

High-Resolution Analysis of (Sc₃C₂)@C₈₀ Metallofullerene by Third Generation Synchrotron Radiation X-ray Powder Diffraction

Eiji Nishibori,^{*,†} Ikuya Terauchi,[†] Makoto Sakata,[†] Masaki Takata,^{‡,||} Yasuhiro Ito,[§] Toshiki Sugai,[§] and Hisanori Shinohara^{§,||}

Department of Applied Physics, Nagoya University, Nagoya 464-8603, Japan, Structural Materials Science Laboratory, Harima Institute, RIKEN SPring-8 Center, 1-1-1 Kyouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan, Department of Chemistry & Institute for Advanced Research, Nagoya University, Nagoya 464-8602, Japan, and CREST JST

Received: March 21, 2006; In Final Form: April 29, 2006

The X-ray structure of Sc₃C₈₂ is redetermined by the MEM/Rietveld method by using synchrotron radiation powder data at SPring-8, where the C₂ encapsulated structure available to discuss the Sc–Sc interatomic distances has been determined. The encapsulated three scandium atoms form a triangle shape. A spherical charge distribution originating from the C₂ molecule is located at the center of the triangle. Interatomic distances between Sc and Sc are 3.61(3) Å in the triangle. The distance between Sc and the center of the C₂ molecule is 2.07(1) Å.

Introduction

Endohedral metallofullerenes have attracted wide interest because of their novel structural and electronic properties.^{1,2} The recent finding of metal carbide (M₂C₂ species) encapsulation by fullerenes³ has provided a brand new series of endohedral fullerenes. The presence of the first metal carbide encapsulated metallofullerene, (Sc₂C₂)@C₈₄, was confirmed by ¹³C NMR measurements and X-ray analyses.³ Recently, the yttrium carbide metallofullerenes, (Y₂C₂)@C₈₂ (isomers I–III), have been synthesized and identified by ¹³C NMR measurements^{4,5} and the Y₂C₂ encapsulation in (Y₂C₂)@C₈₂ has been confirmed by synchrotron radiation (SR) X-ray powder diffraction.⁶

The tri-Sc metallofullerene, Sc₃C₈₂, is one of the most intriguing metallofullerenes since a Sc metal cluster is encapsulated by a fullerene and was first synthesized by arc discharge of Sc-impregnated graphite rods in 1992.^{7,8} Since then a number of studies on Sc₃C₈₂ have been reported such as electron paramagnetic resonance,^{9,10} theoretical calculations,¹¹ and synchrotron X-ray powder diffraction.¹² Sugai et al.¹³ have reported, however, the possibility of an endohedral metal carbide structure of (Sc₃C₂)@C₈₀ instead of Sc₃C₈₂ by gas-phase ion mobility measurements. Actually, Iiduka et al. have recently shown that the fullerene cage of Sc₃C₈₂ is C₈₀-I_h instead of C₈₂ from ¹³C NMR results on the (Sc₃C₈₂)[−] anion,¹⁴ indicating the intact (Sc₃C₂)@C₈₀ carbide structure as in M₂C₂@C₈₂ type carbide metallofullerenes. Single-crystal X-ray structures of chemically functionalized (Sc₃C₂)@C₈₀ molecules with an addition of adamantylidene carbene (Ad) have also been reported.¹⁴ Recently, a density functional theory investigation of the intact (Sc₃C₂)@C₈₀ have been reported by Tan et al.¹⁵ However, X-ray structures of the intact (Sc₃C₂)@C₈₀ fullerenes have not yet been

known. Furthermore, the reported structures of (Sc₃C₂)@C₈₀-(Ad) do not include detailed structural information such as Sc–Sc distances due to multiple disorders of Sc atoms.

