PHYSICAL REVIEW B **69**, 113412 (2004)

Anomalous endohedral structure of Gd@C_{82} metallofullerenes

Eiji Nishibori, Kenichi Iwata, and Makoto Sakata
Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan

Masaki Takata
Japan Synchrotron Radiation Research Institute, 1-1-1 Koto, Mikazuki-cho, Sayo-gun, Hyogo 679-5198, Japan

Hiroshi Tanaka
Department of Material Science, Shimane University, Matsue 690-8504, Japan

Haruhito Kato and Hisanori Shinohara
Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan

(Received 31 October 2003; published 29 March 2004)

An anomalous endohedral structure of Gd@C_{82} metallofullerenes has been revealed by synchrotron radiation powder structure analysis by using the maximum entropy method. The Gd@C_{82} metallofullerene has C_{82}-C_{2V} cage structure as for Sc@C_{82} and La@C_{82} fullerenes. The Gd atom is located in the vicinity of the C-C double bond on the C_2 molecular axis in the C_{82}/C_{2V} cage, which is the opposite end of the six-membered ring where Sc and La atoms in Sc@C_{82} and La@C_{82} are known to be placed. Furthermore, a significant overlap of the electron density distribution has been found between Gd atoms and carbon cages. A significantly polarized distribution of electrons has also been found on the carbon cage around the encapsulated Gd atom.

DOI: 10.1103/PhysRevB.69.113412 PACS number(s): 61.10.Nz, 81.05.Tp

Endohedral metallofullerenes[1] have attracted wide interest during the past decade for their potential applications in the fields of nanomaterials and biomedical science. Among them, Gd@C_{82} is one of the most promising fullerene materials in producing metallofullerene peapods for spintronics devices[2–4] and in synthesizing new types of magnetic resonance imaging (MRI) contrast argents[5,6] owing to its novel Gd^{3+}@C_{82}^{3-} electronic structure. Several important studies have so far been carried out in an effort to elucidate the electronic, structural, and solid-state properties of Gd@C_{82} (Refs. 7–9).

The valency of Gd@C_{82} has been determined as Gd^{3+}@C_{82}^{3-} by *in situ* electron energy loss spectroscopy (EELS) spectra.[10] The result of an extended x-ray absorption fine structure (EXAFS) study has shown that the nearest-neighbor distance from the encaged Gd atom to carbon atom is 2.49(3) Å (Ref. 11). The similarity in UV spectra[12] strongly suggests that Gd@C_{82} possesses C_{82}-C_{2V} cage symmetry similar to those of Sc@C_{82} (Ref. 13) and La@C_{82} (Ref. 14). Thus, as for the metal atom position, Gd@C_{82} has been believed to be situated just above the hexagon on the C_2 symmetry axis as in the case of other M@C_{82} (M = metal atom) monometallofullerenes such as La@C_{82} (Ref. 14). However, the x-ray structure determination of Gd@C_{82} has not yet been reported.

Here, we present the molecular and crystal structure of Gd@C_{82} as determined by the MEM-Rietveld method,[15,16] which is a self-consistent iterative analysis of a combination of the maximum entropy method (MEM) and Rietveld analysis, with synchrotron x-ray diffraction data. Contrary to expectations, the encaged Gd atom is found to be situated adjacent to the C-C double bond on the symmetry axis, which is the opposite side of the molecular symmetry position where group-3 metal atoms (Sc, Y, La) have been reported to exist.[13–15] Furthermore, the MEM charge density reveals the presence of a charge density overlap between Gd and the fullerene cage.

Details of synthesis and purification of metallofullerenes were reported earlier.[1] Briefly, soot-containing fullerenes and Gd endohedral metallofullerenes such as Gd@C_{82} were synthesized by the direct current arc discharge method (500 A, 20–25 V) of Gd/graphite composite rods (0.8 wt % Gd atom, Toyo Tanso Co.) under a 17-l/min flow of helium at 60 Torr. The purification and isolation of Gd@C_{82} metallofullerene was achieved by the two-stage high-performance liquid chromatography (HPLC) method.[1] The purity of Gd@C_{82} metallofullerene (>99%) was quantified by both HPLC and matrix-assisted laser desorption ionization (MALDI) time-of-flight (TOF) mass spectrometry (Shimadzu, UV3100). A Gd@C_{82} powder specimen was grown from toluene solvent. The obtained powder sample was sealed in a silica glass capillary (0.3 mm i.d.).

