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Electrostatic potential and electric field imaging by MEM powder diffraction dada analysis

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Accurate powder diffraction experiment by synchrotron radiation has made progress on the charge density study by the Maximum Entropy Method (MEM). So far, our developed analytical method which is the combination of the MEM and Rietveld refinement, so called MEM/Rietveld method, has been successfully applied to the structure analysis of novel nano materials, ferroelectric materials, manganites and superconductors by synchrotron radiation powder data[1,2]. The obtained MEM charge density enabled us structure refinement as well as observation of interplays between atoms and molecules, such as, bonding nature, charge transfer and etc. The electrostatic potential based on the experimental charge density should be more informative to see the interaction between atoms and molecules. Recently, we have succeeded in developing electrostatic potential and electric field imaging based on MEM charge density analysis[3]. The visualized electrostatic potential of the typical ferroelectric material, tetragonal $PbTiO_3$ has uncovered the feature of electronic polarization in Ti-O and Pb charge densities. In addition, the result shows very good agreement with that obtained from the ab initio calculation[4]. Very recently, we have also succeeded in visualization of charge order associated with orbital order in manganites[5] . Our new method is promising and extending potential of powder diffraction structure refinement. In the talk, the detail of the method and application to the study of the metal-insulator transition of α-(BEDT-TTF)$_2$I$_3$ will be presented.

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Keywords: synchrotron powder diffraction, maximum-entropy method, materials properties

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MAD techniques applied to powder data: The method of the joint probability distribution functions

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The great improvement of the methods for ab initio structure solution from powder diffraction data (PDD) is due to the use of synchrotron radiation: it provides high quality diffraction data, sometimes simulating single crystal data. It also allows a fine wavelength tuning, so giving new emphasis to the Multiple wavelength Anomalous Dispersion (MAD) methods. Phase determination via MAD techniques is usually a three step procedure:
1) estimation of structure factor moduli of the anomalous scatterer substructure [1]
2) location of the anomalous scatterers [2] [3]
3) protein phase estimation [4]
Although with PDD the experimental measure of the Bijvoet differences is lost, MAD techniques can still be usefully applied [5]. The first step of our approach deals with the evaluation of the structure factor moduli $|Foa|$, given the prior knowledge of the moduli measured at two different wavelengths. Direct Methods or Patterson deconvolution techniques are used to locate the anomalous scatterer substructure. The phasing of the whole structure is performed by applying the method of the joint probability distribution functions given the substructure. The procedure has been implemented within the package EXPO [6]. Applications to synchrotron data are discussed.

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Keywords: *ab-initio* structure determination, MAD phasing, powder diffraction data

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Towards routine refinement of hydrogenous materials by neutron powder diffraction

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We have embarked on a substantial programme of research tackling the fact that the accurate determination of the position of hydrogen in a material is usually regarded as a challenging issue unless large single crystals are available for neutron diffraction. We are tackling this problem using the capabilities offered by modern high flux neutron powder diffractometers, such as D20 at the ILL, which average incoherent scattering from hydrogen and allow, through sheer counting statistics, its contribution to the Bragg scattering to be adequately analysed, allowing for structure determination. Results will be presented from successful initial proof-of-concept experiments covering both low hydrogen content inorganic materials, for example in the critical area of water location (Henry et al, Chem Comm, 2008) and also high hydrogen content molecular complex materials in the topical area of temperature-dependent proton migration and transfer (Pulham, Wilson et al, in preparation). The move forward in our studies of hydrogenous compounds using neutron diffraction is demonstrated by this applicability to organic molecular systems; specifically hydrogen-bonded molecular complexes for which it is challenging to grow even X-ray sized single crystals but for which neutron data are vital. In reinforcing the importance of this area, we note not only the fact that powder studies of hydrogenous materials open up new regimes for multi-parameter diffraction studies of structural evolution, but also the study of hydrides rather than deuterides can often mitigate synthesis issues (a major issue for chemically complex materials). Breakthroughs in tackling these issues with neutron powder diffraction on modern instrumentation can have a profound effect on the study of such materials.

