

放射光による分子間相互作用の可視化

Visualization of Inter-molecular Electrostatic interaction in crystal by Synchrotron Radiation Diffraction

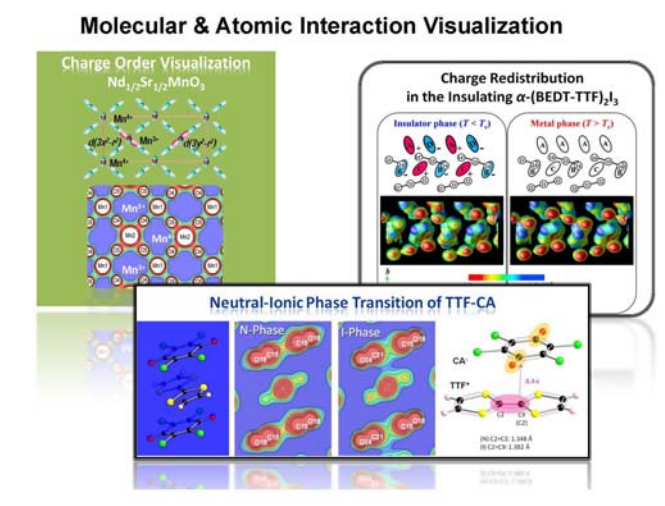
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Our research goal is to develop innovations in Structural Materials Science using Synchrotron Radiation (SR) X-ray diffraction to allow visualization of interactions between atoms and molecules in advanced materials exhibiting novel functional properties. The achievement of this goal will evolve the Structural Materials Science in Molecular Ensemble Development Research from precise structure determination into a direct investigation of structure-property correlations in terms of electrostatic potential (EP). The scientific targets include extensive topical research areas such as superconductivity, metal-insulator/neutral-ionic transition, photo-induced phenomena, thermoelectric materials, and phase change materials. To accomplish this goal, methodologies for both X-ray diffraction experiment and data analysis techniques have been developed. We have constructed a precise SR powder diffractometer at BL44B2, a single crystal diffractometer at BL02B1, and an X-ray pinpoint structure measurement system at BL40XU. A method for EP imaging method using diffraction data has also been developed using our Maximum Entropy Method (MEM) analysis program, ENIGMA. Following are recent examples of topics explored:

1. Visualization of the charge transfers through the M-I transition

To investigate a sample's structural basis at an electron density level of a metal-insulator (M-I) transition of α -(BEDT-TTF)₂I₃ at 135 K, the charge density mapping and EP imaging were performed using Synchrotron Radiation X-ray powder diffraction. The precise charge density that was obtained clearly revealed a significant charge transfer between the I₃ and ET molecules through the M-I transition. In the EP, we found the localized change around the I₃ molecule representing the existence of a charge order of the neighboring ET molecule at a low temperature. The EP on the cross-section of the I₃ molecule successfully allowed visualization of the characteristic conducting layer configuration of ET molecular arrays detached by the insulator I₃ layers. In addition, directional electric field analysis allowed visualization of a potential shield breaking between I₃ insulating and ET conducting channels associated with the local



change of electrostatic interaction. Our present findings in terms of the electrostatic interaction between I_3 and ET molecules will lead to a fuller understanding of the M-I transition of α -(BEDT-TTF) $_2I_3$.

2. Visualization of localized electrostatic interaction in the TTF-CA ionic phase

One of the typical Neutral-Ionic Transition (NIT) materials, tetrathiafulvalene-p-chloranil (TTF-CA), was investigated with EP imaging using the MEM program, based on data from synchrotron radiation powder diffraction data. The EP obtained revealed the structural features of charge transfer from the TTF molecule to the CA molecule through the thermally induced NIT ($T_c = 81$ K). From the charge density change, the degree of charge transfer (CT) was evaluated as 0.30(2) e through the NIT. In the EP, it was found that a significant potential valley appeared at the inter-molecular region connecting between the C2=C9 bonding part in TTF and the C15(21)-O18(24) part in CA. The present findings indicate the existence of a distinct local molecular interaction between TTF and CA in the I phase.

3. The photo-induced commensurate modulated structure in a site-selective spin crossover complex *trans*-[Fe(abpt) $_2$ (NCS) $_2$]

The photo-induced superstructure of polymorph C of *trans*-[Fe(abpt) $_2$ (NCS) $_2$] (abpt = 4-amino-3,5-bis(pyridin-2-yl)-1,2,4-triazole) is discovered as a commensurate modulated structure by single-crystal X-ray diffraction under irradiation. The crystal structure at 25 K before the photo-irradiation is composed of two crystallographically independent iron molecules, one of which exhibits a high spin (HS) state and the other at low spin (LS) state. Under green laser light ($\lambda = 532$ nm) irradiation, the LS molecule (Fe1) is found to be excited to a metastable HS state, giving rise to a commensurate tripled superstructure along the c axis. In addition, it is confirmed that this modulation persists up to the HS \rightarrow LS relaxation temperature beyond 52 K. Our structural findings suggest a high correlation between that the structural modulation and the site-selective LS \rightarrow HS excitation. In the talk, application to the research of hydrogen absorption in Metal Organic Framework(MOF) and the recent development of the Raman spectroscopy measurement system synchronized with the diffraction data collection will be also reported.

