Charge Density Level Structures of Metallofullerenes by the MEM/Rietveld Method.

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Many varieties of fullerene compounds have come up for the last decades of the 20th century and, more and more are coming up. Among them, endohedral metallofullerenes, which encage metal atom in a carbon cage, are novel forms of fullerene-related materials. Since the discovery of C_{60}, the extensive experimental and theoretical researches for metallofullerene have been carried out to explore their unusual structural and electronic properties. However, up to 1995, the endohedral structure had not been determined experimentally. As for the endohedral nature, there had been a long debate whether the metal atoms are really inside the cage or not. Although several theoretical and experimental studies had suggested that the metal atoms are inside fullerene cage, there had been no conclusive and direct evidences for the endohedral nature of metallofullerene, that is, where in the cage the metal atoms exist. In the mean time, we have succeeded in determination of endohedral structure of the metallofullerene, $Y@C_{82}$, by the x-ray structure analysis in 1995. For the structure analysis, we used the new method, the Maximum Entropy Method (MEM)[1)]. The MEM can yield a high-resolution density distribution from a limited number of diffraction data. The obtained density distribution gives detailed structure information without using structural model. The ability of the MEM in terms of a model-free reconstruction of the charge densities from measured X-ray diffraction data can be interpreted as "imaging of diffraction data"[2)]. The method is further developed by combining the MEM with the Rietveld method to create a new sophisticated method of structure refinement in charge density level, that is, the MEM/Rietveld method[2,3)]. The MEM/Rietveld analysis is an iterative way in combination with the MEM and Rietveld analyses. When the MEM charge density at a certain iteration step can provide a better structural model for the Rietveld of the next iteration, the iteration process continues. In this method, the final MEM electron density distribution derived is compatible with the structural model used in the Rietveld refinement. The method has been successfully applied to the structure studies of endohedral metallofullerenes [3,4)]. The difficulties of X-ray structure analysis of fullerene compounds come from the fact that the intrinsic orientational disorder is rather common like other molecular compounds. In such a case, it may be extremely difficult to construct an adequate structural model. The MEM/Rietveld method succeeded in overcoming such difficulties by "imaging of diffraction data", when it is applied to Synchrotron Radiation (SR) powder data. In the talk, the experimentally determined charge densities of $Y@C_{82}$, $Sc@C_{82}$, $La@C_{82}$, $Sc_2@C_{84}$, $La_2@C_{80}$, $Sc_2@C_{66}$, $Sc_3@C_{82}$ and $Sc_2C_2@C_{84}$ will be presented to illustrate an importance of charge density level structure determination of metallofullerenes to discuss the stability of endohedral structure and to presume the electronic properties. In addition, the ability of the MEM/Rietveld method utilizing SR powder diffraction data for the structural study of metallofullerenes in electron density level will be also presented.

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