Structure of Endohedral Dimetallofullerene $Sc_2@C_{84}$

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The endohedral nature of dimetallofullerene $Sc_2@C_{84}$ is determined for the first time by a method which is a combination of the maximum entropy method (MEM) and the Rietveld refinement from synchrotron powder diffraction data. The obtained MEM charge density clearly shows the D_{2d}-symmetry cage structure, indicating the rotation of $Sc_2@C_{84}$ molecules in solid state is almost quenched even at room temperature. From the MEM charge density, the encapsulated Sc-Sc distance and the nearest Sc-C distance are 3.9(1) and 2.4(1) Å, respectively. [S0031-9007(97)03040-8]

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Endohedral metallofullerenes have gained extremely wide interest, because of their unique structural and electronic properties [1,2]. Recently, the endohedral nature of the monometallofullerene $Y@C_{82}$ has been finally confirmed by an x-ray structural study [3]. In the meantime, various metallofullerenes supposed to encapsulate two or three metal atoms within fullerene cages, such as La_2C_{80} [4], Y_2C_{82} [5], Sc_2C_{74} [6], Sc_2C_{82} [6], Sc_2C_{84} [6], and Sc_3C_{82} [7,8], have been successfully synthesized and purified. Among them the dimetallofullerenes are especially interesting, because they might exhibit novel solid state properties due to their very small band gaps [1,6]. *Ab initio* theoretical studies [9,10] and the experimental results on $Sc_2@C_{84}$ including scanning tunneling microscopy [11], transmission electron microscopy [12], and ^{13}C NMR [13] have suggested an endohedral nature. However, to date no x-ray evidence for the endohedral structure of dimetallofullerenes has been reported, which, in fact, has restricted any further study on the solid state properties of the dimetallofullerenes. Here, we report the first result on an x-ray structural study of a dimetallofullerene, $Sc_2@C_{84}$ (isomer III), by using synchrotron powder diffraction data. The result reveals that both Sc atoms are encapsulated within the carbon cage and that the $Sc_2@C_{84}$ (III) molecule has D_{2d} symmetry.

The soot containing $Sc_2@C_{84}$ and other Sc metallofullerenes was produced in direct-current (500 A) spark mode under He flow at 50 Torr and collected under totally anaerobic conditions. The $Sc_2@C_{84}$ fullerene was separated and isolated from the various hollow fullerenes (C_{60}–C_{110}) and other scandium metallofullerenes by the two-stage high-performance liquid chromatography (HPLC) method by using two complementary types of HPLC columns [6,13]. In a previous study [13], we have found that there are three structural isomers of $Sc_2@C_{84}$ (I, II, III) and the present structural analysis was performed on $Sc_2@C_{84}$ (isomer III). The purity of $Sc_2@C_{84}$ (III) relative to other fullerenes was more than 99.9%.

$Sc_2@C_{84}$ powder sample grown from toluene solvent was sealed in a silica glass capillary (0.3 mm inside diam). To collect an x-ray powder pattern with good counting statistics, the synchrotron radiation (SR) x-ray powder experiment with imaging plate (IP) as detectors was carried out at Photon Factory BL-$6A_2$ [14]. The exposure time was 1 hour. The wavelength of incident x-rays was 1.0 Å. The x-ray powder pattern of $Sc_2@C_{84}$ was obtained with a 0.02° step up to 29° in 2θ which corresponds to 2.0 Å resolution in d spacing. The peak positions of present powder pattern show very good accordance with the previous one [3] of $Y@C_{82}$ ($P2_1$) when they are normalized by considering the differences of lattice parameters. Therefore, the space group was assigned to $P2_1$, which is monoclinic [$a = 18.312(1)$ Å, $b = 11.2343(6)$ Å, $c = 11.2455(5)$ Å, and $\beta = 107.88(1)$ Å].

The experimental data were analyzed in an iterative way of combination of the Rietveld analysis and the maximum energy method (MEM). The method has been developed and successfully applied to the previous study [3] of $Y@C_{82}$. It is well know that MEM [15–17] can provide useful information purely from an observed structure factor data beyond a presumed crystal structure model [3,18,19]. The detail of this method is described in the previous paper [3].

In the first Rietveld analysis (considered as a preanalysis), C_{84} molecules were described by homogeneous spherical shells. Then, the central position of the C_{84} sphere, the radius of the sphere, the positions of Sc atoms and the central position of the solvent toluene molecule were refined as structural parameters. Both the number of formula units of $Sc_2@C_{84}$ and toluene molecules are two. As for the temperature factors, the isotropic harmonic model was used. Observed structure factors were evaluated by dividing the observed intensities at each data point according to the calculated contributions of individual reflections by a modified Rietveld-refinement program. The reliability factor (R factor) based on the Bragg intensities, R_I, was 14.6%. The number of structure factors derived in this analysis were 326, which were used for a further MEM analysis.

