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# A transformation of carbon dioxide to nonmolecular solid at room temperature and high pressure

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Raman and infrared absorption spectra of solid carbon dioxide (CO<sub>2</sub>) have been measured at high pressures up to 80 GPa and room temperature. The broadening and weakening of lattice vibrational signals and the disappearance of molecular vibration were detected at 65 GPa by means of the Raman and infrared absorption experiments, respectively. The present Raman spectral feature is exactly the same as that of amorphous CO<sub>2</sub> synthesized around 600 K and 60 GPa [M. Santoro *et al.*, *Nature* (London) **441**, 857 (2006)]. It is demonstrated that the polymerization of CO<sub>2</sub> proceeds even at room temperature and almost independently of temperature. © 2007 American Institute of Physics. [DOI: 10.1063/1.2775539]

## I. INTRODUCTION

Early high pressure studies established the six crystal phases of carbon dioxide (CO<sub>2</sub>) under high pressures and high temperatures.<sup>1–14</sup> Phase I (dry ice) is obtained at room temperature around 0.6 GPa, and transforms to the orthorhombic molecular phase III above 20 GPa through an intermediate phase.<sup>1–3</sup> Since phase III appeared only via low temperature compression of phase I, phase III was suggested to be a metastable phase. Heat treatments of phase III at 30–60 GPa above 1000 K polymerize the CO<sub>2</sub> molecules, resulting in the transformation to the nonmolecular phase V which is fully covalent extended solid, structurally analogous to SiO<sub>2</sub> tridymite.<sup>4,5,12</sup> The polymeric CO<sub>2</sub>-V is maintained even though the temperature is decreased to room temperature. Recently, it was reported experimentally that the heat treatment of phase III with relatively low temperature (~600 K) causes the molecular CO<sub>2</sub> solid to be an amorphous state, which was interpreted with a glassy counterpart of phase V.<sup>13</sup> In more recent study, a covalent extended-solid VI around 600 K and 50–60 GPa,<sup>14</sup> which are almost the same conditions as the amorphous CO<sub>2</sub> (*a*-CO<sub>2</sub>), was observed. This crystal phase VI was interpreted to take a stishovitelike structure in which the carbon atoms maintain an average sixfold coordination. Theoretical studies as well as the experimental ones have been performed for the covalent crystal CO<sub>2</sub>, in aspects of its structure, high pressure stabil-

ity, vibrational properties, and so on.<sup>15–18</sup> According to the theoretical study,<sup>15</sup> a polymeric phase becomes stable above 35 GPa, more than the molecular phase.

Although extensive searches have been performed for exploring the solid phases of CO<sub>2</sub>, the pressure range investigated so far was limited to about 80 GPa, which is lower compared with other simple molecular solids [H<sub>2</sub>, >285 GPa;<sup>19–21</sup> N<sub>2</sub>, >200 GPa (Refs. 22 and 23)]. Furthermore, the phase boundaries in the *P*-*T* phase diagram are still controversial, in particular, for nonmolecular phases V and VI. This seems to originate from the experimental difficulty in determining the temperature and the irreversible nature of the transformation between the polymer and the monomer.

Up to now, the polymerization of CO<sub>2</sub> into phases V and VI, and the amorphous phase is discovered at high temperatures (*T* > ~600 K). Even in room temperature, the polymerization is expected<sup>14</sup> but not confirmed yet. Only a few descriptions based on the Raman signals were found in the previous papers: The molecular phase III remains stable at least up to 60 GPa,<sup>5</sup> and the Raman signals become hardly distinguishable from the background signal above 60 GPa.<sup>12</sup> The disappearance of Raman signals was also reported for the quenched molecular phase IV around 80 GPa.<sup>8</sup> These findings suggest the amorphization of CO<sub>2</sub> at room temperature, but the lack of definitive descriptions is likely to be because the Raman signals from amorphous state are usually very weak and broad, and the transformation to the amorphous state is sluggish. In addition, since the CO<sub>2</sub> molecular phases are unusually stiff,<sup>5</sup> the strain which causes spectral

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broadening and weakening tends to be highly generated in the crystal at high pressures. This has prevented us from studying the intrinsic structural transformation under the room temperature. Apart from the fundamental point of view, the polymerization of CO<sub>2</sub> at room temperature and the irreversible nature are of much interest in the aspect of covalent materials based on light elements which are expected to be superhard materials.

