

## Pressure and temperature dependences of the structural properties of Dy@C<sub>82</sub> isomer I

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Crystals of Dy@C<sub>82</sub> isomer I are studied by x-ray powder diffraction with synchrotron radiation in wide temperature and pressure regions. The isomer I of Dy@C<sub>82</sub> shows a simple cubic structure with lattice constant  $a$  of 15.85(3) Å at 298 K, while the isomer II shows a face-centered cubic structure with  $a$  of 15.75(4) Å. The structural phase transition of the second order is indicated for the isomer I at 300–310 K by the temperature dependence of x-ray diffraction and differential scanning calorimetry. Further, the pressure dependence of the lattice constant is studied for the isomer I up to 60 kbar, which can be fitted by a Murnaghan equation of state.

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Structures and physical properties of metallofullerenes is a very exciting research subject, because their novel physical properties are theoretically predicted.<sup>1</sup> However, the study has hardly been proceeded because of the difficulty in obtaining pure samples of metallofullerenes. Among metallofullerenes, it is relatively easy to obtain the pure samples of metal endohedral C<sub>82</sub> ( $M@C_{82}$ ). The crystal structure of 1:1 toluene solvate of Y@C<sub>82</sub> was first determined by a maximum entropy method (MEM) analysis of x-ray powder diffraction.<sup>2</sup> This shows that the Y atom lies on a six-membered ring of the C<sub>82</sub> cage. Further, the MEM analysis was applied to the structural determination of 1:1 toluene solvates of Sc@C<sub>82</sub> and Sc<sub>2</sub>@C<sub>84</sub>.<sup>3,4</sup> Subsequently, it has been found that the crystals of solvent-free La@C<sub>82</sub> (isomer I) take a face-centered cubic (fcc) structure with the lattice constant  $a$  of 15.78 Å at 300 K.<sup>5</sup> The structural transitions to various phases were observed in a wide temperature region on the basis of x-ray diffraction for single crystals of La@C<sub>82</sub> isomer I: fcc at 180–300 K, rhombohedral at 140–180 K, triclinic at 20–140 K in slow cooling, and simple cubic (sc) at 20–132 K in rapid cooling.<sup>5,6</sup> The various phases are realized by differences in the molecular orientation of the C<sub>82</sub> cage and the molecular electric dipole moment produced by a displacement of metal ion from the cage center. The magnetic property of La@C<sub>82</sub>(CS<sub>2</sub>)<sub>1.5</sub> with a body-centered cubic (bcc) structure ( $I\bar{4}3d$ ) was recently reported.<sup>7</sup> In these crystals, the C<sub>82</sub> cage is disordered.<sup>7</sup> Nevertheless, it is suggested that the long axis of the C<sub>82</sub> cage is oriented along the [111] direction and the La atom is also displaced along [111] inside the C<sub>82</sub> cage.<sup>7</sup> The magnetic property shows a strong antiferromagnetic interaction (Weiss temperature  $\theta \sim -130$  K). A phase transition was observed at 150 K, which originates from an orientational ordering of the C<sub>82</sub> cage.

We recently reported the x-ray powder diffraction and the x-ray-absorption fine structure (XAFS) of a purified solvent-free Dy@C<sub>82</sub> sample that contains at least two isomers of I and II.<sup>8,9</sup> The x-ray-diffraction pattern of the mixed crystals of the isomers I and II at 298 K and 1 bar was indexed with a fcc lattice of  $a = 15.86(1)$  Å. The  $a$  value is close to that of La@C<sub>82</sub>.<sup>5</sup> The XAFS of the Dy@C<sub>82</sub> sample showed that

the valence of Dy atom was +3. Further, it showed that the distance between Dy atom and the first-nearest C atoms, and that between the Dy atom and the second-nearest C atoms were 2.52(2) and 2.86(2) Å, respectively.<sup>8</sup> These results suggest that the Dy atom lies on six-membered ring of C<sub>82</sub> cage. In the present paper, the structural property of isomer I of Dy@C<sub>82</sub> is reported in wide temperature and pressure regions on the basis of x-ray powder diffraction. The structural phase transition is discussed for the isomer I on the basis of x-ray powder diffraction and differential scanning calorimetry (DSC).

