_c continues by elevating pressure in sc, Ca-IV, and Ca-V phases, and it reaches 25 K at 161 GPa, which is the highest recorded among all the elements.[11]

Several theoretical papers related to the high-pressure polymorphs of Ca have also been reported. The sequential transitions found in reported experimental and theoretical studies by four groups, including ours are summarized in Fig. 1, in which the space-group symmetries and transition pressure of each phase are presented.[12–16] Yao *et al.* have previously reported by theoretical calculation a $Pnma$ structure after sc in which they identified the structure as our observed phase Ca-IV. Recently Ishikawa *et al.* also found the $Pnma$ phase after Ca-V, which they introduced from our data. This structure is same as proposed by Yao *et al.* The present study aims to confirm the proposed phase by high-pressure x-ray diffraction using synchrotron radiation.

In situ powder x-ray diffraction experiments were performed on Ca samples with a diamond-anvil cell at pressures up to 172 GPa at room temperature. We used beveled diamond anvils with inner culets of 100 or 150 μm. A rhenium (Re) metal plate of 250 μm was preindented to 10–20 μm in thickness and was used as a gasket. Small pieces of Ca metal cut from a block which had a stated purity of 99.99%
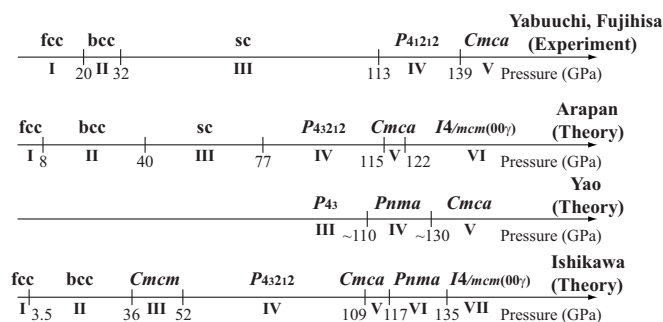

FIG. 1. Schematic views of pressure phase diagrams proposed by experimental (Refs. 6–8) and theoretical (Refs. 12–16) studies on high-pressure phase of Ca.
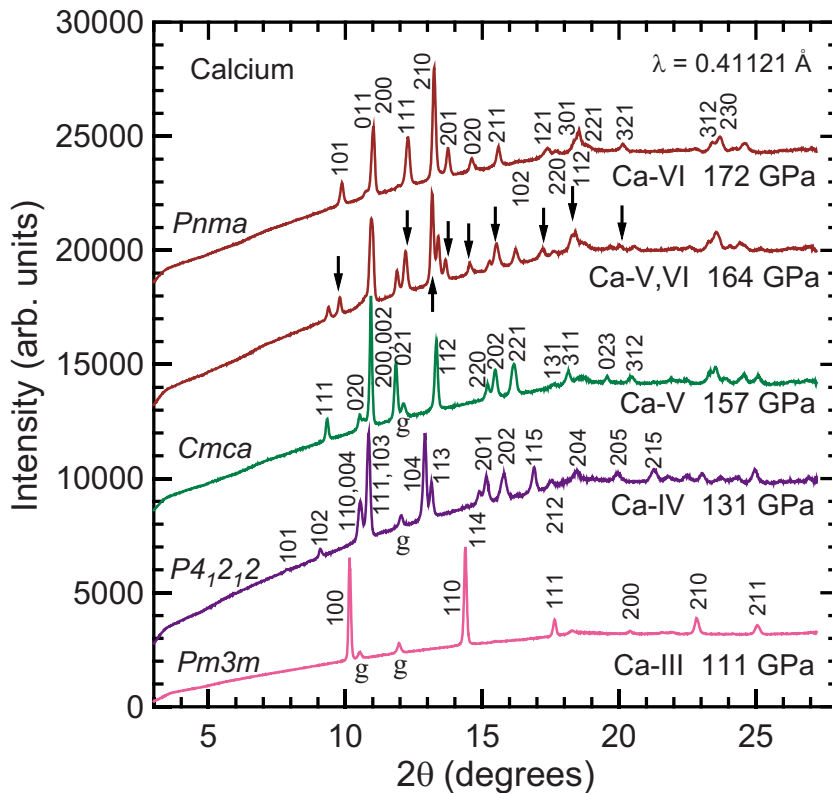
FIG. 2. (Color online) X-ray diffraction patterns of calcium at several pressures. The peaks with arrows show the new phase, Ca-VI. The g denotes the peak from Re gasket. The Miller indices are shown for each phase.

