# Pressure-dependent electronic structure of the A-site ordered perovskite CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> via x-ray Raman scattering

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X-ray Raman scattering (XRS) of the A-site ordered perovskite  $CaCu_3Ti_4O_{12}$  was measured under high pressure up to 13 GPa. Core excitations such as Cu 2p3d and Cu 2p4p, where the underline denotes the core hole, were detected under excitations around the Cu K absorption edge. Unoccupied electronic states were investigated with changing pressure through the XRS. The Cu ion in  $CaCu_3Ti_4O_{12}$  showed mixed valence (Cu<sup>+1</sup> and Cu<sup>+2</sup>) at atmospheric pressure: a divalent component was prevailing, with an increasing monovalent feature at increasing pressure. An electronic state was also revealed between these states at high pressure, without evidence of a structural phase transition from x-ray diffraction study.

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# I. INTRODUCTION

The A-site ordered perovskite  $CaCu_3Ti_4O_{12}$  (CCTO) exhibits a giant dielectric constant (~ 10<sup>4</sup>) over a wide temperature range (100–600 K), and then decreases by two orders of magnitude below 100 K without a structural phase transition [1,2]. The origins of this anomalous behavior remain unclear, despite many reports [3,4]. It was also reported that the CCTO shows photocatalytic activity in the visible light region [5,6]. To understand such a specific property of CCTO, the electronic structure should be investigated; however, methods based on electrons are unsuitable for insulators such as CCTO. Room-temperature angle-resolved photoemission [7] and inverse photoemission [8] were reported by Im *et al.* 

X-ray Raman scattering (XRS), as well as x-ray emission spectroscopy (XES), are suitable for studying electronic states of insulating materials, because both excitation and detection involve photons. XRS has a greater potential for revealing electronic states of insulating materials such as CCTO. An XRS study of CCTO at the Ti *L*, Cu *L*, and O *K* edges was reported by McGuinness *et al.* [9]; however, further study is needed to understand the electronic state of CCTO.

XRS under resonant conditions is often referred to as resonant inelastic x-ray scattering (RIXS), while XRS refers to nonresonant scattering. Here, however, we use XRS to refer to both resonant and nonresonant scattering. We emphasize that it is scattering by elementary excitations, where the selection rules are determined by the symmetry of the elementary excitation [10]. Here, core excitations were observed as elementary excitations. Specifically, Cu 2p3d and Cu 2p4p excitations were observed, where core holes are underlined. Because the energy of the core state is constant, the XRS spectrum reflects the density of states in the conduction band. Selected XRS of CCTO have been reported previously [11].

Here, the pressure dependences of XRS and x-ray diffraction (XRD) were acquired. Hence, the electronic and crystal structures of CCTO were investigated simultaneously. The electronic structure with changing crystal structure under high pressure would be a great help to understand the property of CCTO.

#### **II. BACKGROUND**

Light scattering is described by the nonrelativistic interaction between an electron and the radiation,

$$H_{\rm int} = \frac{e^2}{2mc^2} A^2 - \frac{e}{mc} (\mathbf{pA}), \qquad (1)$$

where **p** is the momentum operator of the electron and **A** is the vector potential of the photon [12–14]. From the perturbation **pA**, the Kramers-Heisenberg (KH) formula is derived. The differential cross section of the photon scattering with respect to the solid angle  $\Omega_{k_2}$  can be expressed as [15]

$$\frac{d^2\sigma}{d\Omega_{k_2}d(\hbar\omega)} \sim \sum_j \left| \sum_i \frac{\langle j|T_2|i\rangle \langle i|T_1|g\rangle}{E_g + \hbar\Omega - E_i + i\Gamma_i} \right|^2 \\ \times \delta(E_g + \hbar\Omega - E_j - \hbar\omega), \tag{2}$$

where  $|g\rangle$ ,  $|i\rangle$ , and  $|j\rangle$  are the initial, intermediate, and final states, respectively;  $E_g$ ,  $E_i$ , and  $E_j$  are their respective energies; and  $\hbar\Omega$  and  $\hbar\omega$  are the photon energies. The operators  $T_1$  and  $T_2$  are the radiative transitions of the incident and emitted