Details for separation of Dy@C<sub>82</sub> isomers I and II are described elsewhere.<sup>8</sup> The characterization of the isomers I and II were performed by high-performance liquid chromatography (HPLC), time-of-flight (TOF) mass spectra, and UV-VIS-NIR absorption spectra. The molecular symmetry of the isomer I is identified to be  $C_{2v}$ ,<sup>8</sup> while that of the isomer II is identified to be  $C_s$  from the similarity in the UV-VIS-NIR spectrum to that of La@C<sub>82</sub> isomer II for which the molecular symmetry has been determined from <sup>13</sup>C NMR.<sup>10</sup> The solid samples of isomers I and II were obtained by evaporating toluene from the finally separated toluene solution of each isomer after five-step HPLC. A trace of toluene was removed from the solid sample by a dynamical pumping under a pressure of 10<sup>-6</sup> Torr for 12 h at room temperature, for 12 h at 473 K, and 48 h at 573 K. The solvent-free solid sample was introduced, without exposure to air in an Ar glove box, into a glass capillary ( $\phi = 0.5$  mm) for x-ray-diffraction measurement at 1 bar and a diamond-anvil cell for the measurement under high pressure. The x-ray powder-diffraction pattern of the isomer I was measured from 17 to 463 K at 1 bar, and from 1 bar to 60 kbar at 298 K with synchrotron radiation [wavelength  $\lambda = 0.8517(5)$  Å] at BL-1B of KEK-PF (Tsukuba, Japan).<sup>11</sup> The x-ray-diffraction pattern of the isomer II was measured at 298 K. The DSC curve was measured for the mixed crystals of isomers I and II from 103 to 473 K at 1 bar by using a differential scanning calorimeter (Perkin-Elmer DSC Pyris I).

Figure 1(a) shows the x-ray-diffraction pattern of the isomer I at 119 K and 1 bar, which can be indexed with a sc lattice of  $a = 15.79(4)$  Å. All x-ray powder-diffraction patterns for the isomer I from 17 to 298 K at 1 bar could be

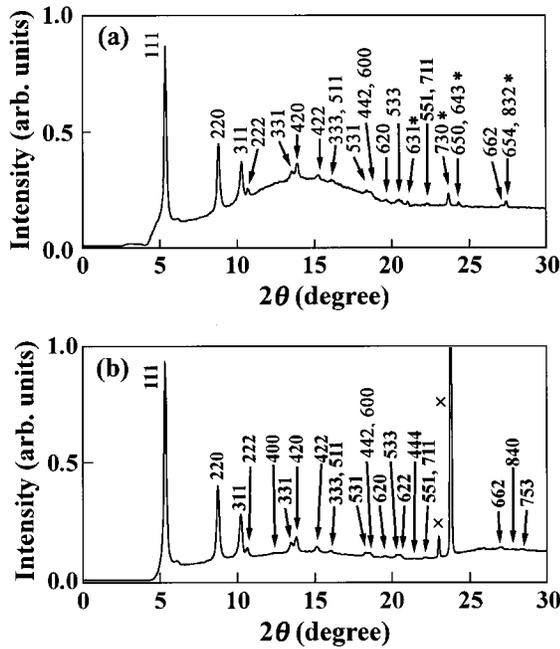


FIG. 1. X-ray-diffraction patterns for the isomer I of  $\text{Dy@C}_{82}$  at (a) 119 and (b) 463 K at 1 bar. The peaks denoted by  $\star$  in (a) are the sc peaks that appear at low temperature below 300 K, while the peaks denoted by  $\times$  in (b) are the peaks due to sample holder.

indexed with the sc lattice. The value of  $a$  at 298 K is  $15.85(3)$  Å. The x-ray-diffraction pattern at 463 K could be indexed with an fcc lattice of  $a = 15.91(3)$  Å [Fig. 1(b)]. Above 298 K no reflections which could be assigned to the sc lattice were observed, and the diffraction patterns could be indexed with the fcc lattice. This shows that the structural phase transition from the sc to the fcc lattice occurs above 298 K. The temperature dependence of  $a$  is shown in Fig. 2. The  $a$  value decreases continuously with a decrease in temperature below 298 K; the  $a$  at 17 K is  $15.75(3)$  Å. An anomaly in the  $a$ - $T$  plots is observed in the temperature region from 310 to 383 K, where the plots deviate from the curve calculated with a Grüneisen relation within the Debye approximation (Fig. 2).

