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The reflection overlap problem is the primary limitation in structure determination from powder diffraction data, and over the last decade, a procedure that addresses this problem experimentally by exploiting preferred orientation has been developed [1]. The intensity variation in the X-ray diffraction pattern obtained from a textured sample as a function of sample orientation (tilt  $\chi$  and rotation  $\varphi$ ) can be applied to resolve the relative intensities of reflections that overlap in a conventional powder diffraction pattern. The availability of a new version of the 1-dimensional Si-microstrip detector (Mythen II) on the Materials Science Beamline at SLS [2] and new features in the computer program *Maud* [3] have allowed both the experimental and the data analysis procedures to be redesigned. By applying these modifications, it was expected that a significant improvement in the quality of the extracted reflection intensities could be achieved.

To test this modified method, two samples of a zirconium phosphate framework material (ZrPOF-pyr) with a known crystal structure [4] were measured: (1) a textured sample using the revised experimental setup and data collection strategy, and (2) an untextured sample in a 0.5mm capillary. Both datasets were collected at the SLS using the Mythen II detector. For the analysis, reflections up to a minimum  $d$ -spacing of 1.0 Å were considered, and a reflection separation factor of 0.5\*FWHM was used to define the overlap groups.

Comparison of the structure factors extracted from conventionally measured powder diffraction data with those derived from a textured sample indeed shows the latter to be significantly better. The agreement between the amplitudes obtained with a LeBail extraction using *Maud* for the untextured data and those calculated from the refined crystal structure [4] can be expressed as an  $R$  value of 0.453. For overlapping reflections (80.2% of the reflections) an  $R$  value of 0.547 was obtained. Amplitudes derived in a joint extraction using 32 powder patterns collected on a textured sample yielded  $R$  values of 0.380 and 0.408 for all and overlapping reflections, respectively. This improvement was obtained even though the peaks in these patterns are broader (presumably a result of multiple measurements of this particular sample) and have 91.9% overlap.

The quality of the extraction could be further improved by combining the amplitudes derived from the textured sample with those derived from the sharper untextured one. This combination results in  $R$  values of 0.326 for all and 0.385 for overlapping reflections. This obvious improvement in the estimation of the structure factor amplitudes should allow some crystal structures that were previously inaccessible to be solved. If the remaining difficulties with the estimation of the background and the description of the peak shapes can also be solved, the method would become even more powerful.

[1] Ch. Baerlocher et al., *Z. Kristallogr.* **2004**, *219*, 803-812. [2] A. Bergamaschi et al., *J. Synchrotron Rad.* **2010**, *17*, 653-668. [3] L. Lutterotti, *Nucl. Inst. Meth. B* **2010**, *268*, 334-340. [4] J. Dong et al. *Microporous Mesoporous Mater.* **2007**, *104*, 185.

**Keywords:** texture, reflection overlap, X-ray powder diffraction

## MS95.P04

*Acta Cryst.* (2011) **A67**, C799

### Patterson-function direct methods for structure solution from powder data

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A new type of direct methods (DM) called Patterson-function DM

are presented that directly explore the Patterson instead of the modulus function. Since they work with the experimental intensities, they are particularly well-suited for handling powder diffraction data. These methods are based on the maximization of the sum function  $S_p = \sum_H (I_H - \langle I \rangle) G_H(\Phi)$  in terms of the phases of the structure factors. The quantity accessible from the experiment is  $I_H$ , the equidistributed multiplet intensity of reflection  $H$ , and  $\langle I \rangle$  is the average intensity taken over all non-systematically absent reflections.  $G_H(\Phi)$  is the calculated structure-factor amplitude of the squared structure that includes the positivity and the atomicity of the density function in its definition. The  $S_p$  sum function can be optimized with the Patterson-function tangent formula (TF) using a variant of the S-FFT algorithm [1]. It is important that overlapped reflections also participate in the phase refinement, so that not only the resolved reflections but the whole pattern contribute decisively to the refinement. The increase in effective data resolution minimizes Fourier series termination effects and improves the accuracy of  $G(\Phi)$ . The Patterson-function TF has been applied to synchrotron powder data of various organic compounds. In all cases the molecules were easily identified in the respective Fourier maps. By way of illustration the method was applied to synchrotron powder data of a dimer formed by 30 symmetry-independent non-H atoms [2]. However, the application field of the method is not restricted to organic compounds. Here some recent results obtained with coordination and inorganic compounds will be discussed. Since single-crystal data may be regarded as overlap-free powder data, it is clear that Patterson-function DM can cope with powder and single crystal data.

[1] J. Rius, A. Crespi, X. Torrelles, *Acta Cryst.* **2007**, *A63*, 131-134. [2] J. Rius *Acta Cryst.* **2011**, *A67*, 63-67.

**Keywords:** powder diffraction, ab-initio structure solution, direct-methods

## MS95.P05

*Acta Cryst.* (2011) **A67**, C799-C800

### PDXL Structure Analysis Wizard

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The integrated X-ray powder diffraction software suite PDXL has been developed as a comprehensive software package for the analysis of X-Ray powder diffraction (XPD) data. PDXL allows the user to perform many types of analysis using a single platform, making it possible to obtain a diverse array of analysis results from XPD patterns [1]. Ab-initio crystal structure analysis based on XPD data can be done using PDXL Structure Analysis Package [2].