The synchrotron radiation x-ray powder experiment with imaging plate (IP) as detectors was carried out by a Large Debye-Scheerer Camera at SPring-8 BL02B2 (Ref. 17). The exposure time was 2 h. The wavelength of incident x rays was 0.9952 Å. The x-ray powder pattern of Gd@C_{82} was obtained with a 0.02° step from 3.0° to 28.0° in 2θ, which corresponds to a 2.06-Å resolution in d spacing.

The experimental data were analyzed by the MEM-Rietveld[15,16] analysis. By using the method, the structures of M@C_{82}-type endohedral metallofullerenes such as Y@C_{82} (Ref. 15), Sc@C_{82} (Ref. 13), La@C_{82} (Ref. 14), and Sc_3@C_{82} (Ref. 18) have been successfully revealed as the precise charge densities from synchrotron radiation powder data. The details of this method are described in the previous studies.[13–15,18]

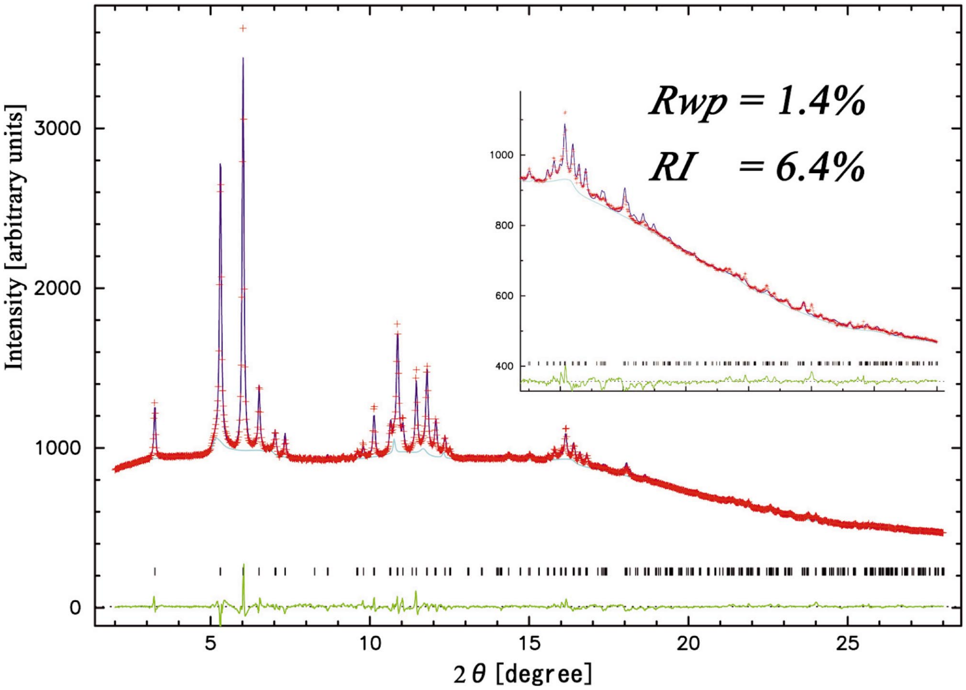

FIG. 1. (Color) The fitting result of Rietveld analysis for Gd@C_{82}. A close-up of the region between 15.0° and 28.5° is shown in the inset.

The cell parameters are determined as $a=18.351(1)$ Å, $b=11.262(1)$ Å, $c=11.282(1)$ Å, and $\beta=107.72(1)°$ (monoclinic: $P2_1$) by the Rietveld analysis. The reliability factor (R factor) based on the Bragg intensities, R_I, and weighted profile R factor R_{wp} were 6.4% and 1.4%, respectively. Figure 1 shows the result of the final Rietveld fitting. The number of structure factors derived in this analysis was 301. The MEM charge density based on Rietveld analysis was derived with the 301 structure factors by dividing the unit cell into 120×90×90 pixels using the MEM program ENIGMA (Ref. 19). The reliability factor of the final MEM charge density was 2.2%.

