

conditions but there exists a narrow phase boundary where for the beta form the major component is always PhNO<sub>2</sub> and in the delta form the major component is always PNO. Even though the packing for the structures is very similar the observed diffuse scattering for these two phases is very different and different phase transitions are observed upon cooling these crystals. Our methods are used to attempt to model the diffuse scattering to explain the ordering of the guests and their dynamical behavior in the host lattice.

[1] E.J. Chan, T.R. Welberry, D.J. Goossens, A.P. Heerdegen, *Journal of Applied Crystallography*, **2010**, *43*, 913-15.

**Keywords:** diffuse scattering, monte-carlo simulations, supra-molecular chemistry.

## MS30.P02

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### Diffuse scattering study of aspirin forms (I) and (II)

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Polymorphism of aspirin crystals has recently become an important issue, following reports of a second polymorph [1], because of the widespread popular use of aspirin as an analgesic. The reported structure appeared to correspond to one of the low-energy structures predicted in energy calculations [2]. Bond et al. [3] at first cast some doubt on the findings and stated ‘form (II) of aspirin as reported . . . may just as easily be derived, to the accuracy and precision reported, . . . from experimental diffraction data collected from . . . a single crystal of the well known form (I)’. Subsequently they investigated a number of different crystals that were supposedly form (II) [4]. In this paper the authors concluded that form (II) crystals consisted of “an intergrowth of two ‘polymorphic’ domains” and that ‘each aspirin crystal is an integral whole in which the domains are intimately connected with each other, with possibly many turnovers of domain within a single crystal’. In order to try to make sense of these findings we have undertaken a diffuse scattering study.

Full three-dimensional diffuse scattering data have been recorded for both polymorphic forms [(I) and (II)] of aspirin and these data have been analysed using Monte Carlo computer modeling [5]. The observed scattering in form (I) is well reproduced by a simple harmonic model of thermally induced displacements. The data for form (II) show, in addition to thermal diffuse scattering (TDS) similar to that in form (I), diffuse streaks originating from stacking fault-like defects as well as other effects that can be attributed to strain induced by these defects. The present study has provided strong evidence that the aspirin form (II) structure is a true polymorph with a structure quite distinct from that of form (I). The diffuse scattering evidence presented shows that crystals of form (II) are essentially composed of large single domains of the form (II) lattice with a relatively small volume fraction of intrinsic planar defects or faults comprising misoriented bilayers of molecular dimers. There is evidence of some local aggregation of these defect bilayers to form small included regions of the form (I) structure. Evidence is also presented that shows that the strain effects arise from the mismatch of molecular packing between the defect region and the surrounding form (II) lattice. This occurs at the edges of the planar defects in the *b* direction only.

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17. [4]. A.D. Bond, R. Boese, G.R. Desiraju, *Angewandte Chemie-International Edition* **2007**, *46*, 618-22. [5]. E.J. Chan, T. R. Welberry, A.P. Heerdegen, D.J. Goossens, *Acta Crystallogr B* **2010**, *66*, 696-707.

**Keywords:** diffuse scattering, monte carlo, aspirin polymorphs.

## MS30.P03

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### $\alpha$ -“NaLuF<sub>4</sub>”: 6 fold twinning with modulation and diffuse scattering

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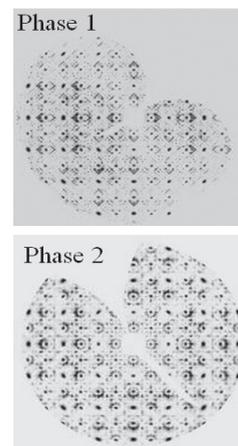
Hexagonal  $\beta$ -NaLuF<sub>4</sub> (Ln=Y,La-Lu) compounds are a family of up-conversion materials which emit visible light upon IR excitation, e.g. show green and blue emission for Er<sup>3+</sup>, Yb<sup>3+</sup> and Tm<sup>3+</sup>, Yb<sup>3+</sup> doping, respectively. Understanding of the properties of these technologically important materials requires a knowledge of their structures at an atomic level. [1] We are presently studying two phases of so-called “cubic  $\alpha$ -NaLuF<sub>4</sub>” obtained from the melt with a likely composition of Na<sub>5</sub>Lu<sub>9</sub>F<sub>32</sub>.

