

## Structural studies of endohedral metallofullerenes by synchrotron radiation powder diffraction

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The endohedral natures of the metallofullerenes Y@C<sub>82</sub> and Sc<sub>2</sub>@C<sub>84</sub> are described based on synchrotron radiation powder diffraction experiments. For structural analysis, a combination of the maximum-entropy method (MEM) and Rietveld refinement was employed to analyse the complicated powder pattern. The obtained MEM charge densities show a clear distinction of the endohedral natures of the mono- and dimetallofullerenes.

**Keywords:** maximum-entropy method; powder diffraction; fullerenes; Rietveld method; endohedral metallofullerene.

### 1. Introduction

Endohedral metallofullerenes have attracted extremely wide interest because of their unique structural and electronic properties (Chai *et al.*, 1991; Bethune *et al.*, 1993). In the past decade, various metallofullerenes supposed to encapsulate one, two or three metal atoms within fullerene cages, such as LaC<sub>82</sub> (Chai *et al.*, 1991; Johnson *et al.*, 1992), YC<sub>82</sub> (Shinohara *et al.*, 1992), ScC<sub>82</sub> (Shinohara *et al.*, 1993), La<sub>2</sub>C<sub>80</sub> (Kikuchi *et al.*, 1993), Y<sub>2</sub>C<sub>82</sub> (Shinohara *et al.*, 1992), Sc<sub>2</sub>C<sub>74</sub>, Sc<sub>2</sub>C<sub>82</sub>, Sc<sub>2</sub>C<sub>84</sub> (Shinohara *et al.*, 1993) and Sc<sub>3</sub>C<sub>82</sub> (Shinohara *et al.*, 1992; Yannoni *et al.*, 1992), have been successfully synthesized and purified. Recently, the endohedral natures of the mono- and dimetallofullerenes, Y@C<sub>82</sub> and Sc<sub>2</sub>@C<sub>84</sub>, have been finally confirmed from synchrotron radiation powder data by using the maximum-entropy method (MEM) (Takata *et al.*, 1995, 1997). Until then, no direct X-ray evidence for the endohedral structures had been reported, which, in fact, had restricted any further study on the solid-state properties of the metallofullerenes.

An X-ray structural study of an endohedral metallofullerene can be very difficult, because only very small amounts of powder samples are generally available and the observable X-ray powder data are limited to the low-angle region. Additional difficulties come from the fact that intrinsic orientational disorder is rather common. Hence, it may be extremely difficult to construct an adequate structural model. The MEM can overcome all these difficulties when it is applied to synchrotron powder data. The success of the structural studies of the metallofullerenes Y@C<sub>82</sub> and Sc<sub>2</sub>@C<sub>84</sub> is possible owing partly to the very high angular resolution and good counting statistics of powder data by using synchrotron radiation and partly to the capability of model-free reconstruction by the MEM.

In the present paper, the work is reviewed to demonstrate that the synchrotron radiation powder experiment is a powerful

method for the MEM structural analysis of endohedral metallofullerenes.

### 2. Experimental

The soot containing Y@C<sub>82</sub> or Sc<sub>2</sub>@C<sub>84</sub> and other metallofullerenes was produced in direct-current (500 A) spark mode under He flow at  $6.7 \times 10^3$  Pa and collected under totally anaerobic conditions. The Y@C<sub>82</sub> or Sc<sub>2</sub>@C<sub>84</sub> fullerene was separated and isolated from the various hollow fullerenes (C<sub>60</sub>–C<sub>110</sub>) and other yttrium or scandium metallofullerenes by the two-stage high-performance liquid chromatography (HPLC) method by using two complementary types of HPLC columns (Shinohara *et al.*, 1993). In previous studies (Shinohara *et al.*, 1994; Yamamoto *et al.*, 1996), we have found two and three structural isomers of Y@C<sub>82</sub> (I, II) and Sc<sub>2</sub>@C<sub>84</sub> (I, II, III), respectively. The MEM structural studies were performed on Y@C<sub>82</sub> (I) and Sc<sub>2</sub>@C<sub>84</sub> (III). The purity of both samples relative to other fullerenes was more than 99.9% in each case.