Following the Rietveld analysis, the MEM analysis was carried out with a computer program, MEED [20], using 58 × 48 × 44 pixels. In the MEM reconstruction, the structure factors were all treated independently as phased values. The MEM map derived in this process provides a lot of information on constructing a better structural model of $Sc_2@C_{84}$. In the MEM charge density, two remarkably high density maxima, which should correspond to the Sc atoms are found inside the carbon cage aligning nearly along the $[1\bar{1}\bar{1}]$ direction of the unit cell. The MEM map shows strong indication of the D_{2d} symmetry represented by many local maxima in the C_{84} cage charge density. The C_2 axis of the carbon cage density is slightly different from the direction connecting the two density maxima inside the carbon cage, i.e., Sc atoms.

Finally, the remodeling of the $Sc_2@C_{84}$ crystal was done as follows: (1) The initial positions of carbon atoms were placed according to an *ab initio* optimized geometry of $C_{84}(D_{2d})$ [9]; (2) The orientation of the C_2 axis was determined from the MEM map; (3) The Sc atom positions were deduced from the maximum positions of the two density maxima inside the cage; (4) The solvent toluene molecule is also remodeled as a CH_3 part and a six-membered ring composed of five CH and one C, providing the directional feature along [201].

By using the new structural model, the Rietveld analysis was redone and a better R factor ($R_I = 12.2\%$) was obtained. Such iterative steps involving the Rietveld and MEM analyses were repeated until no significant improvement of the R factor is obtained. In the series of the procedure, the C_2 axis was finally refined to the $[5\bar{3}\bar{7}]$ direction, and an anisotropic thermal vibrational model was introduced for the Sc atoms to express the elongated feature parallel to the C_2 axis in the MEM map. Eventually, the positional parameters of all carbon atoms and Sc atoms were included as refined parameters in the Rietveld analysis maintaining the D_{2d} symmetry presumed for the $Sc_2@C_{84}$ molecule as suggested by the ^{13}C-NMR study [13]. In the present study, the D_{2d} symmetry constraint is restricted to the $Sc_2@C_{84}$ molecule in the Rietveld analysis to avoid the severe correlations of parameters. Under this particular constraint of the molecule, the carbon atomic sites are reduced from 84 to 11 for one $4b$ site and ten $8d$ sites. In the final stage, the number of structural parameters refined is 54. In the MEM analysis, the D_{2d} symmetry constraint to the $Sc_2@C_{84}$ molecule was released and the lattice symmetry $P2_1$ was used as a constraint. The R_I factor finally became 7.9% (the weighted profile R factor Rwp = 5.3%). In Fig. 1(a), the best fit of the Rietveld analysis of $Sc_2@C_{84}$ is shown. The final MEM map was obtained by using the observed structure factors evaluated from the Rietveld analysis with $R_I = 7.9\%$.

The MEM can produce an electron density distribution map which is consistent with the observed data and least biased with respect to unobserved data. In the MEM analysis, any kind of deformation of electron densities is allowed as long as it satisfies the symmetry requirements. MEM enables us to visualize more detailed features included in observed data like the bonding charge between the carbon atoms, slight distortion of the molecule charge density, etc., which are difficult to express by a crystal model with an assembly of free atoms. Thus, the R_I factor is expected to decrease. To demonstrate this, the calculated intensities from the final MEM map are restored to the powder pattern by inverse process of the observed intensity estimation in our modified Rietveld analysis and are represented as a pattern fitting in Fig. 1(b). The R_I factor calculated in such a process is 2.1%, which proves the validity of the above consideration.