The powder X-ray structure of Sc₃C₈₂ based on the second generation SR data (*d* > 2.1 Å) was reported in 1999 by the present group.¹² In the MEM (maximum entropy method)/Rietveld analysis¹⁶ of that study, the fullerene cage for Sc₃C₈₂ was postulated as C₈₂ (i.e., Sc₃@C₈₂) based on the mass spectral data and the disorder of Sc atoms was not considered. These led us to erroneously assign (Sc₃C₂)@C₈₀ as Sc₃@C₈₂ in the analysis. Since then, the qualities of the powder diffraction data have drastically improved by the third generation SR X-ray source, such as SPring-8, due to their high angular resolutions and intensities. This high-resolution data provides great improvement of the accuracy of the structure analyzed by both Rietveld refinement¹⁷ and MEM¹⁸ for fullerene materials. In a previous La₂@C₈₀ analysis, which was determined by using *d* > 1.66 Å SPring-8 data,¹⁸ a multiple disorder of La atoms has been revealed and the precision of MEM charge density becomes comparable to theoretical calculation.¹⁹ Here we report the structure of Sc₃C₈₂ based on the powder data measured at SPring-8, BL02B2 beamlines.

Experimental Methods

Scandium metallofullerenes were produced by the reported dc arc-discharge method.¹ The soot containing scandium metallofullerenes was collected anaerobically and extracted with *o*-xylene solvent. The scandium metallofullerene (Sc₃C₂)@C₈₀ was separated and isolated from various empty fullerenes and other scandium metallofullerenes by the multistage high-performance liquid chromatography (HPLC) method with toluene as eluent. The purity of (Sc₃C₂)@C₈₀ metallofullerene was checked by both positive and negative laser desorption time-of-flight (LD-TOF) mass spectrometry as well as HPLC analyses. LD-TOF mass spectral data were obtained on a Shimadzu MALDI–IV mass spectrometer.

The (Sc₃C₂)@C₈₀ powder sample grown from toluene solvent was sealed in a silica glass capillary with 0.4 mm inside

* To whom correspondence may be addressed. Telephone: +81-52-789-3702. Fax: +81-52-789-3724. E-mail: o47271a@cc.nagoya-u.ac.jp.

† Department of Applied Physics, Nagoya University.

‡ Structural Materials Science Laboratory.

§ Department of Chemistry & Institute for Advanced Research, Nagoya University.

|| CREST JST.

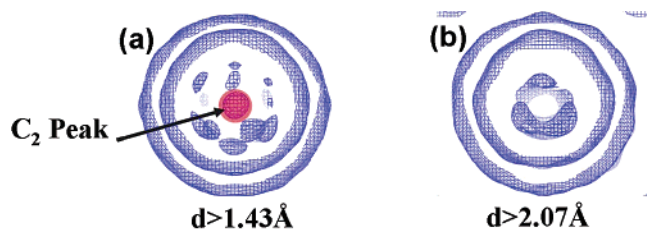


Figure 1. The equicontour ($0.7 \text{ e} \text{ \AA}^{-3}$) mesh of MEM charge densities for the $(\text{Sc}_3\text{C}_2)@C_{80}$ molecules based on the C_{82} spherical-shell model (see text).

diameter. The powder diffraction data of $(\text{Sc}_3\text{C}_2)@C_{80}$ were measured at SPring-8 BL02B2 beamlines at room temperature. An imaging plate with $50 \mu\text{m}$ pixel size was used as a detector. The wavelength of incident X-ray was $1.00123(5) \text{ \AA}$. Exposure time of X-ray was 90 min.

Results and Discussion

First we describe the quality of powder diffraction data measured at SPring-8 as compared with the previous data,¹² since an accuracy of determined structure fully depends on the quality of the data such as counting statistics, peak width, and data resolution. SPring-8, one of the third generation synchrotron sources, has great advantage over previous sources to improve the quality of data due to availability of high flux and high energy resolution X-ray photons. The maximum intensity of Bragg reflection for the present data was around 1 500 000 counts, which are approximately four times larger than that used for the previous data. The widths of Bragg peaks for present data were from 0.04 to 0.08° in 2θ . These are approximately two-thirds of that of the previous data. The larger intensities and higher angular resolution enable us to perform accurate structural analyses because even the weak Bragg intensities become detectable. The data set with $d > 1.43 \text{ \AA}$ d -spacing range was used in the present analysis.

By comparison of the peak positions of the present data and those of $\text{La}_2@C_{80}$,¹⁸ the space group of the present specimen was assigned as $P2_1$ at this stage. The lattice constants were refined by the LeBail method. The lattice constants were $a = 18.1948(2) \text{ \AA}$, $b = 11.14953(9) \text{ \AA}$, $c = 11.13725(9) \text{ \AA}$, and $\beta = 107.733(2)^\circ$. It is well-known^{6,16,18} that this type of monoclinic unit cell includes solvent molecules inside the unit cell. Therefore, the chemical formula of the present powder specimen should be written as $[(\text{Sc}_3\text{C}_2)@C_{80}] \cdot (\text{C}_6\text{H}_5\text{CH}_3)$.