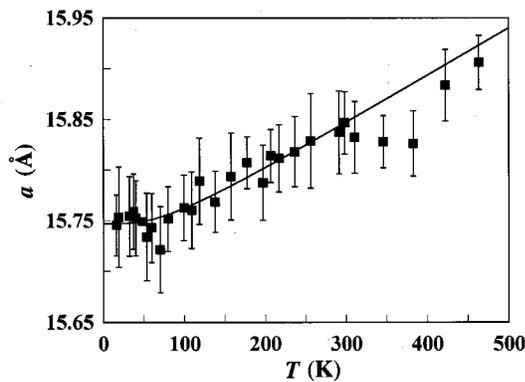


FIG. 2. Temperature dependence of  $a$  for the isomer I at 1 bar. The solid line refers to the Grüneisen curve within the Debye approximation: Debye temperature  $\theta_D = 270$  K.

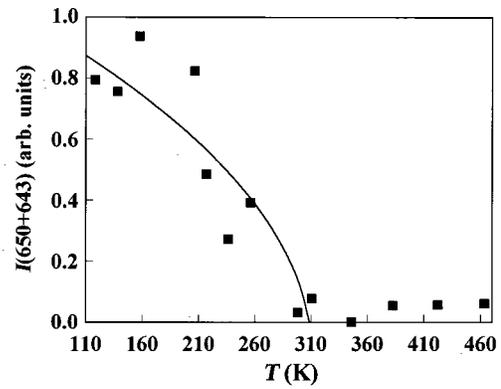


FIG. 3. Temperature dependence of the peak intensity of 650 and 643 reflections for the isomer I at 1 bar. The solid line refers to the curve fitted with the equation,  $I(650+643) = A(T_m - T)^{1/2}$ .

The temperature dependence of an intensity contributed from 650 and 643 reflections,  $I(650+643)$ , which can be observed in the sc lattice, is shown in Fig. 3. The temperature dependence can be fitted by the equation  $I(650+643) = A(T_m - T)^{1/2}$ , where  $A$  and  $T_m$  are constant and the phase-transition temperature, respectively; the  $T_m$  value is estimated to be 310 K. This implies that the structural phase transition is the second-order transition. The continuous deviation from the Grüneisen curve above 300 K in the  $a$ - $T$  plots can also be understood reasonably by the existence of the second-order phase transition. The  $T_m$  value determined from the  $I(650+643)$ - $T$  plots is consistent with the onset temperature 300–310 K of the deviation from the Grüneisen curve in the  $a$ - $T$  plots.

The DSC curve of the mixed crystals of  $\text{Dy@C}_{82}$  isomers I and II is shown in Fig. 4; the fraction of isomer I is larger than 80% in this sample. The small endothermic peak is observed at 302 K. The value of  $\Delta H$  is estimated to be 2.5 J/g. The small endothermic peak suggests the existence of the second-order transition around 302 K; the transition temperature suggested from the DSC curve is consistent with those from the  $a$ - $T$  and  $I$ - $T$  plots. These results show that the structural phase transition occurs from the sc to the fcc phase

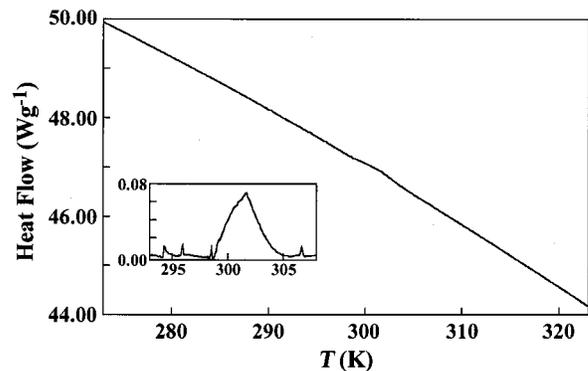


FIG. 4. DSC curve for the mixed crystals of the  $\text{Dy@C}_{82}$  isomers I and II recorded by raising temperature at the rate of  $5 \text{ K min}^{-1}$ .

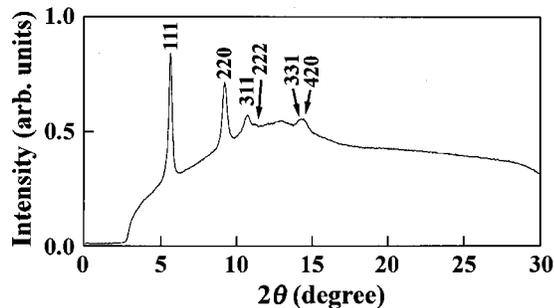


FIG. 5. X-ray-diffraction pattern for the isomer I of Dy@C<sub>82</sub> at 60 kbar and 298 K.