Previous x-ray structural studies on Y@C_{82} (Ref. 15), La@C_{82} (Ref. 14), and Sc@C_{82} (Ref. 13) have shown that these metal atoms are located at an off-center position in the C_{82} cage and are situated adjacent to the hexagonal ring on the C_2 axis of C_{82}-C_{2V} fullerene cage. These experimental results are consistent with theoretical calculations.[20] Under these circumstances, both the cage structure and position of the metal atom of Gd@C_{82} could be the same as those of La@C_{82} (Ref. 14) and Sc@C_{82} (Ref. 13).

The obtained MEM charge density of Gd@C_{82} molecule is shown in Figs. 2(a) and 2(b) together with the previous result for La@C_{82} (Ref. 14) in Figs. 2(c) and 2(d) for reference. The charge density of the metal atom is colored azure and red for Gd and La, respectively. Six- and five-membered rings are clearly seen for both Gd@C_{82} and La@C_{82} molecules. Figures 2(a) and 2(c) show top views of the metallofullerenes from the six-membered rings on the C_2 axis for Gd@C_{82} and La@C_{82}, respectively, and Figs. 2(b) and 2(d) represent the corresponding side views. Because the 5/6 ring networks are exactly the same with each other, Gd@C_{82} also has C_{2V} symmetry as in La@C_{82}. The Ga atom is located on the C_2 axis of the C_{82}-C_{2V} cage.

One of the most important findings of the present study is that the Gd atom is situated adjacent to the C-C double bond on the symmetry axis as in Fig. 2(b). This is the opposite side of the C_{82}-C_{2V} fullerene cage along the C_2 symmetry axis where group-3 metal atoms (Sc, Y, La) have been reported to exist,[13–15] even though the C_{82} cage symmetry is exactly the same for Gd@C_{82} and La@C_{82} as in Figs. 2(b) and 2(d), respectively. The position of Gd in the C_{82} cage is different

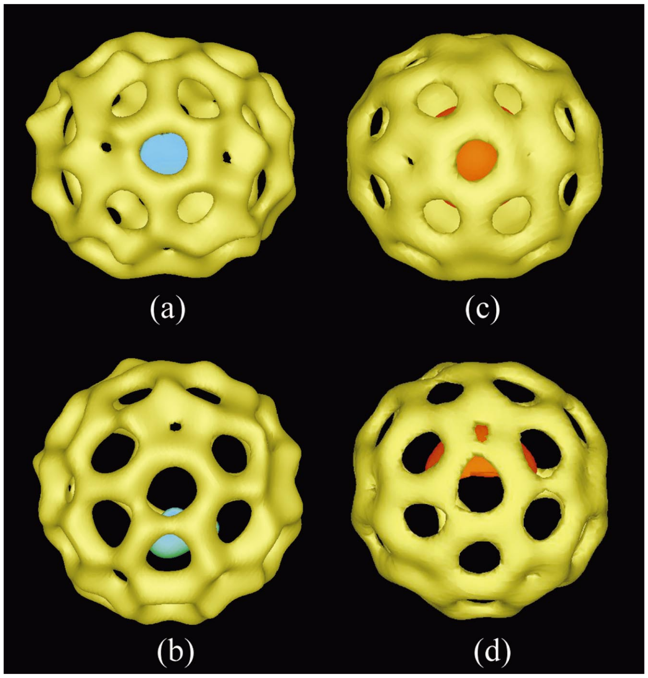

FIG. 2. (Color) The MEM charge densities of Gd@C_{82} and La@C_{82} molecules as the equicontour ($1.7e/\text{Å}^{-3}$) surface: (a),(b) the top view and (c),(d) the side view. The Gd atom charge density is colored azure. The La atom charge density is colored red.