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FIG. 1. Energy diagram of x-ray emissions in the case of Cu *K* resonance [8]. The upper arrows represent x-ray fluorescence processes, while the lower arrows represent x-ray Raman-scattering (XRS) processes. (a) Resonant XRS, (b) quasiresonant XRS, and (c) normal (nonresonant) XRS. The full-length vertical dashed line denotes the Fermi level ( $E_F$ ). The left side corresponds to occupied states and the right side corresponds to unoccupied states. The standard binding energies are shown in parentheses. The shorter vertical dashed lines in the XRS process denote virtual states.

photons, respectively, and  $\tau_i (= \hbar/\Gamma_i)$  is the lifetime of the intermediate state. The energy difference between the initial and the final states corresponds to an elementary excitation in the Raman process (e.g., phonon, magnon, electron excitation). Here, core-level excitations were measured. Under nonresonant conditions, Eq. (2) corresponds to a Raman tensor determined by the symmetry of the elementary excitation. Because the transition via a photon is a dipole transition, the Raman-active excitations are monopoles and quadrupoles, with 0 and  $\pm 2$  changes in the orbital angular momentum  $\ell$ , respectively. When the incident photon energy is near the excitation threshold of a core electron (i.e., a resonant condition), some forbidden dipole excitations ( $\Delta \ell = \pm 1$ ) selected by an intermediate state are enhanced and become observable.

Usually, nonresonant XRS is described by the perturbation  $A^2$ , while the perturbation **pA** is used to describe resonant XRS that is often called RIXS [13]. However, the KH formula not only describes the resonant process, but also the nonresonant process. In practice, the RS process in the visible light region that is in nonresonant condition is described by the KH formula. In this study, XRS spectra were measured widely from the nonresonant to the resonant region and the selection rules in both regions are very important, thus we think the XRS spectra in this study should be described by the KH formula. So, we use the term XRS here.

Figure 1 depicts an energy diagram of x-ray emission processes in the case of Cu K resonance [10]. The Fermi level ( $E_F$ ) is indicated by the full-length vertical dashed line. The vertical solid lines on the left are core levels, and the thin dotted lines on the right are levels of unoccupied states, which consist mainly of Cu 3d and 4p states. The arrows at the top represent Cu K fluorescence processes. When the excitation energy is much greater than the binding energy of the Cu 1s core level, a core electron is emitted, followed by



FIG. 2. Crystal structure of CCTO.  $TiO_6$  clusters are tilted to four directions.

incoherent fluorescence processes ( $K\alpha_1$  and  $K\alpha_2$ ). The lower part of Fig. 1 represents coherent XRS processes. Figure 1(a) depicts resonant XRS where the core electron is excited to an unoccupied state (conduction band), and another electron in an occupied state (valence band or core level) decays to the core hole that was created. The Cu 3*d* levels are shifted to lower energies relative to the *p* levels because of the core-hole potential [16], as indicated by the dotted lines. Figures 1(b) and 1(c) represent the XRS process described here. Because the excitation energy is lower than the absorption edge, the Cu 1*s* core electron is excited to a virtual state represented by the dotted line to the left of  $E_F$  in Fig. 1. If the excited electron decays directly to the 1*s* core hole, the emitted photon undergoes elastic scattering.

If the excited system creates another elementary excitation, such as a Cu 2p3d or Cu 2p4p core excitation (represented in the dotted rectangle) with 2p core holes, the excited state loses its energy and undergoes a transition to another virtual state (the dotted line to the left of the Cu  $2p_{3/2}$  level in Fig. 1). The broad arrow in the middle of Fig. 1 denotes energy transfer to the elementary excitation. As a result, the scattered photon has a lower energy than that of the excitation. When the excitation energy is sufficiently lower than the absorption edge, the normal (nonresonant) XRS process is dominant, and a monopole transition (2p4p) is active  $(P_3-P_5)$ . In nonresonant XRS, such an even parity transition is allowed [17]. In contrast, a dipole excitation such as Cu 2p3d is prohibited in normal XRS. However, it becomes active under excitation near the absorption edge where Cu 3d states exist, and the XRS peak is resonantly enhanced. Here, such enhanced peaks are observed as  $P_1$  and  $P_2$ . In addition, because the Cu 2p level is split largely by spin-orbit interactions, then all the  $P_1-P_5$ peaks are also observed for the Cu  $2p_{1/2}$  state  $(P'_1 - P'_5)$ . These peaks overlap in the case of Ti K XRS, because of the smaller spin-orbit splitting of the Ti 2*p* level [10].