Keywords: neutron powder diffraction, hydrogen, molecular complexes

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Powder diffraction and DFT optimization in structural characterization of macrocyclic compounds

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A series of novel 1,2,4,5,7,8-hexaoxonanes [1], crown-containing compounds Cu(L1)$_2$ and LiNCS.HL1 (HL1 = 4'-[2-(tosylamino) benzylideneamino]-2,3-b15c5; b15c5 = benzo-15-crown-5) [2], and NaNCS.L2, $[M(L2)_2]^{2+}.2PF_6^-$, $[Co(L2)_2]^{2+}.2NCS^-$, $[M(NaNCS.L2)_2]^{2+}.2PF_6^-$, L3 [3], $[M(L3)_2]^{2+}.2PF_6^-$ (L2 = terpyridine-O-CH$_2$-b15c5, L3 = terpyridine-O-b15c5, M = Co, Ni, Cu, Zn) were structurally characterized by powder diffraction methods. For most of these compounds, it was rather difficult to obtain not only single-crystals but even crystalline powders suitable for structure determination, that required either repeat crystallizations or repeat full synthesis. Powder patterns for two compounds - Cu(L1)$_2$ and LiNCS.HL1, respectively - were obtained using synchrotron radiation, and the rest powder patterns were obtained using the laboratory diffractometers. The fourteen new crystal structures of the aforementioned compounds were determined from powder diffraction data, which provide a reliable validation of the molecular structure for each compound. Due to the large molecular dimensions, the structure determination process did not take too much time, in contrast to the subsequent Rietveld refinement because of a large number of variables and unknown (in advance) conformations of flexible macrocycles. To overcome these obstacles in each case, a number of molecular models with various conformations of macrocycles was subjected to DFT optimization. The optimized molecular geometries were used as templates in the bond-restrained Rietveld refinement allowing a choice of the correct conformations of macrocycles.

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Keywords: structure from powder diffraction, rietveld refinement, DFT

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SDPD: A key component in populating the carbamazepine crystal structure landscape

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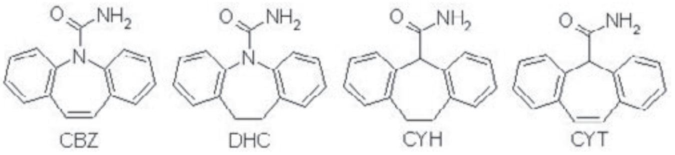
The anticonvulsant agent carbamazepine (CBZ) has received a lot of attention from both those interested in polymorphism and those interested in crystal structure prediction (CSP). Our own interest in CBZ spans both these disciplines; in particular, we are intrigued by the fact that predicted structures for CBZ point to the existence of a favourable C(4) catemer that has yet to be observed experimentally. Given that the C(4) catemer is observed amongst analogues of CBZ, the focus of our work has broadened to include these closely-related compounds, specifically dihydrocarbamazepine (DHC), cyheptamide (CYH) and cytenamide (CYT). This presentation will illustrate the relationships between these four compounds and, in particular, will highlight the role that SDPD has played in obtaining the crystal structures of various polymorphs. Many of the crystal structures have presented considerable challenges to SDPD (Z'=4, V ~ 2400A^3, 72 non-H atoms, 28 DOF) both in the solution and refinement aspects. Evidence for the existence of CBZ in a C(4) catemeric configuration in a CBZ:DHC 1:1 solid solution will also be presented.



Keywords: *ab-initio* structure determination, powder diffraction, pharmaceutical compounds

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Martensitic transformations in the Ni-based ferromagnetic shape memory alloys

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Since Ullakko et al. reported a large magnetic field-induced strain (MFIS) in the Ni$_2$MnGa single-crystalline alloy in 1996, ferromagnetic shape memory alloys (FSMAs) have received much attention as high performance actuator materials. The Ni$_2$MnGa ferromagnetic Heusler-type alloy showing a martensitic transformation has first been found by Webster and Ziebeck in 1984, and several Ni-based FSMAs besides the Ni$_2$MnGa have recently been reported by the present authors in Ni-Mn-Al, Ni-Co-Al, Ni-Co-Ga, Ni-Fe-Ga, Ni-Mn-In and Ni-Mn-Sn based alloy systems. In the present talk, basic features on the martensitic transformations and the magnetic properties in those new FSMAs except the Ni$_2$MnGa alloy will be reviewed.

Keywords: ferromagnetic alloys, martensitic transformation, shape-memory alloys