The powder sample grown from toluene solvent was sealed in a silica glass capillary (0.3 mm diameter.). To collect an X-ray powder pattern with good counting statistics, the synchrotron radiation powder experiment with imaging plates (IP) as detectors was carried out at the Photon Factory BL-6A2 (Takata *et al.*, 1992). The experimental arrangement is shown elsewhere (Takata *et al.*, 1992). The exposure time was 1 h. The wavelength of the incident X-rays was 1.0 Å. The X-ray powder pattern of the Sc<sub>2</sub>@C<sub>84</sub> crystal was obtained with a 0.02° step up to 29° in 2θ, which corresponds to 2.0 Å resolution in *d* spacing. For Y@C<sub>82</sub>, the X-ray powder reflection intensities from 20° to a higher angular region were much weaker than those of Sc<sub>2</sub>@C<sub>84</sub>. Eventually, the data up to 20° in 2θ, which corresponds to *d* = 2.9 Å resolution, were available, which yielded reliable intensities for Y@C<sub>82</sub>.

### 3. Data analysis

The experimental data were analysed in an iterative way by a combination of the Rietveld analysis and the maximum-entropy method (Takata *et al.*, 1995, 1997). It is well known that the MEM (Sakata & Sato, 1990; Collins, 1982; Bricogne, 1988) can provide useful information purely from observed structure-factor data, without a presumed crystal structure model (Takata *et al.*, 1995, 1996; Papoular & Cox, 1996). In MEM analysis, any kinds of deformation of electron densities are allowed as long as they satisfy the symmetry requirements.

The details of the analysis are described in previous papers (Takata *et al.*, 1995, 1997). In this paper, data analysis is mentioned briefly. The space group was assigned as *P*2<sub>1</sub>, which is monoclinic, for both Y@C<sub>82</sub> [*a* = 18.401 (2), *b* = 11.281 (1), *c* = 11.265 (1) Å, β = 108.07 (1)°] and Sc<sub>2</sub>@C<sub>84</sub> [*a* = 18.312 (1), *b* = 11.2343 (6), *c* = 11.2455 (5) Å and β = 107.88 (1)°]. In the preliminary Rietveld analysis where fullerene cages are assumed as homogeneous spherical shells, 105 and 326 observed structure factors were evaluated by dividing the observed intensities at a data point according to the calculated contributions of the individual reflections. At this stage, the reliability factors (*R* factors) based on the Bragg intensities, *R*<sub>i</sub>, were 14.4 and 14.6% for Y@C<sub>82</sub> and Sc<sub>2</sub>@C<sub>84</sub>, respectively.

Following Rietveld analysis, MEM analysis was carried out with the computer program *MEED* (Kumazawa *et al.*, 1993). In the MEM reconstruction, the structure factors were all treated inde-

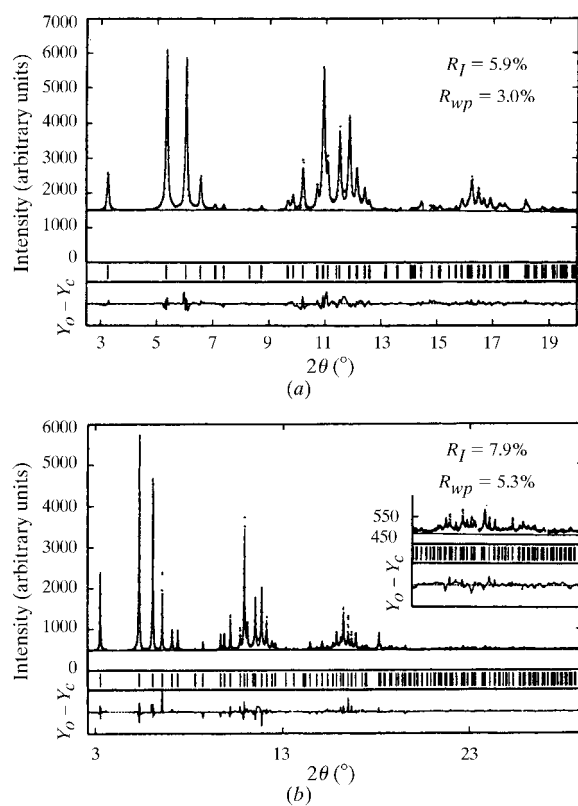
pendently as phased values. The MEM map derived in this process allowed a better structural model to be constructed for  $Y@C_{82}$  and  $Sc_2@C_{84}$ . For example, in the case of  $Sc_2@C_{84}$ , the MEM map shows a strong indication of the  $D_{2d}$  symmetry represented by many local maxima in the  $C_{84}$  cage charge density. After remodelling, the  $R_I$  factors for  $Y@C_{82}$  and  $Sc_2@C_{84}$  finally became 5.9 and 7.9% and the weighted powder profile  $R$  factors,  $R_{wp}$ , were 3.0 and 5.3%. In Fig. 1, the best fits of the Rietveld analysis for  $Y@C_{82}$  and  $Sc_2@C_{84}$  are shown.