### **III. EXPERIMENT**

Figure 2 shows the crystal structure of CCTO, which is an *A*-site ordered perovskite [18,19]. One of four *A* sites is substituted with a  $Ca^{2+}$  ion (alkaline-earth metal), while the other sites are occupied by Cu ions (3*d* transition metal). Ti ions in perovskite materials have covalent bonds with O ions, forming TiO<sub>6</sub> clusters that are tilted in four different directions in CCTO. The unit cell has two formulas and the



FIG. 3. Pressure-dependent x-ray diffraction patterns of CCTO. Values next to each pattern denote the pressure in GPa.

crystal structure has the centrosymmetric space group  $Im\bar{3}$  [2], with a 7.391-Å lattice constant [18]. Half of the lattice constant is less than a standard perovskite material such as SrTiO<sub>3</sub> (3.94513 Å), while the length of O-Ti-O is comparable to that in perovskites because the TiO<sub>6</sub> cluster is tilted (i.e., a similarly sized TiO<sub>6</sub> cluster). Polycrystalline CCTO synthesized via standard solid-state reactions was used in this measurement.

The samples were loaded into the sample chamber of a stainless gasket set in a three-pin diamond-anvil cell. The diamonds had 400-µm diameter culets and mineral oil (Idemitsu, Daphne 7474) was used as the pressure medium. The pressure was calibrated by the ruby  $R_1$  fluorescence line before and after every measurement. The accuracy of the pressure measurement was approximately ±0.1 GPa.

Pressure-dependent x-ray diffraction patterns were acquired at the Taiwan beamline BL12B2 of SPring-8. The synchrotron radiation beam was monochromatized ( $\lambda =$ 0.688 8007 Å) with a Si(111) double-crystal monochromator, and then were collimated on the sample with a 50-µmdiameter pinhole. The XRD pattern was detected with a charge-coupled device at room temperature and analyzed with IPAnalyzer and PDIndexer software [20]. The Rietveld refinement of the XRD pattern was performed using the RIETAN-FP program [21].

XRS measurements were performed at the Taiwan beamline BL12XU of SPring-8 [22]. The undulator beam with horizontal polarization was monochromatized with the Si(111) double crystal and focused on the sample with Kirkpatrick-Baez mirrors. The sample, crystal analyzer, and a Si solidstate detector were arranged horizontally in a Rowland-circle geometry. Both incident and outgoing x rays went through the



FIG. 4. Pressure-dependent lattice constant of CCTO.

Be gasket with in-plane geometry. A Johann-type spherically bent Si(553) analyzer crystal with an approximately 1-m radius was used to analyze the Cu  $K\alpha$  emission  $(2p \rightarrow 1s)$ . The overall energy resolution was estimated to be about 1.2 eV at  $h\nu \sim 9$  keV. X-ray absorption spectra (XAS) were acquired via the partial fluorescence yield method (PFY-XAS). The PFY-XAS spectra were collected by scanning the incident photon energy through the Cu K absorption edge and detecting Cu K $\alpha$  emission [23,24]. The total fluorescence yield (TFY) spectrum using a photo diode was acquired at the same time.

In the resonant condition, XRS spectra are observed with fluorescence spectra. Since the XRS peak loses an energy corresponding to elementary excitation from excitation energy, the XRS peak changes its emission energy with changing excitation energy, while the fluorescence peak has constant emission energy. In this experiment, XES spectra were measured with changing excitation energies, then the spectra were converted to XRS spectra by plotting versus energy loss from excitation energy (Raman shift).

## **IV. RESULTS**

#### A. Pressure-dependent x-ray diffraction

Figure 3 shows pressure-dependent XRD patterns of CCTO. The pressure was increased over the range 0.25–18.80 GPa successively. The patterns had similar structures, although every peak shifted to higher angles and became broader with increasing pressure.