The data were analyzed by the MEM/Rietveld method.¹⁶ A spherical shell composed of 82 carbon atoms and a toluene molecule was used in the first Rietveld refinement to avoid model-biased effects. The model bias is well-known as one of the serious problems for X-ray analysis especially in macromolecule crystallography.²⁰ The model bias may lead to a wrong structure. This also emerges in the powder structural analysis for molecular crystal, which has a large number of atomic positions, such as metallofullerenes. An X-ray diffraction experiment only measures the amplitude of structure factors. The initial phase of structure factors is estimated from a structure model adopted at the beginning of the analysis. The structure obtained by the analysis can be biased by the model adopted at the beginning. In this study, the least biased structure model for a fullerene cage, which must be a spherical shell, was used as an initial model.

A total of 837 observed structure factors were extracted after the refinement. The MEM analysis was carried out by the program ENIGMA.²¹ The MEM charge density at this stage is shown in Figure 1a. There are many peaks due to disorder of

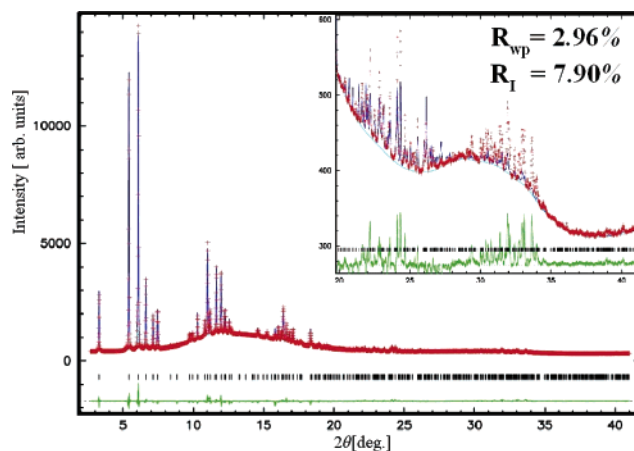


Figure 2. The fitting result of Rietveld analysis using the $\text{Sc}_3@C_{82}$ structure model, which is published in ref 12. A closeup of the region between 19.0 and 41.0° is shown in the inset.

encapsulated Sc atoms in the MEM charge density of fullerene cage. So far, the encapsulated C_2 has been found in the center of a fullerene cage in the previous structural studies of metal carbide endohedral metallofullerene, $(\text{Sc}_2\text{C}_2)@C_{84}$ ³ and $(\text{Y}_2\text{C}_2)@C_{82}(\text{III})$.⁶ These works were also done by the SR powder diffraction experiments. A relatively large peak is located in the center of fullerene cage and is assigned as C_2 . The other peaks are assigned as disordered Sc atoms. Therefore, the fullerene cage is assigned as C_{80} .

In the previous MEM/Rietveld study on Sc_3C_{82} ,¹² only 279 structure factors were used in the MEM analysis because of the very weak Bragg intensities around the $d < 2.1 \text{ \AA}$ d -spacing range. No charge density at the center of fullerene cage was found in that analysis.¹² The lack of the data resolution failed to reveal C_2 encapsulation. To confirm this point, the MEM analysis was performed by using only 279 reflection with $d > 2.1 \text{ \AA}$ d -spacing range of the SPring-8 data. The MEM charge density is shown in Figure 1b. The C_2 peak disappeared in the center of fullerene cage, indicating that $d > 2.1 \text{ \AA}$ resolution is not good enough to reveal a C_2 molecule in the C_{80} carbon cage. In the previous analysis, we put three Sc atoms to the three large electron density peaks in Figure 1b. Then we investigated possible directions of two isomers of $C_{82}-C_{3v}$ cages. The structure with the lowest reliability factors of Rietveld refinement was a final solution. The fitting result of Rietveld refinement using the previous $\text{Sc}_3@C_{82}$ model¹² for present $d > 1.43 \text{ \AA}$ data is shown in Figure 2. In the $d > 2.6 \text{ \AA}$ range, which corresponds to less than 22° in 2θ , the fitting is satisfactory. However, in the $2.6 \text{ \AA} > d > 1.43 \text{ \AA}$ range, there are large deviations indicating incorrect structure. From these facts, it was concluded that the erroneous assignment of the previous analysis is due to the lack of resolution and model-biased effect in the analysis.