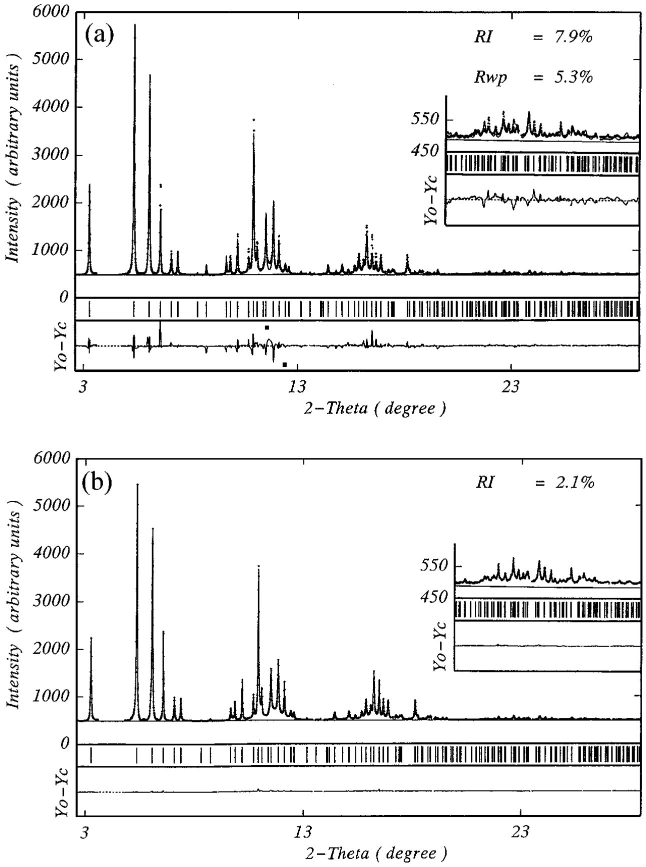

FIG. 1. (a) The Rietveld fitting result for $Sc_2@C_{84}$. (b) The fitting result for $Sc_2@C_{84}$ based on the calculated intensities from the MEM electron density. The nine weak impurity peaks are not included in the figures. A close-up of the profile in the range of 20° to 29° is inserted in each of figures.

In the obtained MEM charge density of the C_{84} cage, there are many local density maxima which are very close to the density distribution with the D_{2d} symmetry, although the MEM analysis was based on the $P2_1$ lattice symmetry. To visualize three dimensional configuration of the endohedral nature of the $Sc_2@C_{84}$, the MEM electron density distributions of $Sc_2@C_{84}$ are shown by

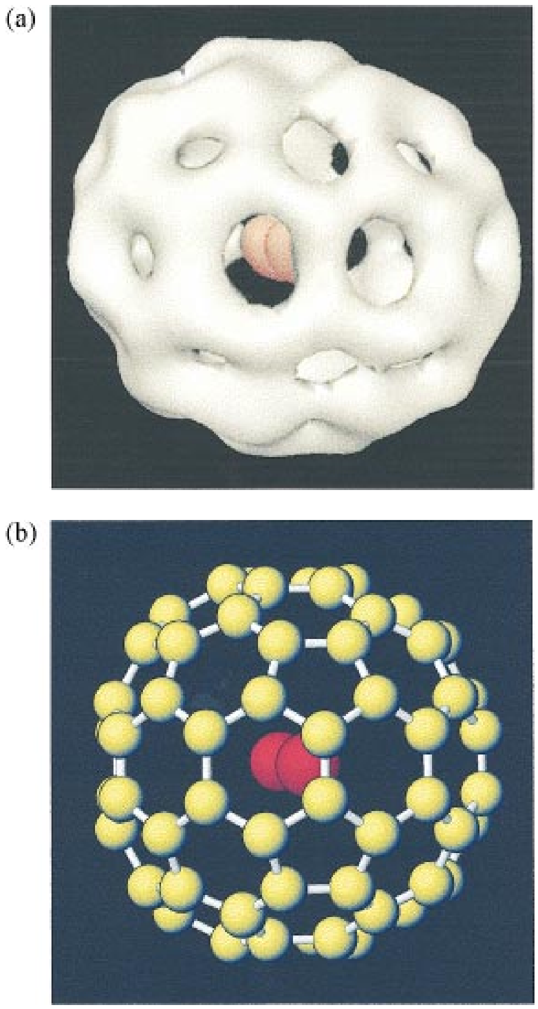

FIG. 2(color). (a) The equicontour ($1.3e$ Å^{-3}) density map of the MEM charge density for the $Sc_2@C_{84}$ molecule. The Sc atoms are colored in red. The C_2 axis connecting two Sc atoms is just off the axis perpendicular to the figure plane. (b) The schematic representation of the theoretically assumed structure model of $Sc_2@C_{84}$.

an equicontour surface of $1.3e$ Å^{-3} in Fig. 2(a). As a reference, a model structure of $Sc_2@C_{84}$ predicted by a theoretical study [9] is also shown in Fig. 2(b). The cage structure clearly exhibits six- and five-membered rings. This configuration of the rings is exactly the same as that of the $C_{84}(D_{2d})$ cage. The two density maxima can be seen through the carbon cage. The number of electrons around each maximum inside the cage is 18.8 which is very close to that of a divalent scandium ion Sc^{2+} (19.0). Evidently, each of the two density maxima at the interior of the C_{84} cage corresponds to a scandium atom, indicating that Sc_2C_{84} is endohedral. A theoretical study has predicted that the formal electronic structure of $Sc_2@C_{84}$ is well represented by $(Sc^{2+})_2@C_{84}^{4-}$, where two $4s$ electrons of each Sc atom are transferring to the C_{84} cage [9]. The positive charge of the Sc atom from the MEM charge density is +2.2 which is good accordance with the theoretical value [9].