The MEM enables us to visualize detailed features included in observed data, like the bonding charge between the C atoms, slight distortion of the molecule charge density and so on, 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 calculated to fit the powder pattern by an inverse process of the observed intensity estimation in our modified Rietveld analysis, and are shown in Fig. 2. The  $R_I$  factors calculated in such a process are 1.4% ( $Y@C_{82}$ ) and 2.1% ( $Sc_2@C_{84}$ ), which prove the validity of the above approach.

#### 4. The MEM charge densities

##### 4.1. $Y@C_{82}$

To visualize the endohedral nature of  $Y@C_{82}$ , the MEM electron density distributions of  $Y@C_{82}$  are shown for (010) in Fig. 3(a). There exists remarkably high density just inside the  $C_{82}$  cage. The number of electrons around the maximum is about 38, which is very close to the atomic number of a Y atom. Evidently, the density maximum in the interior of the  $C_{82}$  cage is the Y atom.



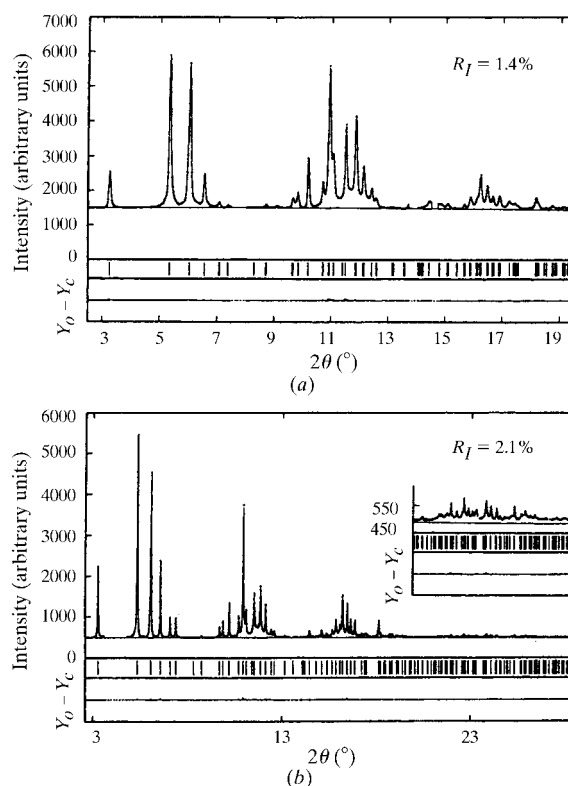
**Figure 1**  
The Rietveld fitting result for (a)  $Y@C_{82}$  and (b)  $Sc_2@C_{84}$ . A close up of the profile in the higher angular range is inserted in (b).

The cage structure of  $Y@C_{82}$  differs from that of the hollow  $C_{82}$  fullerene. There are many local maxima along the cage in  $Y@C_{82}$ , while the electron density of the  $C_{82}$  cage is relatively uniform (Takata *et al.*, 1995). This suggests that in  $Y@C_{82}$  the rotation of the  $C_{82}$  cage is very limited around a certain axis, while that in  $C_{82}$  is almost free. The MEM electron density map further reveals that the Y atom does not reside in the center of the  $C_{82}$  cage but is very close to the carbon cage wall, as suggested theoretically (Laasonen *et al.*, 1992; Nagase & Kobayashi, 1993; Andreoni & Curioni, 1996). Previous electron spin resonance (ESR) (Weaver *et al.*, 1992; Shinohara *et al.*, 1992) and theoretical studies (Laasonen *et al.*, 1992; Nagase & Kobayashi, 1993) suggest the presence of a strong charge-transfer interaction between the  $Y^{3+}$  ion and the  $C_{82}^{3-}$  cage, which may cause the aspherical electron density distribution of Y atoms. The Y–C distance calculated from the MEM map is 2.47 (3) Å, which is almost within the range of the theoretical prediction of 2.55–2.65 Å (Nagase & Kobayashi, 1993).