in the isomer I at 300–310 K. This behavior is different from that of solvent-free La@C<sub>82</sub> in which more complex structural transitions are observed.<sup>5,6</sup> The thermal-expansion coefficient  $\alpha [= (1/a)(da/dT)]$  of the isomer I is evaluated to be  $2.8(1) \times 10^{-5} \text{ K}^{-1}$  from the  $a$ - $T$  plots in the temperature range from 53 to 298 K. This value is close to those of C<sub>60</sub> and metal-doped C<sub>60</sub>:  $2.1 \times 10^{-5} \text{ K}^{-1}$  for C<sub>60</sub>,  $3.1 \times 10^{-5} \text{ K}^{-1}$  for Rb<sub>3</sub>C<sub>60</sub> and  $2.4 \times 10^{-5} \text{ K}^{-1}$  for Rb<sub>6</sub>C<sub>60</sub>.<sup>12,13</sup>

All x-ray-diffraction patterns of the isomer I up to 60 kbar can be indexed with the sc lattice as the x-ray-diffraction pattern at 1 bar; the x-ray-diffraction pattern at 60 kbar is shown in Fig. 5. New Bragg reflections were not observed up to 60 kbar. The pressure dependence of  $a$  for the isomer I is shown in Fig. 6. The curve fitting for the  $a$ - $p$  plots is per-

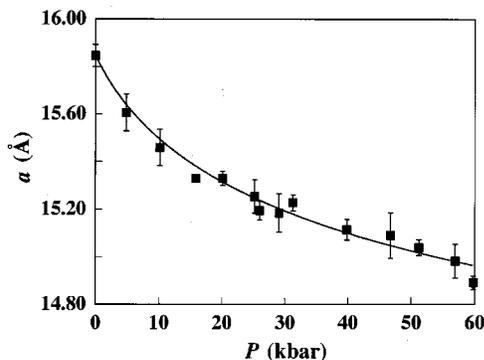


FIG. 6. Pressure dependence of  $a$  for the isomer I at 298 K. The solid line refers to the curve fitted with Murnaghan EOS.

formed with a Murnaghan equation of state (EOS); the  $a$  at 60 kbar is  $14.89(3) \text{ \AA}$ . No indication of any structural phase transition is observed in this pressure region. The bulk modulus  $K_0$  is estimated to be  $284(1) \text{ kbar}$ , which is close to the  $K_0$  values of metal-doped C<sub>60</sub>:  $280 \text{ kbar}$  for Na<sub>2</sub>CsC<sub>60</sub> and  $260 \text{ kbar}$  for Li<sub>3</sub>CsC<sub>60</sub>.<sup>14,15</sup> The compressibility  $\kappa$  of  $a$  [ $= (1/a)(da/dp)$ ] is estimated to be  $2.1(1) \times 10^{-3} \text{ kbar}^{-1}$  by a linear approximation for the  $a$ - $p$  plots up to 16 kbar, which is close to the  $\kappa$  values of C<sub>60</sub> and metal-doped C<sub>60</sub>:  $2.3(2) \times 10^{-3} \text{ kbar}^{-1}$  for C<sub>60</sub> and  $1.52(9) \times 10^{-3} \text{ kbar}^{-1}$  for Rb<sub>3</sub>C<sub>60</sub>.<sup>16</sup> These results show that the behavior of metallofullerene crystals under pressure is similar to that of empty fullerenes and metal-doped fullerenes. The x-ray-diffraction pattern of the isomer II could be indexed with an fcc lattice of  $a = 15.75(4) \text{ \AA}$ . However, the information on details of the structural property was not obtained because only poor quality of x-ray-diffraction data was available for isomer II.

In this study, the structural phase transition from the sc to the fcc phase is indicated for the isomer I of Dy@C<sub>82</sub> at 300–310 K. The jumping in the orientation of the long axis ( $C_2$  axis) of the C<sub>82</sub> cage between different [111] axes should occur randomly in the fcc lattice, if the  $C_2$  axis aligns along the [111] direction and the Dy atom is displaced along the  $C_2$  axis inside the C<sub>82</sub> cage of  $C_{2v}$ . This implies the orientational disorder. Such an orientational disorder is found in the structural phase transition from  $Pa\bar{3}$  to  $Fm\bar{3}m$  in Na-doped C<sub>60</sub>.<sup>17</sup> Further, the jumping motion of the C<sub>82</sub> cage around the  $C_2$  axis along [111] direction is required among at least three preferable orientations to realize a cubic lattice, because it should have the symmetry 3 or  $\bar{3}$  along [111]. The electric dipole moment is expected to disappear by disordering about two orthogonal axes perpendicular to the  $C_2$  axis in the case of fcc lattice of  $Fm\bar{3}m$  or  $Fm\bar{3}$ . Now, the structural analyses are tried for the sc and fcc crystals of the isomer I based on the Rietveld refinements.

