

Visualization of intermolecular interaction by electron density mapping using synchrotron radiation

Hiroyuki Ohsumi, Fumiko Yoshida, Nobuhiro Mizuno, Kennichi Kato, Masaki Takata
RIKEN Harima Institute, SPring-8 Center, Japan

X-ray diffraction data allows us to determine not only an atomic arrangement but also charge density distribution in materials. Low divergent and highly brilliant synchrotron radiation of SPring-8 provides an accurate diffraction data, which has considerably improved the precision of structural materials science. Our developed MEM/Rietveld method[1], which is an analytical method of charge density distribution, has been successfully applied to the structure analysis of organic conductors[2], ferroelectric materials[3], manganites[4] and so on. The obtained MEM charge density enabled us to observe valence state, orbital occupation and bonding nature of atoms and molecules. Recently, we have succeeded in developing electrostatic potential and electric field imaging based on MEM charge density analysis[5, 6]. Our new method is also conducive to visualizing the association between atomic arrangement and materials properties. In the presentation, I will give a talk about following two topics.

1. Direct observation of charge transfer in α -(BEDT-TTF)₂I₃

F. Yoshida, K. Kato (Structural Materials Science Lab.); R. Koto (Condensed Molecular Material Lab.)

A molecular conductor α -(BEDT-TTF)₂I₃ has peculiar physical property, for example, the metal-insulator transition at 135 K, photo-induced transition, and superconductivity under uniaxial pressure. However, the origin of the metal-insulator transition has not yet been revealed. Recent research proposed the charge ordering may be occurred in the insulator phase[7]. To ascertain this model, we conducted the charge density level structure analysis on α -(BEDT-TTF)₂I₃ using MEM/Rietveld method.

We have obtained the reliable powder-diffraction data at BL02B2, Spring-8. Results of the MEM/Rietveld analyses yielded the electrostatic potential and the electric field images of α -(BEDT-TTF)₂I. There were apparent differences in the electrostatic potential at I₃ molecular position between high temperature conducting phase and low temperature insulating phase. Temperature variation of the electric field was also seen around the boundary between conductor layer (ET molecular region) and non-conductor layer (I₃ molecular region). These suggested that the charge transfer from I₃ molecules to ET molecules occurs at the metal-insulator transition of 135 K. This finding revealed the charge doping to the conductor layer is realized in this material.

2. Charge density distribution study on high-molecular-weight organic molecules

N. Mizuno(Structural Materials Science Lab.); Z. Hou(Organometallic Chemistry Lab.)

The application of MEM charge density mapping to protein molecule is our next target. We are now striving to realize a research on charge transfer and related function in protein molecules. Since the MEM charge density mapping requires accurate diffraction data, the reliability of single crystal diffraction data should be validated with close attention. To analyze current condition, we have performed precise structure analyses of two high-molecular-weight organic molecules, the rare earth metal hydride cluster (MW:1500) and the supramolecular porphyrin box (MW:1700).

We have succeeded in visualizing the hydride ligands in the metal hydride cluster. The high quality data, in which standard deviation of integral intensity is less than several %, made it possible to apply the MEM charge density mapping to high-molecular-weight organic molecules. On the other hand, we have attained a remarkable improvement of the structural model of the porphyrin box by means of the MEM charge density mapping. It is noteworthy that the structural model of solvent area has been successfully determined. These accomplishment motivate further studies on relatively large molecules such as Rubredoxin (MW:5700) and Cytochrome c3 (MW:11500).

- [1] M. Takata, *et al.*, *Z. Kristallogr.* **216**, 71 (2001).
- [2] S. Aoyagi, *et al.*, *Angew. Chem. Int. Ed.* **43**, 3670 (2004).
- [3] Y. Kuroiwa, *et al.*, *Phys. Rev. Lett.* **87**, 217601 (2001).
- [4] K. Kato, *et al.*, *J. Phys. Soc. Jpn.* **74**, 2137 (2005).
- [5] H. Tanaka, *et al.*, *Phys. Rev.* **B74** (2006) 172105.
- [6] K. Kato, *et al.*, *Phys. Rev.* **B 77**, 081101 (2008).
- [7] H. Seo, *J. Phys. Soc. Jpn.* **69**, 805 (2000).