PHYSICAL REVIEW B **83**, 220512(R) (2011)

Superconducting state of Ca-VII below a critical temperature of 29 K at a pressure of 216 GPa

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(Received 17 January 2011; revised manuscript received 16 May 2011; published 22 June 2011)

Pressure-induced superconductivity and structural phase transitions in calcium (Ca) were studied by electrical resistance measurements and angular dispersive x-ray diffraction measurements under pressures above 200 GPa. Other alkaline-earth metals, Sr and Ba, have a high-pressure phase with a "host-guest" structure, and the maximum superconducting transition temperature T_c is observed in this phase. However, the high-pressure phase with the host-guest structure has not yet been observed in Ca. In this work, we found a high-pressure phase (Ca-VII) around 210 GPa with a host-guest structure. Furthermore, the T_c onset at Ca-VII increased continuously, reaching 29 K at 216 GPa.

DOI: 10.1103/PhysRevB.83.220512 PACS number(s): 74.62.Fj, 61.05.cp, 64.70.K−, 74.70.−b

Superconductivity in elements under high pressure has been investigated intensively and a relatively high superconducting transition temperature T_c of around 20 K has been observed in several elements such as Li, Ca, Sc, and Y.[1–4] Indications of the superconducting transition of Ca were observed by Dunn and Bundy at 2 K and 44 GPa.[5] The T_c onset of Ca increases linearly as pressure increases from 3 K at 85 GPa and reaches about 25 K at 161 GPa.[2,5,6] This value is the highest T_c onset among single elements at present. The high-pressure electronic and crystallographic properties of alkaline-earth metals, Ca, Sr, and Ba have been discussed in terms of the pressure-induced *s-d* electron transfer.[7] In the case of Ba and Sr, T_c increases with increasing pressure and the maximum appears in the Ba-IV and Sr-V phases. These phases have the same host-guest structure, where the *s-d* electron transfer is considered to be completed.[8,9]

At ambient pressure and temperature, Ca has a face-centered cubic structure (Ca-I). With increasing pressure, it undergoes successive phase transitions into a body-centered cubic phase (Ca-II) at 20 GPa and to a simple-cubic (sc) phase (Ca-III) at 32 GPa (reported by Olijnyk *et al.*).[10] Recently, there have been several theoretical and experimental studies on the structure of Ca-III. In theoretical investigations, Errea *et al.*[11] and Yao *et al.*[12] introduced the stability of the sc structure of Ca at 300 K, respectively. Teweldeberhan *et al.* suggested no sc structures such as the crystal structure of space group *Cmmm* at 0 K and room temperature.[13] Experimentally, Gu *et al.* suggested that the Ca-III phase has an sc structure at room temperature.[14] Mao *et al.* suggested that the structural transition from an sc-like, primitive unit by rhombohedral distortion to a monoclinic phase at 30 K under a pressure of around 40 GPa.[15] We have also suggested that the Ca-III phase has a *Cmmm* structure at low temperature and at room temperature.[16] We have previously reported that two more forms have been found: the Ca-IV phase and the Ca-V phase above 113 GPa and 139 GPa, respectively.[17–19] Furthermore, very recently we reported the high-pressure phase "Ca-VI" with a crystal structure of space group *Pnma* above 158 GPa.[16] However, Ca shows no phase transition to the host-guest structure up to around 170 GPa.

Many theoretical papers related to the high-pressure polymorphs of Ca have been reported. Yao *et al.* have reported a *Pnma* structure above Ca-III in which they identified the structure as our observed phase Ca-IV.[20] Ishikawa *et al.* also found the *Pnma* phase above Ca-V, which they introduced from our data.[21] Our observed Ca-VI has the same *Pnma* structure as Yao's *Pnma* model. Therefore, the sequence of pressure-induced phases by Ishikawa *et al.* agrees well with our experimental sequence until Ca-VI. The interesting suggestion in Ishikawa's study is that they predicted the high-pressure phase Ca-VII with the host-guest structure, which was introduced by Arapan *et al.*[22]

From these experimental and theoretical results on Ca and related elements, Sr and Ba, it is predicted that, in Ca, the phase with host-guest structure has the highest T_c. In this study, we performed powder x-ray diffraction and electrical resistance measurements of Ca under high pressure in order to search for the higher-pressure phase of Ca-VII with a host-guest structure and superconductivity.