Recently Rigaku Corporation has included the easy-to-use Structure Analysis Wizard into PDXL software suite. The PDXL Structure Analysis Wizard is a user interface type that presents a user with a sequence of dialog boxes that lead the user through a series of well-defined steps in ab-initio crystal structure analysis. PDXL software suite including the Structure Analysis Wizard makes it possible to easily perform the task of ab-initio crystal structure analysis even for those who are not specialists in the field of X-ray diffraction. The PDXL Structure Analysis Wizard is working together with other PDXL software suite features like indexing programs (DICVOL, ITO, N-TREOR), software tools for space group determination and a easy-to-use Rietveld analysis package (used to perform pattern decomposition and refining the initial crystal structure model).

Several initial crystal structure model construction routines can be used within PDXL Structure Analysis Wizard. PDXL Structure

Analysis Wizard offers three methods for initial structure determination: a) Direct method, b) Direct space method and c) Charge flipping method.

[1] *The Rigaku Journal* (English version), **2010** 26(1), 23-27. [2] *The Rigaku Journal* (English version) **2010**, 26(2), 10-14.

**Keywords:** Ab-initio crystal structure analysis, charge flipping method, rietveld method

## MS96.P01

*Acta Cryst.* (2011) **A67**, C800

### Recent Progress in joint charge and spin densities refinement

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Electron density, in all its representations, plays a key role in the understanding of the nature of interatomic interactions and chemical bonds. In case of molecular magnetic materials, as the experimental electron densities rely on high resolution X-ray diffraction experiments, it is necessary to go further and enrich the electronic model by the use of complementary techniques such as unpolarized and polarized neutron (PND) diffraction or Compton scattering. This implies to be able to include all these different experimental contributions into a unique electronic model, and to carry out a joint refinement. In this respect we are developing a new program to model the charge, spin and momentum densities (ANR CEDA project [\*]).

We will report on the first charge and spin densities joint refinement applied to the molecular magnetic compound MnCuPba, (Fig. 1 [1],[2]). The results are consistent with the previous separated studies of spin and charge densities. This method can bring new insights in the nature of interactions in the solid.

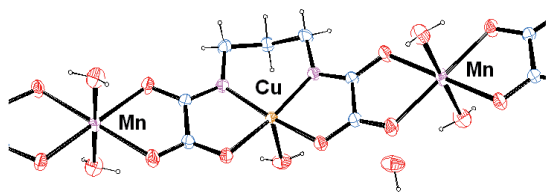


Fig. 1. ORTEP view of the MnCuPba complex chain structure at 100K

[1] S. Pillet, M. Souhassou, C. Mathonière, C. Lecomte, *J. Am. Chem. Soc.* **2004** 126, 1219–1228. [2] V. Baron, B. Gillon, A. Cousson, C. Mathoniere, O. Kahn, A. Grand, L. Ohrstrom, B. Delley, M. Bonnet, J.-X. Boucherle, *J. Am. Chem. Soc.* **1997**, 119, 3500-3506.

**Keywords:** charge, spin, densities

## MS96.P02

*Acta Cryst.* (2011) **A67**, C800

### Structure and magnetic order in CrOCl at low temperatures

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The metal(III) oxyhalide  $MOX$  structures with  $M = \text{Ti, V, Cr}$  and  $X = \text{Cl, Br}$  are isostructural with  $\text{FeOCl}$  at room temperature [1-7] (they are built by slabs consisting of  $M_2O_2$  bilayers enclosed by layers of  $X$  atoms; the interaction between the slabs is of the van der Waals type; the symmetry is orthorhombic, space group  $Pmmm$ ), but they show different magnetic order at low temperatures [8-15]. In  $\text{CrOCl}$  one phase transition was observed towards antiferromagnetic ordering [13].

We have performed low-temperature single-crystal X-ray diffraction experiments at the synchrotron Hasylab/DESY (Hamburg, Germany) to explore the nuclear structure and the development of nuclear superstructure peaks ( $h, k+\frac{1}{2}, l$ ) below  $T_N = 13.5$  K. We found the phase transition at  $T_N$  to be associated upon cooling with a loss of symmetry from orthorhombic towards monoclinic [16]. We also have observed by magnetic susceptibility measurements a second phase transition at  $T_{c2} = 27.8$  K.

Our low temperature powder neutron diffraction experiments at the neutron reactor FRM-II (Garching, Germany) indicate the low temperature phase below  $T_N$  as a monoclinic fourfold magnetic superstructure ( $\mathbf{a} \times 4\mathbf{b} \times \mathbf{c}$ ) with respect to the room temperature phase and the intermediate phase ( $T_N \leq T \leq T_{c2}$ ) as an incommensurately modulated magnetic superstructure. Both magnetic phases are analyzed with Rietveld refinements against the powder neutron diffraction data. For the structure of the low temperature phase the extended magnetic superspace group symmetry  $P 2_1/m 1' (0\sigma_2\sigma_3) 0ss$  (monoclinic,  $\mathbf{a}$ -unique) is applied, the extended magnetic superspace group symmetry of the intermediate phase is  $P m m n 1' (0\sigma_2 0) s0ss$  (orthorhombic). The additional symmetry operator ( $1', s$ ) in the extended symbol stands for the time inversion operator combined with an additional shift of  $\frac{1}{2}$  of the modulation function to describe antiferromagnetic order [17].

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**Keywords:** phase transition, magnetic order, superstructure

## MS96.P03

*Acta Cryst.* (2011) **A67**, C800-C801

### Probing the local sense of the Dzyaloshinskii-Moriya vector: neutrons vs x-rays

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