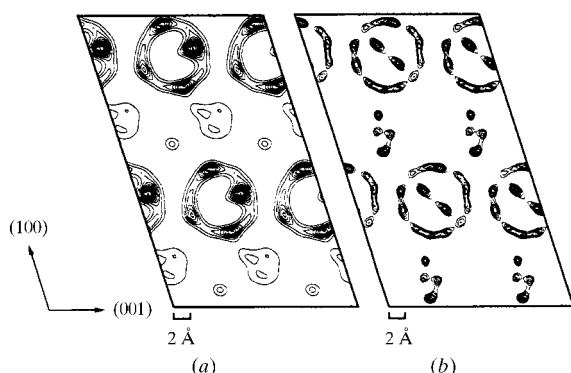
##### 4.2. $Sc_2@C_{84}$

In Fig. 3(b), the section of the MEM charge density including the engaged Sc atoms is shown for the (010) plane. In the MEM charge density of the  $C_{84}$  cage, there are many local density maxima with a density distribution that is very close to  $D_{2d}$  symmetry, although the MEM analysis was based on the  $P2_1$  lattice symmetry. From the configuration of the local maxima, it is concluded that the symmetry of the endohedral  $Sc_2@C_{84}$  molecule has  $D_{2d}$  symmetry, as suggested by the  $^{13}C$  NMR study (Yamamoto *et al.*, 1996).

Two density maxima can clearly be seen inside the section of the carbon cage and are located in symmetric positions with respect to



**Figure 2**  
The profile fitting based on the calculated intensities from the MEM electron density for (a)  $Y@C_{82}$  and (b)  $Sc_2@C_{84}$ .



**Figure 3**

The MEM electron density distribution of (a)  $Y@C_{82}$  and (b)  $Sc_2@C_{84}$  for the (010) section. The contour lines are drawn for 4 unit cells with  $0.5 \text{ e } \text{Å}^{-3}$  ( $Y@C_{82}$ ) and  $0.3 \text{ e } \text{Å}^{-3}$  ( $Sc_2@C_{84}$ ) intervals.

the center of the 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 in the interior of the  $C_{84}$  cage corresponds to an Sc 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 transfer to the  $C_{84}$  cage (Nagase & Kobayashi, 1994). The positive charge of the Sc atom from the MEM charge density is +2.2, which is in good agreement with the theoretical value (Nagase & Kobayashi, 1994).

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 the theoretical value of 4.029 Å (Nagase *et al.*, 1996). The nearest Sc–C distance is 2.4 (2) Å, while the theoretical value is 2.358 Å (Nagase *et al.*, 1996). One of the most intriguing observations in Fig. 3(b) is that the charge density of the Sc atoms shows a salient tear-drop 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 the theoretical value of 1.434 (9) Å, indicating some significant distortion of the polar regions of the  $C_{84}$  cage. Such an anomalously large C=C distance [1.90 (15) Å] has been reported for the polymeric fullerene  $RbC_{60}$  (Stephens *et al.*, 1994). The present result suggests a strong indication of the elongation of the C=C distance, although a further study is required to confirm such an unusual distance by using higher-resolution data. The elongation of the C=C distance is 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.

## 5. Conclusions

The variety in endohedral natures of mono- and dimetallofullerenes, *i.e.* the  $Sc_2@C_{84}$  molecule has a centered nature in terms of molecular symmetry whereas  $Y@C_{82}$  has a strong off-centered nature, was revealed for the first time by the synchrotron radiation powder structure analyses using the maximum-entropy method. For structure analysis, it was not possible to make a structural model as an arrangement of atoms without the MEM map. The very high angular resolution and good counting statistics of synchrotron radiation powder data brought the detailed and firm

features of the MEM maps into relief. From the methodological viewpoint, the combined MEM and Rietveld analysis will become a key method, particularly for structural studies of metallofullerenes, higher fullerenes and other fullerene-related compounds, for which the construction of the appropriate structural model is not always easy.

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