In the present analysis, we pick up all 12 peak positions inside the fullerene cage in Figure 1a. Then the scandium atoms were put at all peaks by considering disorder of metal atoms. The occupancy of atoms was adjusted by the peak value of the MEM charge density. The existence of each charge density peak was verified by omit-MEM map analysis. The flowchart with a schematic figure of omit-MEM analysis is shown in Figure 3.

The procedure of the omit-MEM map analysis is as follows. The structural model omitted a few Sc atoms from 12 Sc positions was used for Rietveld refinement. Then the amplitudes of structure factors are extracted from powder profile by the refinement. The phases of structure factors calculated by the

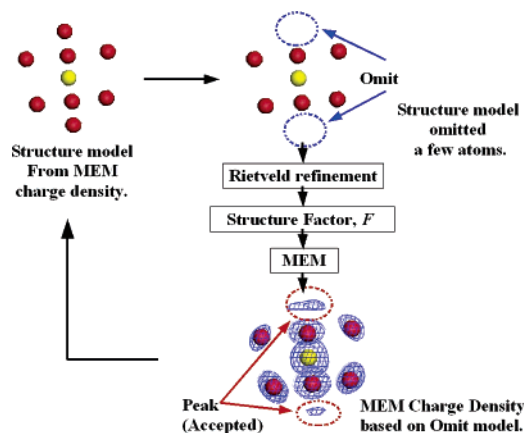


Figure 3. The flowchart of omit-MEM map analysis for disorder Sc atoms in $(\text{Sc}_3\text{C}_2)@\text{C}_{80}$.

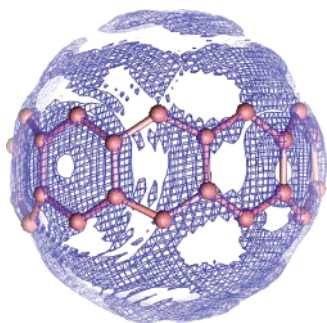


Figure 4. The equicontour ($2.4 \text{ e } \text{\AA}^{-3}$) mesh of MEM charge densities for $(\text{Sc}_3\text{C}_2)@\text{C}_{80}$ molecule with cyclance-like belt of C_{80} cage.

structure model omitted a few atoms. The obtained structure factors were used for MEM analysis. We investigated the MEM charge density of omitted Sc atom position. If a charge density peak was found, the position was accepted as a disordered Sc atom. If the peak disappeared, the atomic position was removed from the structure model. When the additional peaks were found, the peak positions were added to the structural model. The omit-MEM map analysis had been continued until no inconsistency occurs between the MEM map and the structure model. The omit-MEM map analysis is similar to the omit-Fourier map analysis used in macromolecule crystallography. The MEM charge density was utilized to reveal weak peaks of disordered Sc atom. Eventually, the 12 Sc positions had been found and confirmed by the analysis.

At this stage of the analysis, an additional symmetry of the structures has been found for the positions of Sc atoms. There were two candidates of the space groups, which are $P2_1/m$ and $Cmcm$. By consideration of the additional symmetry, the space group has been finally determined as $P2_1/m$. With this new space group, the number of Sc atoms in the crystallographic asymmetric unit amounts to eight. Judging from the arrangement and occupancy of 12 Sc peaks, it was found that Sc atoms with the same occupancies are forming triangles and are disordered in five directions. There are two different kinds of the shared Sc positions. One is shared by the three triangles and the other is shared by the two triangles. Thus the number of Sc position is 12.