In this work, we explored the polymerization and amorphization of CO<sub>2</sub> at room temperature by means of Raman and IR absorption spectroscopies at high pressures up to 80 GPa. The vibrational data give clear evidence that the polymerization from O=C=O to -C-O-C- and the amorphization simultaneously proceed at 65 GPa and room temperature. The pressure dependence of vibrational properties of *a*-CO<sub>2</sub> is similar to those of the stishovitelike covalent solid VI. The *a*-CO<sub>2</sub> formed above 65 GPa is maintained down to about 30 GPa, and then changes to unknown molecular phase, and finally returns to phase I below 10 GPa.

## II. EXPERIMENT

For pressure generation in this work, a diamond anvil cell (DAC) with a metal gasket was used. As the pressure medium, we examined indium (In), known as a compressible metal. Prior to the preindentation of the tungsten (W) gasket, an In film was placed onto the gasket. Then, a hole of 0.03 mm in diameter serving as the sample chamber was drilled in the gasket coated with In. The diamond anvils used here are of the beveled type with a 0.1 mm culet. The loading of CO<sub>2</sub> was carried out by spraying its vapor into the hole of the gasket that was cooled by liquid N<sub>2</sub>. Actually at high pressure, the In sandwiched in between the anvil and gasket was squeezed into the sample chamber, and reduced the strain. This was confirmed by the Raman-peak widths of CO<sub>2</sub> which became narrow, half as those for the case without In. The effects of the pressure medium were described in our recent paper.<sup>24</sup> Raman spectra were measured in a back-scattering geometry with a spectrometer (JASCO NR1800) equipped with a triple polychromator and a charge-coupled device detector. Radiation of 532 nm from an YVO<sub>4</sub> laser (Coherent Japan) was used with output power of about several tens of milliwatts for the excitation of the Raman spectra. The Raman apparatus has been improved through overcoming the previous severe experimental conditions of metallic samples in DAC.<sup>25,26</sup> For high quality Raman measurements, the synthetic high purity diamonds (type IIa) with little background signals were used as the anvils. The pressure was estimated using the first order diamond-Raman signal simultaneously obtained on the Raman measurements of the sample.<sup>27</sup> IR transmission spectra were measured with a microscopic Fourier transform infrared (FTIR) spectrometer (JASCO FTIR-460Plus/IRT-30-16) equipped with mirror objectives to focus the light onto the sample in DAC. The reference signals were measured without placing the DAC. Thus, the obtained IR absorption spectra contain the signals from diamond anvils as well as the sample.

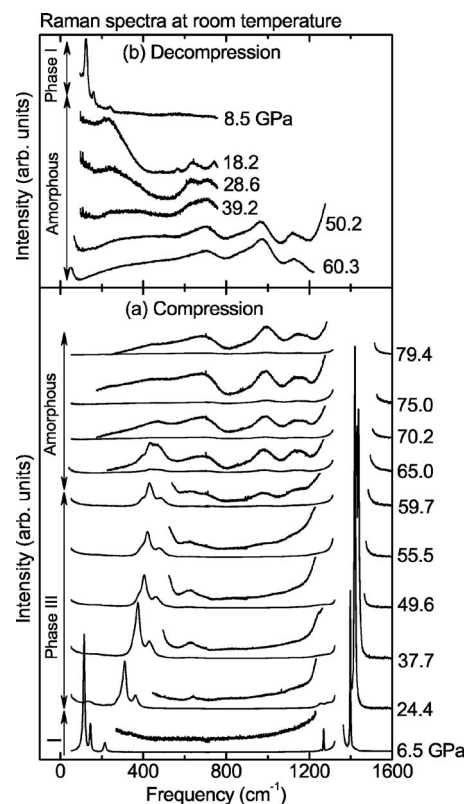


FIG. 1. Raman spectra of CO<sub>2</sub> obtained up to 80 GPa at room temperature. The processes of compression (a) and decompression (b) are presented. Compression: phase I  $\rightarrow$  phase III  $\rightarrow$  amorphous, decompression: amorphous  $\rightarrow$  phase I. The indium was used as a pressure medium. For the frequency range of 400–1200 cm<sup>-1</sup> in (a), the spectra expanded vertically are also indicated.