(Aldrich) were loaded into the gasket hole of 40 μm in diameter without a pressure transmitting medium. All sample preparation and loading procedures were performed in an Ar atmosphere to prevent sample oxidization or any other chemical reaction. Pressure was determined by the diamond Raman method using the calibration curve proposed by Akahama and Kawamura.[17] An angle dispersive diffractometry was adopted using monochromatized synchrotron radiations with an imaging plate detector in the SPring-8 or the Photon Factory (PF). The x-ray beam of wavelength $\lambda=0.41121$ Å was focused by using a polymer compound refractive lens (SU-8 produced by ANKA) at the undulator beamline BL10XU in the SPring-8. The x-ray beam with wavelength $\lambda=0.41210$ Å was used at bending magnet beam line NE1 in the PF. The x-ray beams were radiated through pinhole collimators of 10 μm (SPring-8) or 15 μm (PF) in diameter.

Selected x-ray diffraction patterns obtained under a compression process at room temperature at the SPring-8 are shown in Fig. 2. The peaks marked "g" represent the diffractions from a Re-metal gasket. The sample shows the phase transitions from sc to the Ca-IV phase and from the Ca-IV phase to the Ca-V phase with an increase in pressure below 157 GPa at room temperature. Under further compression to 172 GPa, a new spectrum appeared at 164 GPa, indicating a transition to a new higher-pressure phase from the Ca-V phase. We named this phase "Ca-VI." The peaks marked by arrows in Fig. 2 indicate the Ca-VI phase. In another experimental run at the PF, we observed the transition from Ca-V phase to Ca-VI phase at around 158 GPa. Gathering these data, we conclude that Ca-V is stable in a narrow pressure region and a new higher-pressure phase exists at room tem-

perature. By the increase in applied pressure, the diffraction peak intensities of the Ca-V phase gradually became weaker and those of the Ca-VI phase became stronger. At 172 GPa, as shown in Fig. 2, the diffraction pattern of the single phase of the Ca-VI is obtained.

We performed a structure analysis with a normal procedure of an indexing, a space-group determination, and a Rietveld refinement without using Yao's model. The Ca-VI pattern at 172 GPa in Fig. 1 was indexed with 13 peaks using the program X-CELL (Ref. 18) from Accelrys, Inc. The most probable candidate for the unit cell is an orthorhombic lattice of $a=4.28$ Å, $b=2.88$ Å, and $c=3.23$ Å with a cell volume of $V=39.8$ Å^3. This cell could be considered to contain four atoms since the atomic volume V_1 of Ca-V at 154 GPa was 10.50 Å^3.[8] The following 18 space-group numbers were allowed for the orthorhombic cell from the extinction rule: 16–19, 25, 26, 28, 29, 31–33, 47, 51, 52, 55, 57, 59, 62. A structure model with the space group $Pna2_1$ (33) could fit the diffraction intensities. By raising the symmetry and swapping the b and c axes, the space group $Pnma$ (62) could finally be obtained without worsening the fit. The main misfit was found at the strongest peak at $2\theta=13.2°$. This misfit could not be improved by changing the atomic coordinates or by breaking the orthorhombic symmetry. After employing a preferred orientation correction of the March-Dollase type, the misfit was eliminated as shown in Fig. 3. Thus, the structural parameters were determined to be $a=4.276\pm0.001$ Å, $b=3.229\pm0.001$ Å, $c=2.881\pm0.001$ Å, and $V=39.77$ Å^3, and the Ca atom at the 4c Wyckoff position of ($x=0.1704\pm0.0002$, 1/4, $z=0.1148\pm0.0006$).

To check the energy stability of the experimentally obtained structure of Ca-VI, density-functional theory calcula-
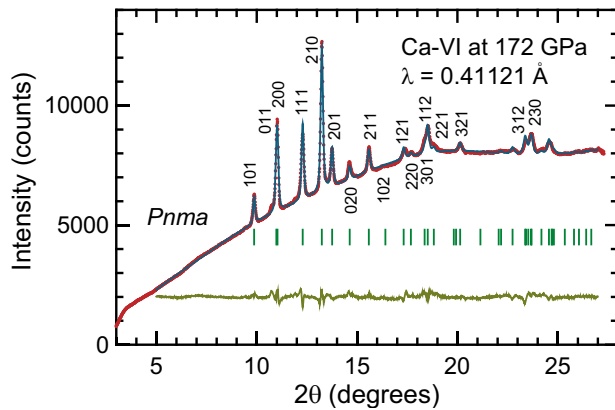
FIG. 3. (Color online) The observed diffraction pattern of Ca-VI at 172 GPa (dot) and the calculated profile of the *Pnma* model (curve) after the Rietveld refinement. The tick marks show the calculated peak positions for the proposed *Pnma* structure. The differences between the observed and calculated profiles are shown below the tick marks. The preferred orientation direction and the R_0 value for the March-Dollase function were converged to $(0.932 \pm 0.001, \ 0.285 \pm 0.002, \ 0.224 \pm 0.002)$ and 0.447 ± 0.006, respectively. The final fit resulted in reliability factors of R_{wp} =1.06%, R_p=0.78%, and R_{wp} (without background) =14.17%.