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<sup>1</sup>See, for example, H. Shinohara, in *Fullerenes*, edited by K. M. Kadish and R. S. Ruoff (Wiley, New York, 2000), p. 357.

<sup>2</sup>M. Takata, B. Umeda, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, and H. Shinohara, *Nature (London)* **377**, 46 (1995).

<sup>3</sup>E. Nishibori, M. Takata, M. Sakata, M. Inakuma, and H. Shinohara, *Chem. Phys. Lett.* **298**, 79 (1998).

<sup>4</sup>M. Takata, E. Nishibori, B. Umeda, M. Sakata, E. Yamamoto, and H. Shinohara, *Phys. Rev. Lett.* **78**, 3330 (1997).

<sup>5</sup>T. Watanuki, A. Fujiwara, K. Ishii, Y. Matsuoka, H. Suematsu, K.

Ohwada, H. Nakao, Y. Fujii, T. Kodama, K. Kikuchi, and Y. Achiba, in *Electronic Properties of Novel Materials Science and Technology of Molecular Nanostructures*, edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth (AIP, Melville, 1999), p. 124.

<sup>6</sup>T. Watanuki, A. Fujiwara, K. Ishii, Y. Matsuoka, H. Suematsu, K. Ohwada, H. Nakao, Y. Fujii, T. Kodama, K. Kikuchi, and Y. Achiba, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **340**, 639 (2000).

<sup>7</sup>C. J. Nuttall, Y. Inada, K. Nagai, and Y. Iwasa, *Phys. Rev. B* **62**, 8592 (2000).

- <sup>8</sup>S. Iida, Y. Kubozono, Y. Slovokhotov, Y. Takabayashi, T. Kanbara, T. Fukunaga, S. Fujiki, S. Emura, and S. Kashino, *Chem. Phys. Lett.* **338**, 21 (2001).
- <sup>9</sup>In this paper, the numbering of the isomers, I and II, is the same as that in Ref. 8.
- <sup>10</sup>T. Akasaka, T. Wakahara, S. Nagase, K. Kobayashi, M. Waelchli, K. Yamamoto, M. Kondo, S. Shirakura, Y. Maeda, T. Kato, M. Kako, Y. Nakadaira, X. Gao, E. V. Caemelbecke, and K. M. Kadish, *J. Phys. Chem. B* **105**, 2971 (2001).
- <sup>11</sup>A. Fujiwara, K. Ishii, T. Watanuki, H. Suematsu, H. Nakao, K. Ohwada, Y. Fujii, Y. Murakami, T. Mori, H. Kawada, T. Kikegawa, O. Shimomura, T. Matsubara, H. Hanabusa, S. Daicho, S. Kitamura, and C. Katayama, *J. Appl. Crystallogr.* **33**, 1241 (2000).
- <sup>12</sup>P. A. Heiney, G. B. M. Vaughan, J. E. Fischer, N. Coustel, D. E. Cox, J. R. D. Copley, D. A. Neumann, W. A. Kamitakahara, K. M. Creegan, D. M. Cox, J. P. McCauley, Jr., and A. B. Smith III, *Phys. Rev. B* **45**, 4544 (1992).
- <sup>13</sup>O. Zhou and D. E. Cox, *J. Phys. Chem. Solids* **53**, 1373 (1992).
- <sup>14</sup>S. Margadonna, C. M. Brown, A. Lappas, K. Prassides, K. Tanigaki, K. D. Knudsen, T. Le Bihan, and M. Mezouar, *J. Solid State Chem.* **145**, 471 (1999).
- <sup>15</sup>S. Margadonna, K. Prassides, K. D. Knudsen, M. Hanfland, M. Kosaka, and K. Tanigaki, *Chem. Mater.* **11**, 2960 (1999).
- <sup>16</sup>O. Zhou, G. B. M. Vaughan, Q. Zhu, J. E. Fischer, P. A. Heiney, N. Coustel, J. P. McCauley, Jr., and A. B. Smith III, *Science* **255**, 833 (1992).
- <sup>17</sup>T. Yildirim, J. E. Fischer, A. B. Harris, P. W. Stephens, D. Liu, L. Brard, R. M. Strongin, and A. B. Smith III, *Phys. Rev. Lett.* **71**, 1383 (1993).