Complex host-guest structure of calcium phase VII at high pressure

Thirty elements are known to show superconductivity at atmospheric pressure. Another 23 elements are currently known to show superconductivity at high pressures. The superconductivity transition temperature (T_c) increases with the pressure in some of these elements. Among these elements, Li, Ca, Y, and Sc have high T_c values near 20 K, and their highest T_c values are observed at high pressures. The highest T_c of the alkaline earth elements Sr and Ba are observed when these elements have a complex host-guest structure. The relation between the crystal structure and T_c is very interesting. As shown in Fig. 1, six crystalline phases of calcium, phases I (fcc), II (bcc), III (simple cubic, sc), IV ($P4_12_12$), V (*Cmca*), and VI (*Pnma*), have been found to exist at room temperature at ambient pressure and high pressures of 20 GPa, 32 GPa, 119 GPa, 143 GPa, and 158 GPa, respectively [1]. Superconductivity for Ca was first reported at about 44 GPa and 2 K. The T_c of Ca has been predicted to increase with the occupancy of *d*-electrons and would continue to occur with successive phase transitions. The T_c of phases IV and V increased with pressure and reached 25 K at 161 GPa and exceeded the previous highest recorded values of 20 K for Li at 48 GPa, 17.2 K for V at 120 GPa, and 19.5 K for Y at 115 GPa.

Recently, Sakata *et al*. have performed an X-ray powder diffraction experiment and discovered a new phase VII at around 210 GPa [2]. They measured the electrical resistance at low temperatures and found that phase VII has the highest T_c among all the elements at 29 K and 216 GPa. Its crystal was thought to have a typical host-guest structure as predicted by some theoretical studies [3,4]; however, the structure did not provide good quality upon Rietveld refinement. The purpose of this study is to clarify the fascinating structure of phase VII using the data obtained by synchrotron X-ray diffraction and density functional theory (DFT) calculation, and then to compare it with the previous host-guest structure to understand the relation between the crystal structure and its highest T_c.

Powder diffraction patterns of calcium samples up to 241 GPa were measured by using a diamond-anvil high-pressure cell (DAC) with a beveled diamond anvil of 100 μm inner diameter and 300 μm outer diameter and an imaging plate detector (IP) at beamline **BL10XU**. The X-ray wavelength was 0.41231 Å. The X-ray beams were collimated using a 10-μm-diameter pinhole. The typical exposure time was 10 min. A one-dimensional powder pattern was obtained by averaging all the intensities along the Debye-Scherrer rings recorded on the IP. Peak indexing and Rietveld analysis were performed with the Materials Studio (MS) software of Accelrys, Inc. DFT calculations for structural optimizations and enthalpies were carried out using the MS CASTEP program.

Structure analysis was performed on the pattern obtained at 241 GPa. Some tetragonal candidates were obtained by indexing 14 strong peaks from this pattern. However, none of these candidates were found to be appropriate since they could not fit the observed pattern. Instead of these candidates, the theoretically predicted model of *I*4/*mcm*-32 [3,4] with a=5.51 Å and c=9.18 Å shown in Fig. 2 fitted the observed strong peaks; however, some weak peaks remained unfitted. We attempted to fit these peaks with the *I*4/*mcm*(00γ) model by adjusting the incommensurability γ using Jana2006 software, but were unable to fit them. We tried to expand the cell size of the *I*4/*mcm*-32 model in the *ab*-plane and created tetragonal supercells. Finally, all diffraction peaks were fitted successfully in a 2×2×1 model by optimizing the *z*-coordinates of the guest chains. The converged structure has two *z*-coordinates as shown in Fig. 3. Since this model, which is assumed to be

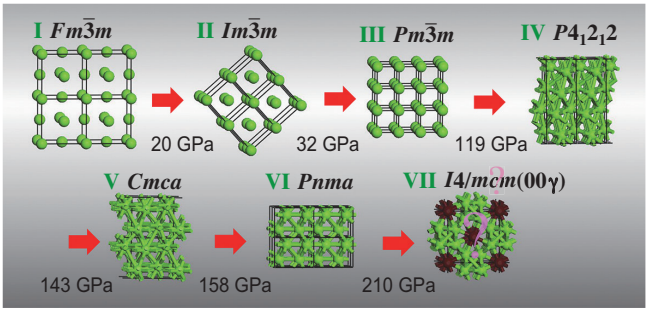

Fig. 1. Successive phase transitions of calcium under pressure [1]. The question marks in the crystal structure of phase VII [2] indicate that its structure is theoretically predicted but not established yet.