The MEM charge density at this stage is shown in Figure 4. The structure model of Rietveld refinement for the C_{80} fullerene cage is still a spherical shell. There is one relatively large occupancy of a Sc triangle in five disordered triangles. The occupancy of this Sc atom is 1.2 times larger than that of the others. In Figure 4, the triangle is located on the horizontal plane

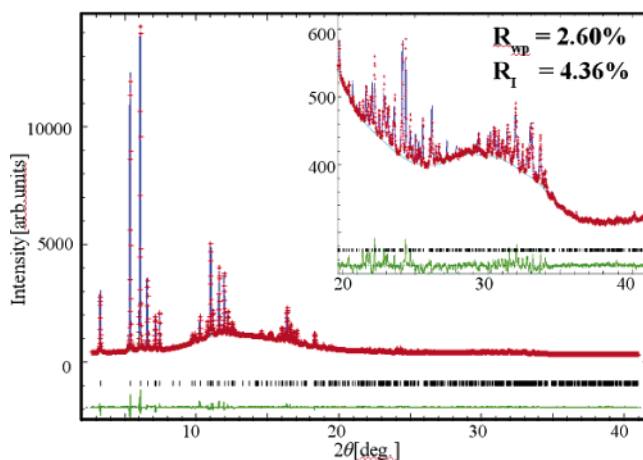


Figure 5. The fitting result of Rietveld analysis for $(\text{Sc}_3\text{C}_2)@\text{C}_{80}$. A closeup of the region between 19.0 and 41.0° is shown in the inset.

that passes through the center. There are periodical charge density holes on the horizontal plane of the fullerene cage. The arrangement of these holes fit the cyclance-like belt, which is composed of six-membered rings, of the $\text{C}_{80}-I_h$ cage. The orientation of the $\text{C}_{80}-I_h$ molecule was determined by the fitting of the cyclance-like belt to the MEM charge density as shown in Figure 4. A few unfitted parts on the cage remained after assuming a $\text{C}_{80}-I_h$ cage. To express these parts, an additional $\text{C}_{80}-I_h$ cage was assumed as disorder. The occupancy of the newly assumed $\text{C}_{80}-I_h$ cage was 0.2. The omit-MEM map analysis was also utilized in the determination of cage orientation.

The peaks of carbon and Sc atoms in the MEM charge density are expanded like circular arcs, indicating rotational motions of a $(\text{Sc}_3\text{C}_2)@\text{C}_{80}$ molecule. To express the rotational motion, the C_{80} cage and disordered Sc triangles have been assumed as the mixture of spherical shell and atoms, respectively. The C_2 atoms have been assumed to be a spherical shell. The atoms composed of both C_{80} fullerene cage and Sc have been treated as a rigid-body in the next Rietveld refinement. The combination of spherical shell and rigid body is effective to reduce the number of the parameters in the refinement. The number of structure parameters in the final Rietveld refinement is as small as 39. They are 5 position parameters, 25 orientation parameters, 3 radius of spherical shells, and 6 thermal parameters. Similar treatments have already been successfully used in previous studies of $\text{La}_2@\text{C}_{80}$ ¹⁸ and $(\text{Y}_2\text{C}_2)@\text{C}_{82}(\text{III})$ ⁶ for improvement of the accuracy of the results.

The fitting result of the final Rietveld refinement is shown in Figure 5. The reliability factors based on weighted profile, R_{wp} , and Bragg intensities, R_I , are as small as 2.60% and 4.36%, respectively. These values are lower than those of the previous study¹² even in high-resolution analysis. The small number of parameters and lower reliability factors are satisfactory for the current precise structure determination.

The crystal structure of $[(\text{Sc}_3\text{C}_2)@\text{C}_{80}] \cdot (\text{C}_6\text{H}_5\text{CH}_3)$ is shown in Figure 6a. As described above, the $\text{C}_{80}-I_h$ and Sc_3C_2 molecules exhibit disordered structure. The solvent toluene molecules have also shown a disorder with two directions. The occupancy in this disordered structure is not equal. In Figure 6a, all the disordered structure is included. In Figure 6b, the crystal structure of the highest occupancy for each molecule is shown. It is clear that the planer Sc_3C_2 cluster is parallel to the six-membered ring of toluene molecules. The cyclacene-like belt of the $\text{C}_{80}-I_h$ molecule is also parallel to the six-membered ring of toluene molecules. From these facts, the