Figure 4 shows the pressure-dependent lattice constant derived from the XRD pattern by means of the Rietveld method. The lattice constant changed from 7.40 to 7.27 Å, continuously. The pressure dependence indicated that CCTO did not undergo a structural phase transition until 18.80 GPa, while the lattice constants decreased continually. The result is consistent with both previous pressure-dependent XRD [25,26] and Raman-scattering studies [27] showing no structural phase transition. The bulk module in this study is larger than that in previous studies. It might be caused by decreased hydrostaticity at high pressures. The narrower pressure range in this study would also result in the larger bulk module. However, it would not affect the result about the absence of phase transition in this pressure range.



FIG. 5. X-ray absorption spectra of CCTO at atmospheric pressure. Lower: Total fluorescence yield. Upper: Partial fluorescence yield x-ray absorption spectra using Cu  $K\alpha$  fluorescence. Inset shows the preedge region. Vertical bars and numbers denote excitation energy in measurement.

## B. Resonant x-ray Raman scattering

Figure 5 shows the x-ray absorption spectra of CCTO at atmospheric pressure obtained at the Cu K absorption edge. TFY and PFY-XAS spectra were acquired at the same time. The PFY-XAS spectrum had high resolution, such that very strong preedge peaks were observed relative to the TFY spec-



FIG. 6. Cu *K*-resonant x-ray emission spectra of CCTO at atmospheric pressure. The top spectrum shows the Cu  $K\alpha$  fluorescence spectrum. Numbers beside the spectra denote excitation energies in Fig. 5.



FIG. 7. Cu *K*-resonant x-ray Raman-scattering spectra (RXRS) of CCTO at atmospheric pressure. Upper: Intensity mapping of RXRS. Lower: RXRS spectra. Numbers beside spectra denote excitation energies in Fig. 5.

trum. Preedge peaks  $A_1$  and  $A_2$  originated from quadrupole transitions involving Cu 3d states, while the main structures originated from dipole transitions involving Cu 4p states. In particular, the peak at 8977.7 eV  $(A_1)$  is a typical peak in divalent  $(Cu^{2+})$  compounds [28,29], so that the Cu in CCTO is thought to be divalent mainly. On the other hand, the peak at 8982.3 eV  $(A_2)$  is thought to be a peak in monovalent (Cu<sup>1+</sup>) compounds, since monovalent Cu compounds show a peak enhancement in resonant XRS excited there [30]. The  $A_2$  peak is thought to be originated from the Cu 3d state at the absorption edge, even if the Cu ion is monovalent (mainly  $3d^{10}$ ). It should be pointed out that the  $A_2$  peak was observed in the PFY-XAS spectra, while it became the tail structure in standard TFY spectra. The Cu ion in CCTO would have both monovalent and divalent features. XRS spectra were acquired with excitations near the preedge region, and the excitation energies were denoted by vertical bars in Fig. 5.

Figure 6 shows the Cu *K*-resonant XES spectra of CCTO at atmospheric pressure. The XES spectra were acquired with excitation at the preedge region of Cu *K* absorption. The excitation energies are shown in Fig. 5. The spectrum at the top of the figure shows the x-ray fluorescence of Cu, with  $K\alpha_1$  and  $K\alpha_2$  peaks. The XES spectra below show a duplicated



FIG. 8. Cu *K*-resonant x-ray Raman spectra of CCTO at 9.7 GPa. Upper: Intensity mapping of RXRS. Lower: RXRS spectra. Numbers beside the spectra denote excitation energies in Fig. 5.

structure that reflected spin-orbit interactions in the Cu 2p core state. Several peaks were observed and shifted to lower energy with decreasing excitation energies.