A Ca block with a stated purity of 99.99% was purchased from Aldrich Chemical Company. The sample was set in a diamond anvil cell (DAC) for x-ray diffraction and electrical resistance measurements were performed in an Ar atmosphere to prevent sample oxidization or any other chemical reaction. Pressure was determined by using the diamond Raman method described by Akahama and Kawamura.[23] *In situ* x-ray diffraction experiments for a powder Ca sample were performed with the DAC at pressures up to 241 GPa at room temperature. The diamond anvils had an inner culet diameter of 100 μm, a beveled angle at 8 degrees, and an outer culet of 300 μm. A metal gasket plate of rhenium (Re) of 250 μm was pre-indented to 15 μm in thickness. The sample was cut into small pieces and loaded into a gasket hole 40 μm in diameter without a pressure-transmitting medium. The x-ray diffraction experiments were carried out by an angle-dispersive method using an image-plate detector. High-quality powder patterns of Ca in the high-pressure region above 200 GPa were obtained by synchrotron radiation at BL10XU in SPring-8, which was monochromated to a wavelength of $\lambda = 0.4123$ Å focused by using a polymer compound refractive lens (SU-8 produced

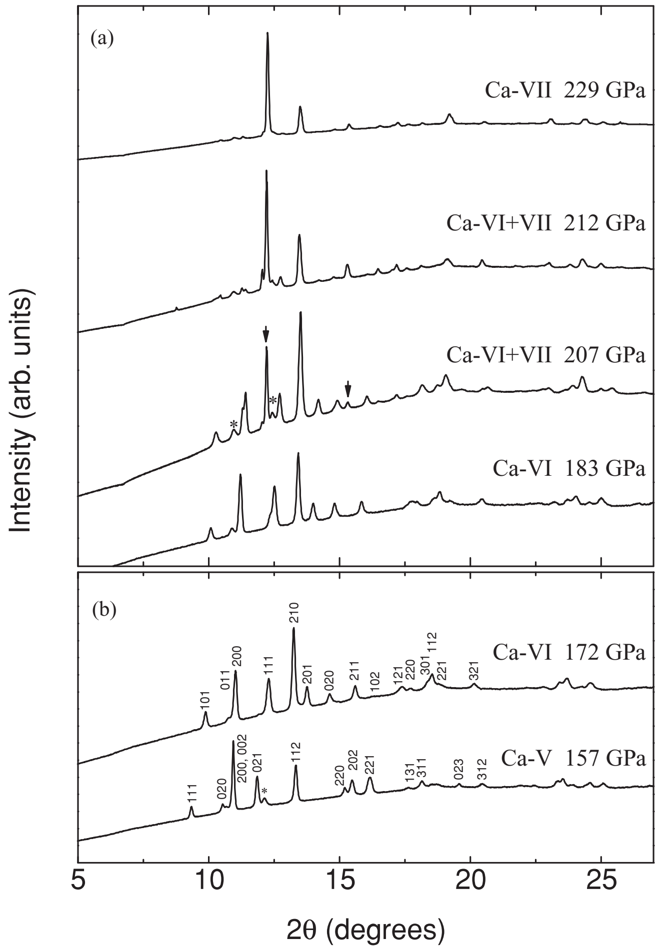

FIG. 1. Pressure variation in x-ray diffraction profiles for Ca at room temperature up to 241 GPa. The peaks marked with an asterisk were the reflections from the Re metal gasket. (a) Data obtained with wavelength $\lambda = 0.4123$ Å at pressures above 183 GPa. (b) Data for $\lambda = 0.4112$ Å in lower-pressure regions.

by ANKA). The x-ray diffraction data in the lower-pressure region were also obtained with a wavelength of $\lambda = 0.4112$ Å. The electrical resistance measurements of Ca were separately performed up to 216 GPa without a pressure-transmitting medium with diamond anvils having a 50–300 μm beveled culet. We aligned the electrodes made of platinum foil in a four-probe configuration. The insulating layer on the Re gasket was made from Al_2O_3 without any binder to prevent chemical reactions. The electrical resistance was measured by using an ac resistance bridge (LR-700) with a 3 μA excitation current.