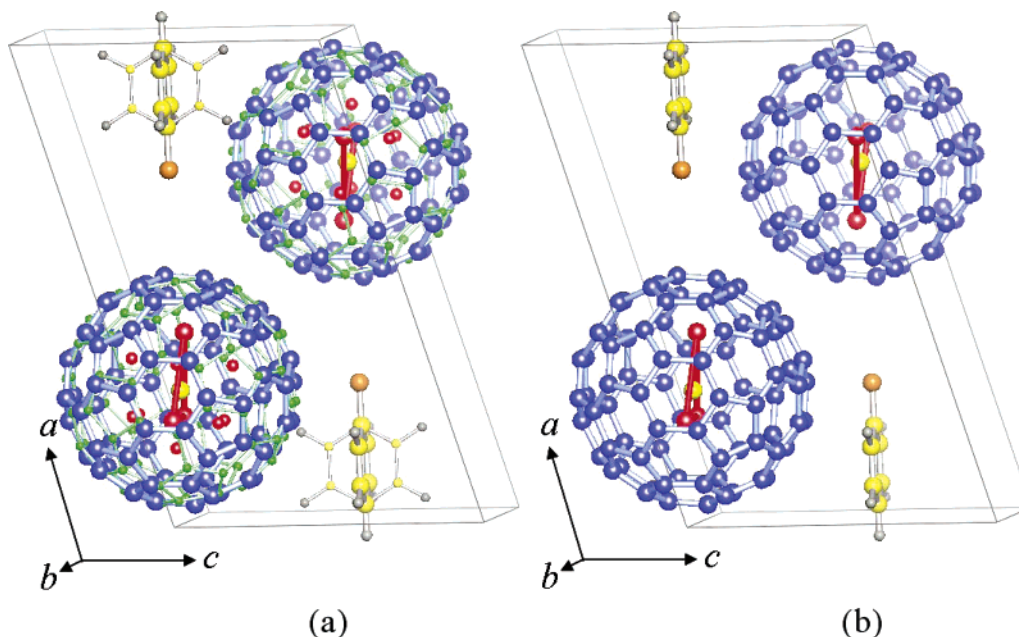


Figure 6. The crystal structure of $[(\text{Sc}_3\text{C}_2)@C_{80}]$, $(\text{C}_6\text{H}_5\text{CH}_3)$. The all atoms including disorder parts are shown in Figure 5a. The size of atom in the figure was adjusted by their occupancies. The major part of the structure is shown Figure 5b.

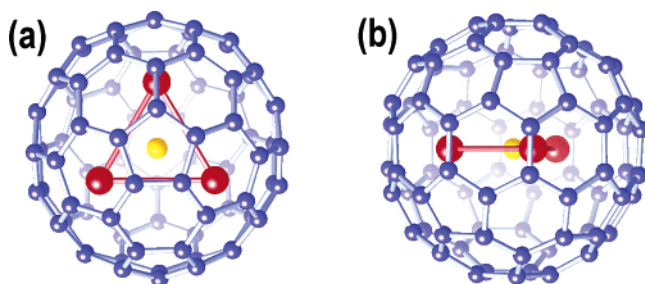


Figure 7. The molecular structure models of $(\text{Sc}_3\text{C}_2)@C_{80}$ along the (a) S_{10} and (b) C_2 axes determined by the MEM/Rietveld method from the present synchrotron X-ray powder diffraction data.

toluene molecules affect the positions of not only fullerene cage but also encapsulated Sc_3C_2 cluster. The positions of encapsulated metal atoms are affected by an external field of fullerene molecules.

The molecular structure of the major part for $(\text{Sc}_3\text{C}_2)@C_{80}$ determined by the MEM/Rietveld method is shown in Figure 7. The C_2 molecule is shown as one yellow sphere, since the MEM charge density for C_2 appears as one peak. The encapsulated three Sc atoms form a triangle shape as in the previous study.¹² A sphere due to C_2 is located at the center of the triangle. In Figure 7b, the three Sc atoms and C_2 are located on the belt of the six-membered ring. The interatomic distance between Sc and Sc is 3.61(3) Å in all five disordered triangles. The distance between Sc and the center of C_2 is 2.07(1) Å.

The present structure is similar to one of the five theoretically predicted structures by recent density functional (DFT) calculations.¹⁵ The positions of Sc atoms are almost identical to **1a** isomer reported by Tan et al.¹⁵ The planer Sc_3C_2 cluster is located at cyclacene-like belt, which is composed of six-membered rings, in the present results. This is consistent with **1a** structure. The average nearest-neighbor interatomic distances between Sc and carbon atoms on the fullerene cages in the present structure is 2.27(20) Å, which is very close to a reported theoretical value of 2.349 Å. The average distances from the center of C_2 to Sc and from Sc to Sc in the theoretical study are 2.181 and 3.748 Å, respectively. The deviations of the distances between the present and the theoretical structures are

within 0.15 Å. It has not been possible to identify the direction of C_2 linear cluster from the MEM charge density because of severe disorder of carbon atoms. However, the direction of the C_2 molecular axis is perpendicular to the plane of the Sc_3 triangles judging from the observed interatomic distances and the reported theoretical calculations.