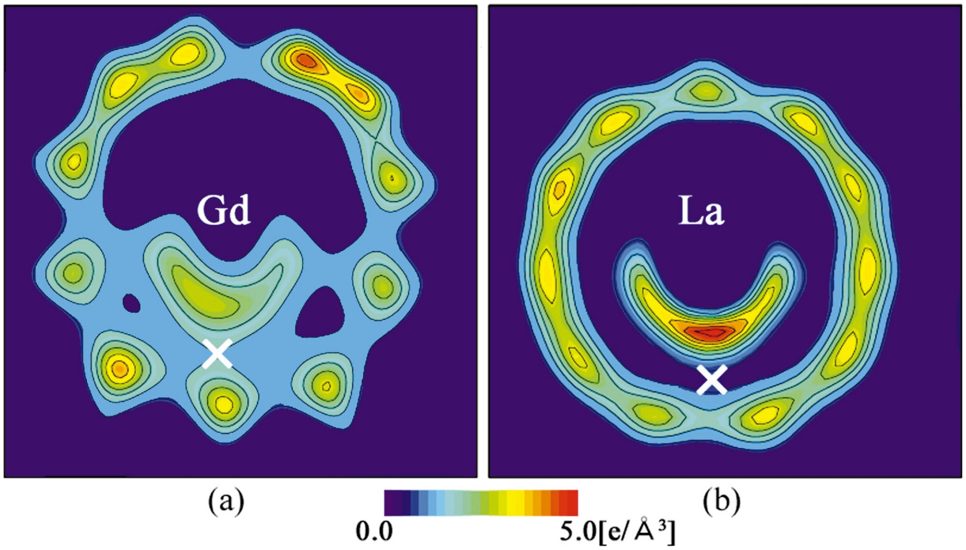

FIG. 3. (Color) The MEM charge density sections of Gd@C_{82} and La@C_{82} molecules. The contour lines are drawn from 0.0 to 5.0 with a 0.5 [e/Å^{-3}] step.

from that of La in the same cage. In the C_{82}-C_{2V} fullerene cage, the C_2 axis goes through the center of a six-membered ring and that of a C-C double bond. The Gd atom is located in the vicinity of the C-C bond, whereas the La atom is located adjacent to the six-membered ring.[14]

Experimental and theoretical studies have shown that charge transfer from metal atoms to the carbon cage plays crucial roles in stabilizing endohedral metallofullerenes. In fact, for La@C_{82} and Sc@C_{82} the position of Sc and La atoms as well as the cage structure as determined by x-ray diffraction are consistent with theoretical predictions[20] based on charge transfer interactions. Moreover, the charge density of the La atom exhibited clear evidence for a large-amplitude motion occurring in the C_{82} cage. The MEM charge density of La resembles the minimum-point region of a calculated electrostatic potential inside C_{82}^{3-}-C_{2V} anion.[20] From these facts, although the structure of La@C_{82} is known to be stabilized by ionic bonding between La^{3+} and C_{82}^{3-}, the present finding that the Gd atom is located in an opposite position inside the C_{82}-C_{2V} cage suggests that Gd@C_{82} should be stabilized by a much more complicated interaction.

The number of electrons of Gd $(60.4e)$ was counted from the obtained MEM charge density, which is close to the trivalent state of the Gd^{3+} ion $(60.0e)$. The electronic structure of Gd@C_{82} can, thus, formally be expressed as Gd^{3+}@C_{82}^{3-}. This is consistent with the result obtained from EELS measurements.[10]

The MEM charge density sections of Gd@C_{82} and La@C_{82} molecules are shown in Figs. 3(a) and 3(b), respectively, where the direction of the C_2 axis is vertical and that of the C-C double bond at the C_2 axis is perpendicular to the figure plane. A widely spread charge density of Gd, which should be due to disorder and/or thermal smearing, is seen inside the C_{82}-C_{2V} cage in Fig. 3(a). A hemispheric charge density distribution of the La atom is also seen in Fig. 3(b) (Ref. 14). It is noted that a significant charge density overlap between Gd and the nearest carbon atom is observed in Fig. 3(a). In contrast, virtually no such overlap of the charge density is seen for La@C_{82} in Fig. 3(b).

The charge density at the middle point between Gd and the nearest carbon atom is 0.996[e/Å^3], which is twice as high as that of La@C_{82} (0.404[e/Å^3]). Such a high charge density suggests the presence of covalency between Gd and the nearest carbon atoms. A similar but somewhat weaker overlap of charge density also exists between Gd atom and other carbon atoms [cf. Fig. 3(a)]. The existence of the charge density overlap between Gd and the adjacent carbon atoms stabilizes the endohedral structure of Gd@C_{82} molecules.