## III. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra observed up to 80 GPa at room temperature. For the compression process (a), the spectra below 60 GPa are essentially in accord with the previous Raman data.<sup>3</sup> At 65 GPa, all the Raman bands in the region studied here almost disappear. At the same time, very weak and broad bands grow up at 1000 and 1150 cm<sup>-1</sup>, as seen in the vertically expanded spectra. Considering that these bands are not observed below 65 GPa, these are to be distinguished from the background signals. The present Raman spectrum obtained at 75 GPa is exactly the same, concerning the shape and the peak frequencies, as that recently reported for amorphous CO<sub>2</sub> which has been synthesized at high temperatures from 500 to 600 K at 50–70 GPa by Santoro *et al.*<sup>13</sup> From the x-ray diffraction measurements, they presented the structural data characteristic of the amorphous state. They also compared the Raman spectra of *a*-CO<sub>2</sub> with those of *a*-SiO<sub>2</sub> and *a*-GeO<sub>2</sub>. The analogy of the spectral feature has been confirmed and the 1000 cm<sup>-1</sup> band was assigned to the symmetric C–O–C stretching mode.<sup>13</sup> Thus, we see that the present spectral change at 65 GPa is due to the amorphization of CO<sub>2</sub>. Figure 2(a) indicates the IR absorption spectra obtained on the compression process. The molecular vibrations are observed as a saturating band around 2400 cm<sup>-1</sup> for the fundamental anti-symmetric mode ( $\nu_3$ ) and a weak peak around 3900 cm<sup>-1</sup> for the combination mode ( $\nu_1 + \nu_3$ ).<sup>2</sup> These signals disappear si-

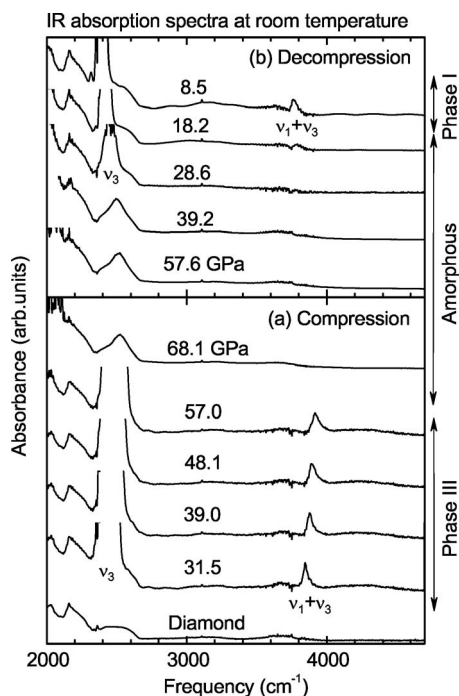


FIG. 2. IR absorption spectra of  $\text{CO}_2$  at high pressures and room temperature. The processes of compression (a) and decompression (b) are presented. Compression: phase I  $\rightarrow$  phase III  $\rightarrow$  amorphous, decompression: amorphous  $\rightarrow$  phase I. The indium was used as a pressure medium. In (a), IR signal from diamond anvil is indicated for comparison.  $\nu_1$  and  $\nu_3$  mean the symmetric and antisymmetric molecular vibrations, respectively.

multaneously with the amorphization, demonstrating that the transformation to nonmolecular state (polymerization) triggers the amorphization.

Usually, the pressure of the amorphization depends on the hydrostatic condition of the sample. However, for the case without pressure medium,<sup>24</sup> the spectral change due to the amorphization was observed at the identical pressure, apart from the fact that the Raman bands in phase III were much more broadened. This can be explained in terms of the amorphization triggered by the molecular dissociation. From IR results, the phase transition observed at 65 GPa is also identified as a change from the molecular solid to the covalent solid, i.e., the molecular dissociation. Since the pressure of the molecular dissociation is not very sensitive to the hydrostaticity, the transition pressure to the amorphous state is independent of the hydrostaticity.

Figure 3 shows the pressure dependence of Raman frequencies upon compression. For comparison, the data reported for the polymeric phase V (Ref. 12) and phase VI (Ref. 14) are also indicated by dotted and solid curves, respectively. The Raman bands of  $a\text{-CO}_2$  at  $\sim 1000$  and  $\sim 1200 \text{ cm}^{-1}$  above 65 GPa (solid circles) are found to be peculiar to the nonmolecular phase because all the molecular phases (I–IV) exhibit no fundamental vibration in this frequency region.<sup>3,7–9</sup> Phases V and VI show the Raman peaks near those in  $a\text{-CO}_2$ . In particular, for phase VI, the Raman bands around 700, 1000, and  $1050 \text{ cm}^{-1}$  were exactly the same as those observed for  $a\text{-CO}_2$ , with respect to the frequencies and pressure dependence, indicating that  $a\text{-CO}_2$  is closely related with phase VI. Since, however, the present