tions were performed by using the program CASTEP (Ref. 19) from Accelrys, Inc. The lattice parameters were set to the experimental values. The atomic positions were optimized to minimize the total energy. We employed the GGA (generalized gradient approximation)-PBEsol (Perdew-Burke-Ernzerhof for solids) exchange-correlation functionals[20] and used an ultrasoft pseudopotential.[21] The atomic position after the optimization converged to (x=0.1720, 1/4, z=0.1192) as displayed in Fig. 4. The experimental structures and the energetically optimized ones were confirmed to be an excellent match. The geometrical optimization without space-group constraint and the dynamics simulation created with CASTEP proved that the *Pnma* structure is stable.

The nearest-neighbor distances for Ca-VI at 172 GPa were investigated. There are fourfold d_1=2.268 Å, twofold d_2=2.273 Å, and twofold d_3=2.275 Å. The next-nearest distance d_4=2.881 Å is located much further than d_3. Therefore the coordination number for Ca-VI is found to be 8. The result seems to be natural compared to the seven coordinated structures of Ca-IV and Ca-V.[8] Our Ca-VI model was compared to the theoretically predicted model of Ca-IV by Yao.[13] Their structural parameters were given as a=4.420, b=3.386, c=2.959, x=0.326, and z=0.614 at 120 GPa as shown by dashed lines and dark balls in Fig. 4. Yao's model matched ours very well.

Very recently, Yao *et al.*[22] proposed a new tetragonal $I4_1/amd$ model for Ca-III. This model is quite different from previous simple-cubic models. We think this model is incorrect since it gives a completely different diffraction pattern from the experimental one. Gu *et al.*[23] reported that the simple-cubic model for Ca-III was confirmed to be correct.
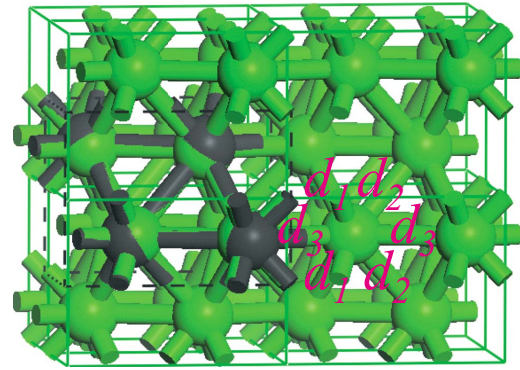

FIG. 4. (Color online) The crystal structure of the calcium phase VI at 172 GPa for $2 \times 2 \times 2$ unit cells. The interatomic distances of less than 2.3 Å are shown by the sticks. Labels d_1 to d_3 on the sticks represent the first to third nearest distances. The dark balls, sticks, and dashed lines represent Yao's *Pnma* model at 120 GPa (Ref. 13).

We have noticed that the 100 and 200 peaks of Ca-III are always sharp and 110 and 111 peaks are broader. This tendency can also be seen in Gu's data. We recently performed low-temperature x-ray diffraction experiments and observed a clear splitting of the peaks. The structure was determined to be an orthorhombic *Cmmm*, a=3.814, b=3.669, and c=2.625 with atoms at $2a$ (0, 0, 0) at 47 GPa and 7 K. The Rietveld refinement of the Ca-III pattern at room temperature with the *Cmmm* model could improve the fit greatly. We think the orthorhombic distortion still remains at room temperature. Teweldeberhan and Bonev[24] and Yin *et al.*[25] calculated the phonon density of states for the simple cubic and its related structures, however, this *Cmmm* model has not been tested. Our preliminary calculation with GGA-PBEsol (Ref. 20) successfully gave the phonon dispersion with no imaginary frequency.

We reported that the highest T_c of 25 K in the element was observed at 161 GPa. The phase at this point was previously considered to be Ca-V.[11] However, the phase could possibly be a mixture of Ca-V and Ca-VI judging from the present x-ray measurement. Phase study at low temperature and high pressure is necessary. Further experiments at higher pressure are also needed to elucidate the existence of the host-guest structure predicted by Arapan *et al.*[12] and Ishikawa *et al.*[14–16]

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