The electron distributions on the C_{82}-C_{2V} cage were in-

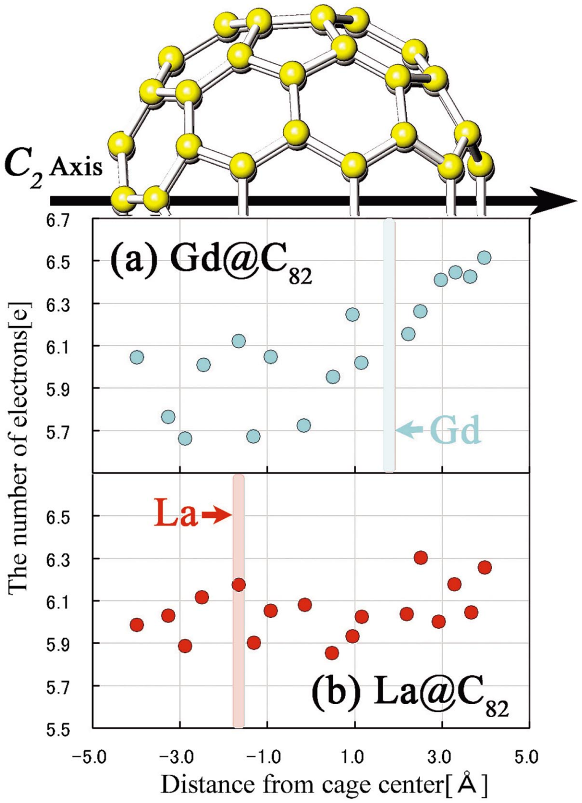

FIG. 4. (Color) The plot of the number of electrons for carbon atoms as a function of distance from the cage center to positions projected onto the C_2 axis.

vestigated by counting the number of electrons for each carbon atoms from obtained the MEM charge density. Figures 4(a) and 4(b) show the number of electrons for the carbon atoms of Gd@C_{82} and La@C_{82} projected onto the C_2 axis, where the origin of the x coordinate coincides with the C_2 axis. A schematic structure of the C_{82}-C_{2V} cage is superimposed on these figures. The metal atom positions are shown as bars colored azure and red for Gd and La, respectively, in the figures. As seen in Fig. 4(a), the electron numbers of carbon atoms apparently increase around the Gd atom. Such a significantly polarized distribution of electrons is not observed in La@C_{82} [cf. Fig. 4(b)]. The Gd@C_{82} metallofullerene has a significant charge localization on the fullerene cage, indicating the existence of electronic polarization.

The present results on the endohedral structure of Gd@C_{82} show that stabilization of endohedral metallofullerenes accompanies not only the charge transfer between Gd and the C_{82} cage but also Gd-C covalent bonding like charge density overlap. A similar charge density overlap between the encaged atoms and fullerene cage was reported in the recent finding of an isolated pentagon rule (IPR) (Refs. 21 and 22) violated metallofullerene Sc_2@C_{66} (Refs. 23 and 24), in which covalent bonding between Sc_2 dimer and carbon atoms has been revealed by the MEM charge density. The endohedral fullerene structures of Sc_2@C_{66} and Gd@C_{82} obtained from x-ray diffraction differ substantially from existing theoretical calculations.[25] Further theoretical considerations which include covalency of the metal-carbon interaction are needed to acquire a better understanding for structural stability and the polarization of the electron distribution of endohedral metallofullerenes.

The present finding on the charge density level structure also provides crucial information for ongoing applications of Gd@C_{82} molecules in spintronics devices using peapods[2–4] and MRI contrast agents using the water-soluble Gd fullerene Gd@$C_{82}(OH)_n$ (Refs. 5 and 6).

This work has been supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Science, Sports and Technology of Japan, the Advanced Processes Research for the Future Program of JSPS. The Nippon Sheet Glass Foundation for Materials Science and Engineering also supported this work. The synchrotron radiation experiments were performed at SPring-8 BL02B2 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI).

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