To investigate the possibility of the other four isomers reported by Tan et al.,¹⁵ we performed Rietveld refinement by using molecular structures of **1b**, **1c**, **2a**, and **2b** isomers. In the case of **1b**, **2a**, and **2b** isomers, R_{wp} and R_1 increased by 0.1–0.7% and by 1.5–3.8%, respectively, from the present final result. These isomers are not consistent with the present X-ray data. The three Sc atoms in these isomers form triangles with different interatomic distances and Sc₃ in **1a** almost forms an equilateral triangle. Three Sc atoms in the **1c** isomer almost form an equilateral triangle. The R_{wp} and R_1 for the **1c** isomer are 2.7% and 4.79%, respectively. However, the direction of the fullerene cage is not consistent with **1a** isomer of the DFT calculations.

The structure of planer Sc_3C_2 cluster is disordered with five directions. The all of five planes are located at a cyclacene-like belt of the $C_{80}-I_h$ cage. This suggests that the planer Sc_3C_2 cluster is hopping along the cyclacene-like belt of the fullerene cage. When such a hopping mechanism is considered, the present structure is compatible with ¹³C NMR observation, which indicates I_h symmetry.¹⁴ There are in total six cyclacene-like belts on the $C_{80}-I_h$ cage. We were not able to find the peaks of Sc atoms on one of six belts in the MEM charge density. This is probably due either to limitation of data resolutions or to the interaction with toluene molecules.

Since the distances reported by Iiduka et al.¹⁴ for Sc–Sc range widely from 3.56 to 3.94 Å and 3.14 to 3.69 Å for $(\text{Sc}_3\text{C}_2)@C_{80}(\text{Ad})$ and $n\text{-Bu}_4\text{N}^+[(\text{Sc}_3\text{C}_2)@C_{80}(\text{Ad})]^-$, respectively, it is not possible to compare the present results to those reported distances. Furthermore, the two of three Sc atoms have been assumed as eight or six split-atom positions with individual anisotropic thermal factors in that study.¹⁴ The structures have at least more than ten Aleart_level_A in checkcif²² of IUCr, which is related only to very fundamental structure parameters, i.e., the atomic distances and thermal factors. Friese et al.

reported that the structure determination of endohedral fullerenes is complicated and beyond the black box level even in single-crystal X-ray analyses.²³ They have suggested that a rigid-body model with TLS approach based on a difference Fourier synthesis map is effective for improvement of accuracy of the structure. The current approach, which is comprised by the rigid-body and spherical shell based on MEM and difference-MEM maps, is very powerful to increase accuracy of the determined structure and reduces the number of structure parameters in the refinement.

Conclusions

We have determined the structure of Sc₃C₈₂ metallofullerene by using the third generation SR powder data collected at SPring-8. The obtained structure reveals the C₂ encapsulation in the C₈₀ cage together with the Sc–Sc interatomic distances. We have shown that the erroneous assignment of the previous analysis is due to the lack of resolution of the powder data and the model bias in the process of analysis. The available data resolution of powder data is dramatically increased by the third generation SR such as SPring-8. The analytical technique in the MEM/Rietveld method has also been developed by confirmation using omit-MEM map analysis. The high-resolution SPring-8 powder diffraction data with the MEM/Rietveld method can determine the structures of endohedral metallofullerene at a charge density level including disorder and/or motion of metal atoms such as the present (Sc₃C₂)@C₈₀ study and La₂@C₈₀ already reported.¹⁸

Acknowledgment. The authors thank K. Kato for experimental help at SPring-8. This work has been supported by the JST CREST Program, the Funds of Ministry Education, Culture, Sports, Science and Technology, the Iketani Foundation, and the Toyota Riken Foundation. The synchrotron radiation experiments were performed at beam line BL02B2 at SPring-8.