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 using Jana2006 software converged to 1.333 and could also be regarded as 4/3. This supercell can be assigned to the 3-dimensional space group $P4_2/ncm$. The model containing 128 atoms is called $P4_2/ncm$-128. Its atomic coordinates for all 12 sites were refined by Rietveld analysis and DFT calculation. The refined coordinates closely matched and the structure was confirmed to be a valid energy minimum. 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 matched the experimental pressure of 241 GPa very well. Our phonon calculation for the $P4_2/ncm$-128 model confirmed the absence of an imaginary frequency.

Although all guest chains of the previous model aligned similarly, as shown at the bottom of Fig. 2, there are two guest chains that can be distinguished by their *z*-coordinates as shown by brown and blue atoms in Fig. 3. We can conclude that the appearance of the different chains is the origin of the 2×2×1 supercell. It would be very difficult to predict the $P4_2/ncm$-128 model only by theoretical calculation since the difference in enthalpy from that of the $I4/mcm$-32 model is too small and the number of atoms of 128 is too large for *ab initio* structure prediction. The volume per atom decreased by 22% from phase I at 1 bar to phase VII at 241 GPa. The corresponding first nearest interatomic distance decreased from 3.92 Å to 2.10 Å.

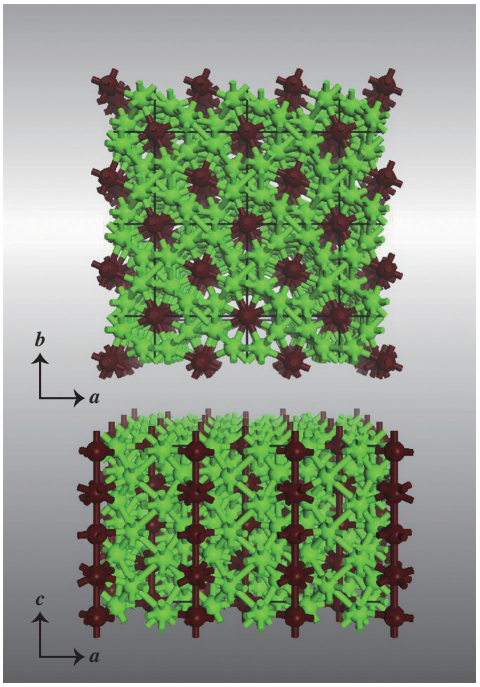

Fig. 2. Known and theoretically predicted host-guest structures [3,4] such as that observed in potassium phase III. The top and bottom figures show different views of the same structure. All spheres indicate calcium atoms; the atoms forming the host structure are in green and those forming the guest structures are in brown.

Our present work [5] is expected to stimulate theoretical investigations such that the T_c value of calcium phase VII may be calculated using this novel $P4_2/ncm$-128 model. Calcium, while being a single element, was found to show a new complex host-guest structure. The results of this study will lead to the design of new high-temperature superconducting materials.

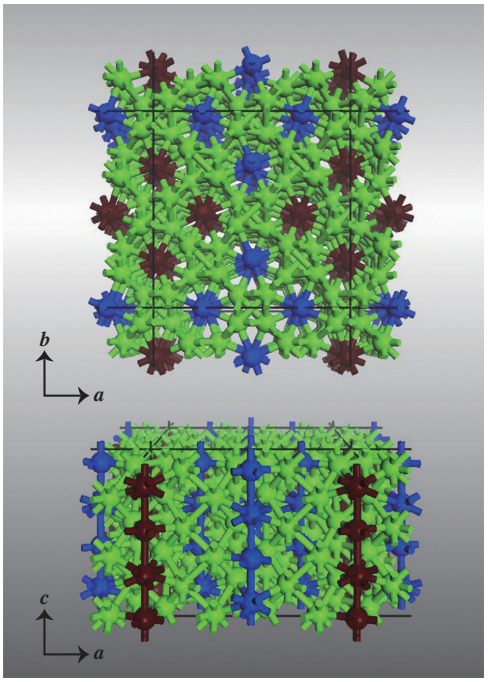

Fig. 3. Crystal structure of phase VII calcium at 241 GPa analyzed in this study [5]. All spheres indicate calcium atoms; the atoms forming the host structure are in green and those forming the guest structures are in blue and brown.

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