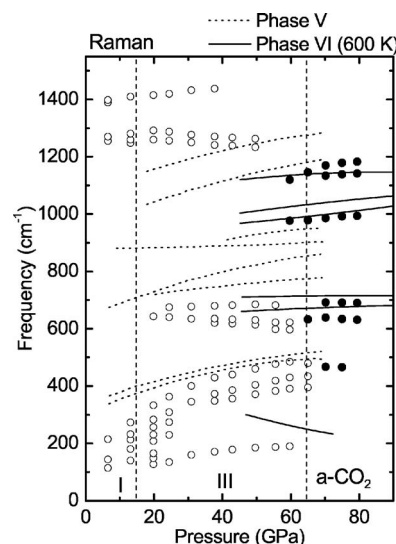


FIG. 3. Pressure dependence of vibrational frequencies of  $\text{CO}_2$  measured at room temperature by Raman scattering experiments upon compression. The present Raman data are plotted by open and solid circles. Vertical dashed lines indicate the pressure of transformations observed on the compression process. Solid circles correspond to amorphous  $\text{CO}_2$  ( $a\text{-CO}_2$ ). Dotted curves (Ref. 12) correspond to polymeric crystal phase V quenched from high temperature. Solid curves indicate the data of phase VI measured at 600 K (Ref. 14).

Raman spectra above 70 GPa show no intense and sharp peak in phase VI ( $1010 \text{ cm}^{-1}$  at 50 GPa),<sup>14</sup> the present spectra should be distinct from that of phase VI. Thus, it is concluded that  $a\text{-CO}_2$  is the glassy counterpart of the stishovite-like phase VI rather than tridymite phase V, as suggested also in the recent paper.<sup>14</sup>

As seen in Figs. 1(b) and 2(b), the forming of covalent-bonding network causes irreversible spectral changes. Upon decompression after pressurizing to 80 GPa, phase I was confirmed below 10 GPa, but phase III was not. Before transformation to phase I, we observed unknown Raman spectra below 30 GPa, i.e., a broadened lattice mode about  $200 \text{ cm}^{-1}$  and three molecular modes around  $600\text{--}800 \text{ cm}^{-1}$ . Correspondingly, in the IR spectra [Fig. 2(b)], the  $\nu_3$  band appears again, indicating the formation of the  $\text{CO}_2$  molecules below 30 GPa. The observations of the broadened lattice modes and distinct molecular modes suggest the molecular amorphous state, in which the  $\text{CO}_2$  molecules are randomly oriented. In the lower pressure (18.2 GPa), three bending peaks are observed in the Raman spectrum [Fig. 1(b)]. This is reminiscent of phase IV which appears at high temperature in this pressure region and shows a triplet bending mode in the Raman spectrum.<sup>8,10</sup>

In the previous studies for  $a\text{-CO}_2$  (Ref. 13) or polymeric crystals  $\text{CO}_2$  [phases V (Refs. 4, 5, 12, and 17) and VI (Ref. 14)], the forming of C–O single bonding network was observed under high temperatures above 600 K. It should be emphasized in the present work that the C–O network is formed without heat treatment at 65 GPa and the transformation to the amorphous state is not so sluggish. In Fig. 4 which shows the  $P$ - $T$  phase diagram of  $\text{CO}_2$ , we plotted the pressure-temperature conditions for the transformation to  $a\text{-CO}_2$  by a solid circle, together with the previous data for  $a\text{-CO}_2$  (Ref. 13) and phase VI.<sup>14</sup> The arrows in this figure



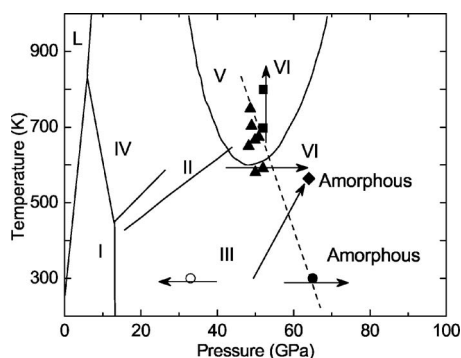


FIG. 4. Phase diagram of carbon dioxide (Refs. 7 and 12–14). The boundary for phase V is in debate, but here it is drawn according to Ref. 12. The molecular  $\leftrightarrow$  nonmolecular transformation observed in the present work is marked with the solid and open circles, which correspond to compression and decompression processes, respectively. The solid diamond corresponds to the formation of the  $a$ -CO<sub>2</sub> reported in Ref. 13. Solid triangles and squares (Ref. 14) correspond to the formation of phase VI on the isobaric-heating and isothermal-compression processes, respectively. The boundary for the formation of the polymeric CO<sub>2</sub> is drawn with a dashed line.