Figure 7 shows the resonant XRS spectra of CCTO. The XES spectra in Fig. 6 are plotted vs energy loss from excitation energies (Raman shifts). The upper panel of Fig. 7 shows XRS intensity mapping and the lower panel shows XRS spectra, where a total of ten peaks were observed. Because these were duplicated structures originating from spin-orbit interactions of the Cu 2p state, the peaks were labeled  $P_1 - P_5$ and  $P'_1 - P'_5$ , which originated from Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , respectively.  $P_1$ ,  $P_2$ , and  $P_3$  originated from Cu 2p3d excitations, while  $P_4$  and  $P_5$  originated from Cu 2p4p excitations. In the case of low-energy excitations, where  $\overline{XR}S$  is nonresonant, Cu 2p4p excitations were observed because of XRS selection rules. The spectra of Cu 2p4p excitations were almost independent from excitation energy. If the excitation energy was close to the absorption edge, where Cu 3d states exist, Cu 2p3d excitations were resonantly enhanced. The peak  $P_1$  was enhanced under excitation at the preedge peak  $A_1$  of Cu K XAS (Fig. 5), which was divalent  $Cu^{2+}$ . The  $P_1$  peaks also originated from a  $Cu^{2+}$  state, as reported previously [11,28]. The peak  $P_2$  was enhanced under excitation at the preedge





FIG. 9. Cu *K*-resonant x-ray Raman spectra of CCTO at 3.6 GPa. Upper: Intensity mapping of RXRS. Lower: RXRS spectra. Numbers beside the spectra denote excitation energies in Fig. 5.

peak  $A_2$  of Cu K XAS (Fig. 5), which was monovalent Cu<sup>1+</sup>. We also observed these peaks corresponding to  $P_1$  and  $P_2$  in XRS measurements of CuO and Cu<sub>2</sub>O, respectively. Hence, CCTO is thought to be a mixed valence (Cu<sup>1+</sup> and Cu<sup>2+</sup>) compound.

### C. X-ray Raman scattering under high pressure

Figures 8 and 9 show Cu *K*-resonant XRS spectra of CCTO under pressures of 9.7 and 3.6 GPa, respectively. The  $P_1$  peak became weak relative to the XRS at atmospheric pressure (Fig. 7). In addition, a new peak  $P_h$  was observed between  $P_1$  and  $P_2$ . It was enhanced under the median energy of the  $A_1$  and  $A_2$  XAS peaks (Fig. 5); it was very clear at 9.7 GPa, but weak at 3.6 GPa. The results indicated that the electronic state changed under high pressure.

#### D. Pressure-dependent x-ray Raman scattering

Pressure-dependent XAS and XRS were acquired at various pressures. Figure 10 shows pressure-dependent XAS spectra. Very similar spectra were observed at every pressure. No significant changes were observed at the median energy of  $A_1$  and  $A_2$ , where the new peak  $P_h$  was enhanced in XRS



FIG. 10. Pressure-dependent partial fluorescence yield x-ray absorption spectra of CCTO. Values beside each spectrum denote the pressure in GPa.

spectra at high pressure. Because XAS is a one-photon process and is affected by the final-state lifetime, weak preedge structures would not have been detected.

Figure 11 shows pressure-dependent XRS spectra. The excitation energy was 8977.5 eV (#10 in Fig. 5), where there was an  $A_1$  peak. Since each spectrum was obtained under respective experimental condition, these spectra were normalized by  $P_4$  intensity. The  $P_h$  peak increased with pressure, while the  $P_1$  peak decreased.

Figure 12 shows the energy dependence of XRS peak intensities at three pressures. The intensities were integrated over each peak in the XRS spectra in Fig. 11. The integration ranges are shown with horizontal lines at the bottom of Fig. 11. The  $P_1$  and  $P_2$  peaks were enhanced under excitation of the XAS  $A_1$  and  $A_2$  peaks (Fig. 5), while  $P_3$ ,  $P_4$ , and  $P_5$  exhibited monotonic changes. The  $P_h$  peak did not change significantly at atmospheric pressure or 3.6 GPa, but was greatly enhanced at 9.7 GPa, while the  $P_1$  peak enhancement decreased. It also can be seen that the  $P_2$  peak becomes slightly stronger at 9.7 GPa. Therefore, the spectral weight transferred from  $P_1$  to  $P_h$  and  $P_2$  under high pressure.

Figure 13 compares XAS and XRS under various pressures. The XRS spectra were normalized by  $P_4$  intensity.  $P_1$  weakened and  $P_h$ ,  $P_2$ , and  $P_3$  strengthened, while  $P_5$  did not change very much.  $P_2$  and  $P_3$  increased under high pressure, indicating an increased monovalent feature of CCTO.