Supporting Information Available: X-ray crystallographic details including CIF files of (Sc₃C₂)@C₈₀. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843–892.

- (2) Chai, Y.; Guo, T.; Jin, C. M.; Haufler, R. E.; Chibante, L. P. F.; Fure, J.; Wang, L. H.; Alford, J. M.; Smalley, R. J. *Phys. Chem.* **1991**, *95*, 7564–7568.
- (3) Wang, C. R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 397–399.
- (4) Inoue, T.; Tomiyama, T.; Shinohara, H. *Chem. Phys. Lett.* **2003**, *382*, 226–231.
- (5) Inoue, T.; Tomiyama, T.; Sugai, T.; Okazaki, T.; Suematsu, T.; Fujii, N.; Utsumi, H.; Nojima, K.; Shinohara, H. *J. Phys. Chem. B* **2004**, *108*, 7573–7579.
- (6) Nishibori, E.; Narioka, S.; Takata, M.; Sakata, M.; Inoue, T.; Shinohara, H. *ChemPhysChem* **2006**, *7*, 345–348.
- (7) Shinohara, H.; Sato, H.; Ohkohchi, M.; Ando, Y.; Kodama, T.; Shida, T.; Kato, T.; Saito, Y. *Nature* **1992**, *357*, 52–54.
- (8) Yannoni, C. S.; Hoinkis, M.; DeVries, M. S.; Bethune, D. S.; Salem, J. R.; Crowder, M. S.; Johnson, R. D. *Science* **1992**, *256*, 1191–1193.
- (9) Kato, T.; Bandow, S.; Inakuma, M.; Shinohara, H. *J. Phys. Chem.* **1995**, *99*, 856–858.
- (10) Van Loosdrecht, P. H. M.; Johnson, R. D.; De Vries, M. S.; Kiang, C.-H.; Bethune, D. S.; Dorn, H. C.; Burbank, P.; Stevenson, S. *Phys. Rev. Lett.* **1994**, *73*, 3415–3418.
- (11) Kobayashi, K.; Nagase, S. *Chem. Phys. Lett.* **1999**, *313*, 45–51.
- (12) Takata, M.; Nishibori, M.; Sakata, M.; Inakuma, M.; Yamamoto, E.; Shinohara, H. *Phys. Rev. Lett.* **1999**, *83*, 2214–2217.
- (13) Sugai, T.; Inakuma, M.; Hudgins, R.; Dugourd, P.; Fye, J. L.; Jarrold, M. F.; Shinohara, H. *J. Am. Chem. Soc.* **2001**, *123*, 6427–6428.
- (14) Iiduka, Y.; Wakahara, T.; Nakahodo, T.; Tsuchiya, T.; Sakuraba, A.; Maeda, Y.; Akasaka, T.; Yoza, K.; Horn, E.; Kato, T.; Liu, M. T.; Mizorogi, N.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **2005**, *127*, 12500–12501.
- (15) Tan, K.; Lu, X. *J. Phys. Chem. A* **2006**, *110*, 1171–1176.
- (16) Takata, M.; Umede, B.; Nishibori, E.; Sakata, M.; Saito, Y.; Ohno, M.; Shinohara, H. *Nature* **1995**, *377*, 46–49.
- (17) Arvanitidis, J.; Papagelis, K.; Margadonna, S.; Prassides, K.; Fitch, A. N. *Nature* **2003**, *425*, 599.
- (18) Nishibori, E.; Takata, M.; Sakata, M.; Taninaka, A.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2998–2999.
- (19) Shimotani, H.; Ito, T.; Iwasa, Y.; Taninaka, A.; Shinohara, H.; Nishibori, E.; Takata, M.; Sakata, M. *J. Am. Chem. Soc.* **2004**, *126*, 364–369.
- (20) For example, Hodel, A.; Kim, S.-H.; Brünger, A. T. *Acta Crystallogr.* **1992**, *A48*, 851–858.
- (21) Tanaka, H.; Takata, M.; Nishibori, E.; Kato, K.; Iishi, T.; Sakata, M. *J. Appl. Crystallogr.* **2002**, *35*, 282–286.
- (22) <http://journals.iucr.org/services/cif/checkcif.html>.
- (23) Friese, K.; Panthoufer, M.; Guang, W.; Jansena, M. *Acta Crystallogr.* **2004**, *B60*, 520–52.