represent the directions of the experimental paths. Referring to the recent observations for forming of  $a$ -CO<sub>2</sub> (closed diamond)<sup>13</sup> and phase VI (closed triangles and squares),<sup>14</sup> we can draw a boundary for the formation of the nonmolecular CO<sub>2</sub> with a dashed line in the  $P$ - $T$  phase diagram shown in Fig. 4. From the boundary for the formation of the covalent CO<sub>2</sub>, we can see that the polymerization proceeds almost independently of the temperature and even in lower temperature than room temperature. This suggests that the polymerization of CO<sub>2</sub> is triggered only if the intermolecular distance reaches a minimum value.

From the relationship between the  $P$ - $T$  domains in which phase VI and  $a$ -CO<sub>2</sub> were discovered,  $a$ -CO<sub>2</sub> is most likely to be crystallized into phase VI by heat treatment. This consideration is well consistent with the interpretation of  $a$ -CO<sub>2</sub> as the glassy counterpart of phase VI. Therefore, it is considered that the short-range structure of  $a$ -CO<sub>2</sub> is the same as phase VI. According to the recent paper,<sup>14</sup> carbon atoms in phase VI maintain an average sixfold coordination, but are disordered and microscopically form a tetrahedral  $sp^3$  bonding network. Therefore,  $a$ -CO<sub>2</sub> probably has a distorted- $sp^3$  bonding network. Thus, upon the transformation from the molecular phase III to  $a$ -CO<sub>2</sub>, the linear CO<sub>2</sub> molecule should be bent to form the  $sp^3$  bonding. We should note in Fig. 3 that, in phase III, the vibrational modes assigned with O=C=O bending vibrations ( $\sim 600$  cm<sup>-1</sup>) and those overtones ( $\sim 1200$  cm<sup>-1</sup>) indicate negative frequency shifts. This may be because the linear CO<sub>2</sub> molecules tend to bend before making the tetrahedral bonding of C atoms.

As mentioned above, once the polymer is formed, it is maintained down to about 30 GPa [Fig. 2(b)]. The pressure at which the CO<sub>2</sub> molecules are recovered is indicated by an open circle in the  $P$ - $T$  phase diagram (Fig. 4). Considering that the polymeric phase V was synthesized above 30 GPa, the polymeric state is likely to be favorably stable in this pressure range. This is roughly consistent with the previous theoretical prediction<sup>15</sup> that a polymeric phase becomes stable above 35 GPa, rather than the molecular phase. In the  $P$ - $T$  phase diagram of CO<sub>2</sub>, there is still an unknown field of

the pressure higher than 80 GPa and temperature higher than several hundreds of Kelvin. In analogy with SiO<sub>2</sub> which shows a variety of polymorphs, there is a possibility of discovering the unknown crystal phase(s) of CO<sub>2</sub> on heating the amorphous at very high pressure.

#### IV. SUMMARY

The high pressure Raman and IR experiments of CO<sub>2</sub> at room temperature demonstrate that (1) the pressurization causes the transformation from the molecular solid CO<sub>2</sub> to nonmolecular (polymeric) amorphous state at 65 GPa even at room temperature and (2) the polymeric CO<sub>2</sub> is not returned to the molecules down to 30 GPa on decompression. The forming of the nonmolecular CO<sub>2</sub> without heating makes us aware that the CO<sub>2</sub> molecule generally considered as an inert molecule becomes much reactive under the high pressure. This means that the CO<sub>2</sub> under high pressure can react with other elements or materials, leading to exotic and useful materials. This is very important from the aspects of the synthesis and modification of CO<sub>2</sub> based covalent solids. Apart from the interest for the practical application, the knowledge of the phase diagram at very high pressure and temperature will be significant for better understanding of CO<sub>2</sub> embedded into ice forms in the outer planet and asteroids.

<sup>1</sup>K. Aoki, H. Yamawaki, M. Sakashita, Y. Gotoh, and K. Takemura, *Science* **263**, 356 (1994).