Selected x-ray diffraction patterns obtained under a compression process at SPring-8 are shown in Fig. 1. The peaks marked with an asterisk represent the diffraction from a Re metal gasket. Ca shows phase transitions from phase Ca-V to Ca-VI as pressure increases up to 172 GPa in Fig. 1(b). The reflections were all assigned to the phase Ca-V and Ca-VI.[16–19] Figure 1(a) shows the x-ray diffraction data above 183 GPa and the structural phase transition from phase Ca-VI at around 210 GPa. Distinguishing reflections with arrows appear at around $2\theta = 12.2$ and 15.3 degrees. We named this phase "Ca-VII." We can see from Fig. 1(a) that the relative intensity

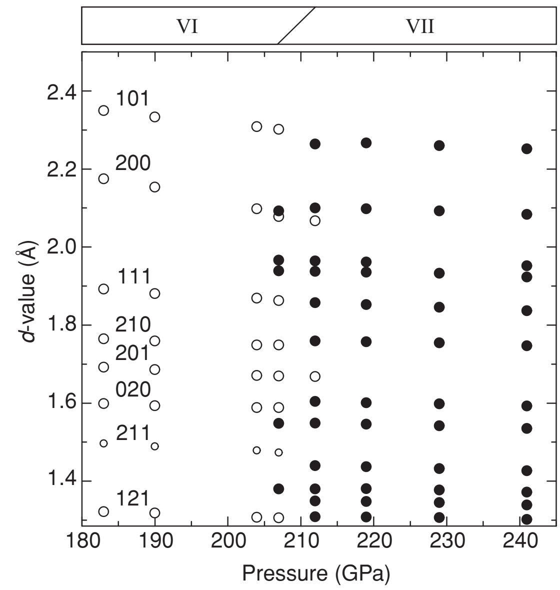

FIG. 2. Pressure dependence of d values for Ca from phases of Ca-VI and Ca-VII up to 241 GPa. This indicates a structural phase transition at around 210 GPa.

of the diffraction lines changed slightly after the transition. At 229 GPa, the diffraction pattern of the single phase of the Ca-VII phase is obtained. In Fig. 2, the pressure dependence of the d value for each line is shown up to 241 GPa. It is also clear from the dependence that a structural phase transition occurs around 210 GPa.

The pressure dependence of electrical resistance $[R(P)]$ at room temperature is shown in Fig. 3. The main features of $R(P)$ are consistent with our previous report.[2] Structural phase transitions affect the $R(P)$ curve; for example, the sudden increase and decrease around 110 and 140 GPa indicates phase transitions Ca-III → Ca-IV (at 113 GPa from powder x-ray diffraction) and Ca-IV → Ca-V (at 139 GPa), respectively. The resistance was nearly independent of pressure from 160 to 190 GPa in Ca-VI. Above 190 GPa, a rapid increase in resistance was observed. This increase indicates a start of the phase

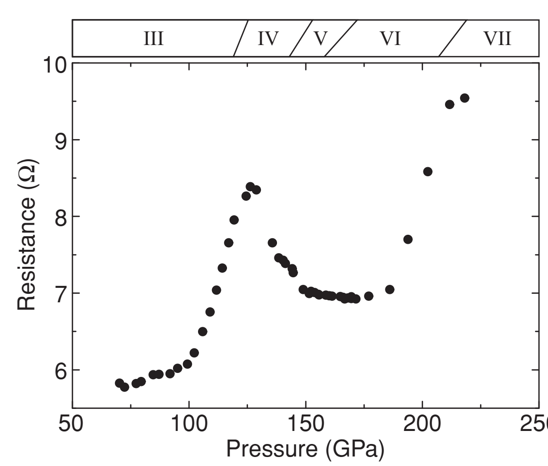

FIG. 3. $R(P)$ plots at room temperature. The upper band indicates the pressure regions of each phase determined by x-ray diffraction measurements.

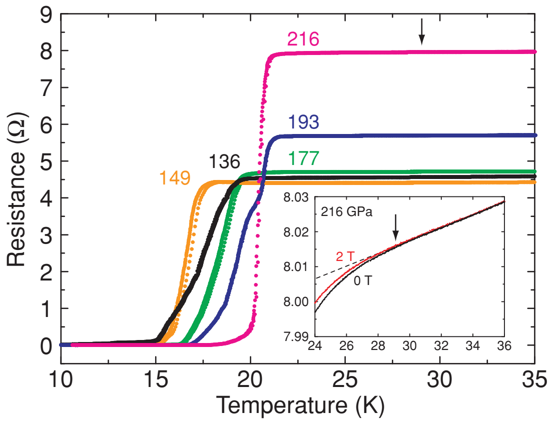

FIG. 4. (Color online) $R(T)$ curves showing superconducting transitions under several different pressures. The numerals indicate the pressure in GPa. The arrows indicate the T_c onset at 216 GPa. The inset shows an enlarged view of the $R(T)$ curve at 216 GPa under a magnetic field of 0 or 2 T. The dashed line in the insertion indicates the extrapolation of the linear temperature dependence of resistance.