Figure 14 shows the pressure dependence of XRS peak intensities. Each peak intensity was obtained by integrating



FIG. 11. Pressure-dependent x-ray Raman-scattering spectra of CCTO. The excitation energy was 8977.5 eV. Values beside each spectrum denote the pressure in GPa. Horizontal lines at the bottom show integrated ranges for peak intensities in Fig 12.

spectra in the range shown in Fig. 11. Since the spectra in Fig. 11 were normalized by  $P_4$  intensity, the  $P_4$  intensity is constant in this figure and the  $P_5$  intensity did not change very much. On the other hand,  $P_1$  became weaker, while  $P_h$ ,  $P_2$ , and  $P_3$  became stronger. In particular, the changes were clear around 8.5 GPa, indicating a phase transition of the electronic state. Because no significant changes were observed in the XRD pattern in Fig. 3, the CCTO structure did not change at that pressure.

#### V. DISCUSSION

Generally, the Cu ion in CCTO is thought to form CuO<sub>4</sub> plaquettes isolated from each other [31] and the covalency of the Cu ion is divalent basically. However, the O ion also forms a covalent bond with the Ti ion and thus the Cu ion would be mixed valence in practice. Since the lattice constant decreases with increased pressure without phase transition, the Cu-O bond length becomes short simply and thus the electronic state of the Cu ion would be changed. The result in this study is that the typical divalent peak became weak and the monovalent structures became strong. The  $P_h$  peak was observed between these structures. Though the origin of the  $P_h$  peak cannot be identified in this work, it suggests the new electronic phase, which is not metallic, at high pressure.

Fagan *et al.* predicted structural phase transition around 3–4 GPa [32], but the phase transition was not found by XRD studies [25,26]. On the other hand, Tyagi *et al.* suggested an



FIG. 12. Peak intensity in resonant x-ray Raman-scattering spectra. Each peak intensity was obtained by integrating spectra in the range shown in Fig. 9. Bottom: atmospheric pressure. Middle: 3.6 GPa. Upper: 9.7 GPa.

isostructural phase transition between 8 and 9 GPa by means of high-pressure Raman spectroscopic study [33]. The result would be in very close relation with this study. The change in electronic state that concerns the atomic bond would affect lattice vibration, as well as dielectric properties. Jara *et al.* reported a slight increase of band gap energy, which is associated with the O to Cu charge transfer, from 0 to 10 GPa by optical absorption measurement [27]. Although the band gap cannot be discussed here, since the XRS spectra does not reflect ground state, the charge transfer energy would be affected by the valence of the Cu ion.

Ferroelectric phase transitions of perovskite materials have a close correlation with Ti-O bonding [34]. The giant dielectric constant in CCTO would be caused by displacement of the Ti ions. On the other hand, because the  $TiO_6$  clusters are tilted in four different directions, long-range ordering of



FIG. 13. Comparison between x-ray absorption and resonant x-ray Raman-scattering spectra at various pressures.

polarization is not allowed in CCTO. Although no structural phase transition was observed under high pressure, the distance between the Ti and O ions would decrease with increasing pressure and the electronic structure of the Ti 3d state would be affected. Although the high-pressure XRS around the Ti K absorption edge is very difficult because of the low x-ray transmittance through diamond, the pressure-dependent electronic structure of the Ti ion should be studied.



FIG. 14. Pressure-dependent XRS peak intensity of CCTO. Each peak intensity was obtained by integrating spectra in the range shown in Fig. 11.

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# VI. CONCLUSIONS

XRS and XRD of CCTO were acquired under high pressure. XRD did not exhibit significant changes under high pressure suggesting the absence of structural phase transition. By acquiring XRS via core excitations, such as Cu 2p3dand Cu 2p4p, the densities of unoccupied states were observed. XRS showed that the Cu 3d state changed under high pressure. The CCTO electronic structure exhibited divalent (Cu<sup>2+</sup>) features under atmospheric pressure, while it exhibited an increase of monovalent (Cu<sup>1+</sup>) features at high pressure. In addition, a new Cu 3d state was observed between the Cu<sup>2+</sup> and Cu<sup>1+</sup> states. The electronic state changed significantly at

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around 8.5 GPa, suggesting an electronic phase transition that is different from metal transition at high pressure.

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