<sup>2</sup>R. Lu and A. M. Hofmeister, *Phys. Rev. B* **52**, 3985 (1995).

<sup>3</sup>H. Olijnyk and A. P. Jephcoat, *Phys. Rev. B* **57**, 879 (1998).

<sup>4</sup>V. Iota, C. S. Yoo, and H. Cynn, *Science* **283**, 1510 (1999).

<sup>5</sup>C. S. Yoo *et al.*, *Phys. Rev. Lett.* **83**, 5527 (1999).

<sup>6</sup>J. Dong, J. K. Tomfohr, and O. F. Sankey, *Science* **287**, 11a (2000).

<sup>7</sup>V. Iota and C. S. Yoo, *Phys. Rev. Lett.* **86**, 5922 (2001).

<sup>8</sup>C. S. Yoo, V. Iota, and H. Cynn, *Phys. Rev. Lett.* **86**, 444 (2001).

<sup>9</sup>C. S. Yoo, H. Kohlmann, H. Cynn, M. F. Nicol, V. Iota, and T. LeBihan, *Phys. Rev. B* **65**, 104103 (2002).

<sup>10</sup>J.-H. Park, C. S. Yoo, V. Iota, H. Cynn, M. F. Nicol, and T. Le Bihan, *Phys. Rev. B* **68**, 014107 (2003).

<sup>11</sup>F. A. Gorelli, V. M. Giordano, P. R. Salvi, and R. Bini, *Phys. Rev. Lett.* **93**, 205503 (2004).

<sup>12</sup>M. Santoro, J. F. Lin, H.-K. Mao, and R. J. Hemley, *J. Chem. Phys.* **121**, 2780 (2004).

<sup>13</sup>M. Santoro, F. A. Gorelli, R. Bini, G. Ruocco, S. Scandolo, and W. A. Crichto, *Nature (London)* **441**, 857 (2006).

<sup>14</sup>V. Iota, C. S. Yoo, J.-H. Klepeis, Z. Jenei, W. Evans, and H. Cynn, *Nat. Mater.* **6**, 34 (2007).

<sup>15</sup>S. Serra, C. Cavazzoni, G. L. Chiarotti, S. Scandolo, and E. Tosatti, *Science* **284**, 788 (1999).

<sup>16</sup>B. Holm, R. Ahuja, A. Belonoshko, and B. Johansson, *Phys. Rev. Lett.* **85**, 1258 (2000).

<sup>17</sup>J. Dong, J. K. Tomfohr, and O. F. Sankey, *Phys. Rev. B* **61**, 5967 (2000).

<sup>18</sup>J. Dong, J. K. Tomfohr, O. F. Sankey, K. Leinenweber, M. Somayazulu, and P. F. McMillan, *Phys. Rev. B* **62**, 14685 (2000).

<sup>19</sup>C. Narayana, H. Luo, J. Orloff, and A. L. Ruoff, *Nature (London)* **393**, 46 (1998).

<sup>20</sup>A. F. Goncharov, E. Gregoryanz, R. J. Hemley, and H.-K. Mao, *Proc. Natl. Acad. Sci. U.S.A.* **98**, 14234 (2001).

<sup>21</sup>P. Loubeyre, F. Occelli, and R. LeToullec, *Nature (London)* **416**, 613 (2002).

<sup>22</sup>M. I. Erements, R. J. Hemley, H.-K. Mao, and E. Gregoryanz, *Nature (London)* **411**, 170 (2001).

- <sup>23</sup>E. Gregoryanz, A. F. Goncharov, R. J. Hemley, H.-K. Mao, M. Somayazulu, and G. Shen, *Phys. Rev. B* **66**, 224108 (2002).
- <sup>24</sup>T. Kume, Y. Ohya, S. Sasaki, and H. Shimizu, *High Press. Res.* **26**, 309 (2006).
- <sup>25</sup>T. Kume, H. Fukuoka, T. Koda, S. Sasaki, H. Shimizu, and S. Yamanaka, *Phys. Rev. Lett.* **90**, 155503 (2003).
- <sup>26</sup>T. Kume, T. Hiraoka, Y. Ohya, S. Sasaki, and H. Shimizu, *Phys. Rev. Lett.* **94**, 065506 (2005).
- <sup>27</sup>L. Sun, A. L. Ruoff, and G. Stupian, *Appl. Phys. Lett.* **86**, 014103 (2005).