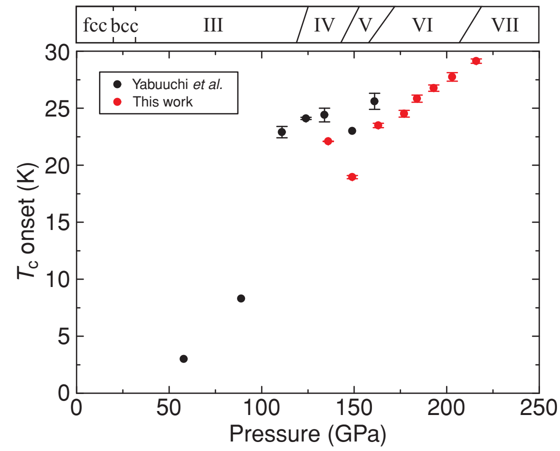

FIG. 5. (Color online) $T_c(P)$ plots from the present work and from previous works. The upper band indicates the pressure regions of each phase determined by x-ray diffraction measurements.

transition from Ca-VI to Ca-VII. Furthermore, the increase was nearly saturated from about 210 GPa, and the pressure was consistent with the results of x-ray diffraction. Therefore, we can claim that the electrical resistance measurement above 210 GPa was performed at Ca-VII.

The temperature dependence of electrical resistance [$R(T)$] up to 216 GPa is shown in Fig. 4. The pressure was determined at room temperature and at low temperature (i.e., around 20 K) by the diamond Raman method using the calibration curve proposed by Akahama and Kawamura.[23] The pressure change during temperature cycle was smaller than 5 GPa. In Fig. 4, we show the pressure determined at low temperature. The superconducting transition shifts to low temperature only once at 149 GPa and then shifts to high temperature continuously with the application of pressures above 160 GPa. At around 190 GPa, a clear step was observed in the superconducting transition. This step indicates the coexistence of two phases, Ca-VI and Ca-VII, and began to disappear with increasing pressure. Finally, no step was observed at 216 GPa. Therefore, the major part of the sample already transitioned to Ca-VII and the superconductivity at 216 GPa is assignable to Ca-VII.

T_c at each pressure was determined from the onset of the drop as shown in the inset of Fig. 4. We defined the onset as the temperature at which the resistance curve starts to deviate from the linear temperature dependence. We used the same definition of T_c as in our previous work to compare the results. This definition reflects T_c at the highest pressure region in the sample. The magnetic field dependence of $R(T)$ is also shown in the inset. The $R(T)$ curves at 0 and 2 T deviated from each other below the determined T_c onset. The pressure dependence of the , onset is shown in Fig. 5 with the pressure dependence obtained in previous work,[2] and the phase diagram is determined by x-ray diffraction at room temperature. Observed T_c onsets in this work were somewhat lower than that in previous works; however, tendencies in the pressure dependence of T_c onset [$T_c(P)$] were the same. The T_c onset in Ca-V is lower than that in neighboring phases and the T_c onset around 25 K at 160 GPa is assignable to Ca-VI, which corresponds to Ishikawa's suggestion.[21]

In Ca-VI, the T_c onset continuously increased as pressure increased. At 216 GPa, the highest pressure in this work, the T_c onset reached 29 K in Ca-VII. The x-ray diffraction pattern of Ca-VII is similar to that in Ba-IV and Sr-V, which have a host-guest structure. It is suggested that Ca-VII also has a host-guest structure. Full analysis of the crystal structure using our x-ray diffraction pattern in Ca-VII is now being performed by Fujihisa.[24] Preliminary results of the crystal structure analysis suggested that Ca-VII has the host-guest structure theoretically predicted by Ishikawa *et al.* and Arapan *et al.*[21,22] We claim that the crystal structure at low temperature is the same as that at room temperature because no anomalies in the $R(T)$ curve were observed from low temperature to room temperature. The T_c onset in Ca-VII suggested that Ca has the highest T_c onset in phases with a host-guest structure, which is the same as for the other alkaline-earth metals, Ba and Sr.

In summary, we succeeded in electrical resistance and x-ray diffraction measurements of Ca under pressures above 200 GPa. We found a structural phase transition from Ca-VI to Ca-VII, which may possibly have a host-guest structure. Furthermore, we have observed a T_c onset of Ca at 29 K at 216 GPa in Ca-VII.

This work was supported by the Scientific Research (S) 19104009 and Global COE Program (Core Research and Engineering of Advanced Materials-Interdisciplinary Education Center for Materials Science), MEXT, Japan and carried out under Proposal 2009A1893 of SPring-8.

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