The charge density of the present $Sc_2@C_{84}$ molecule shows a distinct feature which is in very sharp contrast to that of $Y@C_{82}$ [3]. The 5/6 ring structure of C_{84} can be seen very clearly, although the present experiment was performed at room temperature, whereas only averaged charge density of C_{82} was obtained for $Y@C_{82}$. This suggests that rotations of the C_{84} cage are virtually quenched even at room temperature in a $Sc_2@C_{84}$ solid, while the $Y@C_{82}$ molecule is still in a hindered rotation.

In Fig. 3(a), the section of the MEM charge density including the encaged Sc atoms is shown for the (010) plane. Two density maxima can be clearly seen inside the section of the carbon cage and are located in a symmetric position with respect to the center of the cage. The Sc-Sc distance in C_{84} derived from the MEM charge density is 3.9(1) Å which is a bit smaller than that of a theoretical value of 4.029 Å [9]. The nearest Sc-C distance is 2.4(2) Å (2.358 Å theoretical value [9]) [Fig. 3(b)]. One of the most intriguing observations in

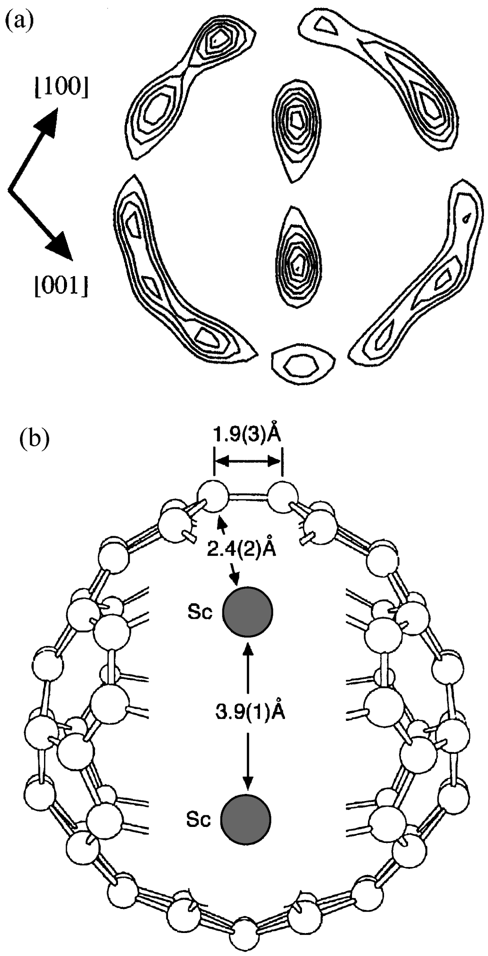

FIG. 3. (a) The MEM electron density distribution of $Sc_2@C_{84}$ for (010) section. The contour lines are drawn with $0.3e$ Å^{-3} intervals from $1.0e$ Å^{-3}. The endohedral nature of $Sc_2@C_{84}$ is clearly shown in this figure. (b) The schematic representation of the Sc-Sc, Sc-C, and double bonded C-C distances obtained from the MEM charge density.

Fig. 3(a) is that the charge density of the Sc atoms shows a salient teardrop feature as if the two Sc atoms (ions) are in a stretching vibration within the C_{84} cage. The C-C distance of the double bond adjacent to the Sc atom is 1.9(3) Å which is considerably longer than a theoretical value of 1.43 Å [9], indicating some significant distortion of the polar regions of the C_{84} cage. Such anomalous large C-C distance [1.90(15) Å] has been also reported for polymeric fullerene, RbC_{60} [21]. Although a further study will be required for such an unusual distance with the higher resolution data, the present result suggests a strong indication of the elongation of C-C distance. Such an indication is also recognized even in the Rietveld analysis. This might be closely related to the thermal motion of the Sc atoms in the C_{84} cage, and to the existence of some localized interaction caused by the charge transfer between the encapsulated Sc atoms and the C_{84} cage.

A rotational vibration of the Sc atoms along the C-C double bonds, which is predicted from the distribution of the potential minima in the electrostatic potential of C_{84}^{4-} by a recent *ab intio* calculation [22], is not obvious in the present MEM charge density. The theoretical calculation was done at 0 K. Therefore, low temperature experiments should be required to confirm the existence of the rotational vibration mode of the Sc atoms. The variety of thermal behavior of metal atoms inside the carbon cage may lead to the discovery of novel physical property of the material. In conclusion, the salient thermal behavior of encapsulated Sc atoms as well as endohedral nature are revealed by the x-ray powder structure analysis using the maximum entropy method.

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