Phase 1 show strong Bragg scattering, commensurate satellite reflections, significant diffuse scattering, while phase 2 shows just strong Bragg reflections with diffuse scattering. The strong, apparently cubic, reflections in reciprocal lattice rows are not collinear and they are split at high angles. This suggests that the crystal is a multiple twin of a structure of lower symmetry with near overlap of reflections. If the satellites are treated as Bragg peaks, an orthorhombic supercell and six fold twinning follow with likely a space group of *Cmmm*.

The apparently cubic main reflections vary in size and position on going from low angle to high angle. To account for this variation an increased mask size was used to integrate the main reflections. To avoid problems arising from the different peak profiles of main and satellite reflections the latter were integrated with an absence condition that eliminates the mains.

Considering only the positions of heavy atoms in the asymmetric unit of the small cell (based on the apparently cubic reflections), the average structure may be described equally well in two different ways for both the phases. The presence of residual electron density in the difference Fourier map of both descriptions was interpreted in terms of disordered fluorine atoms. Their positions are chemically more meaningful for one of the two heavy-atom models.

For the phase 1 structure, the phases of the superstructure reflections were determined by band flipping [2] implemented in the program Superflip. [3] The reconstructed difference electron density map shows two distinct commensurately modulated parallel columns of cations: one with varying Na<sup>+</sup>/Lu<sup>3+</sup> occupancy and one with positional displacements of the ions from the average structure positions. Interestingly, two different solutions result from the band flipping with equal probability. These two solutions differ only by the details of positional and occupational modulation. The two solutions are distinct and the correct one can be identified by subsequent structure refinements.



## Poster Sessions

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#### Short range order in ferroelectric triglycine sulphate

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Triglycine sulphate (TGS)  $[(\text{NH}_2\text{CH}_2\text{COOH})_3\text{H}_2\text{SO}_4]$  is a hydrogen-bonded ferroelectric with a phase transition temperature of 322K [1]. The phase transition is reversible and second-order, order disorder type, making TGS of fundamental interest in the field of phase transitions [2]. Above the critical temperature, one of the glycine molecules is disordered across a mirror plane and below the critical temperature, it chooses a side, breaking the symmetry. The ferroelectric state is obtained through the ordering of the glycine orientations on neighbouring sites, but the mechanism for the phase transition is not well understood.

We have investigated the short range order in TGS by collecting single crystal diffuse scattering data on TGS (x-ray) and fully deuterated TGS (neutron). We have also developed a model of the short-range order using the program ZMC [3] by creating a model crystal in which the molecules can interact and bringing it to equilibrium using a Monte Carlo algorithm. The validity of the model crystal was assessed by calculating the x-ray and neutron diffuse scattering patterns and comparing them with the experimental data.

This approach has yielded new insights into the behaviour of the disordered glycine molecule. For example, above the critical temperature, the correlations in the orientation of the disordered glycine molecule persist over short range rather than being completely random as suggested by the average structure. This is important information because understanding the behaviour of the disordered glycine molecule is crucial to understanding the phase transition and influences the ferroelectric properties of TGS.

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**Keywords:** short range order, diffuse scattering, modelling

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#### Diffuse scattering and superstructures in brownmillerites and related materials

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Brownmillerite-type materials exhibit a wide range of structures, which vary in the arrangement of tetrahedral chains. In brownmillerites perovskite-like layers of octahedra alternate with layers of tetrahedral chains. The tetrahedral chains can adopt two mirror-related configurations, which allow different inter- and intra-layer ordering patterns to form. The simplest of which result in space groups *Pnma* and *I2mb*. More complicated ordering patterns show commensurate or incommensurate intra-layer ordering sequences. Variants with alternating intra-layer order exhibit stacking faults [1] and commensurate or incommensurate stacking sequences. Apart from that, domain structures (anti-phase and twin domains) are possible and cause diffuse scattering to appear.

Diffuse scattering related to stacking faults is observed in layered brownmillerites  $\text{Ca}_4(\text{Fe,Al})_2(\text{Mn,Ti})\text{O}_9$ , which exhibit separated blocks (OTO) of the brownmillerite structure. Similar to  $\text{Sr}_2\text{Fe}_2\text{O}_5$  [1], the layered brownmillerites show a certain degree of order according to superstructures with different stacking sequences, as evident by electron diffraction experiments. All possible superstructures can be described in superspace group  $A2_1/m(0\beta\gamma)0s$  utilising different modulation wave vectors.

In order to explain the observed diffuse scattering intensities, computer simulations were performed. For example, Fig. 1 shows the (3kl) layer of the reciprocal space of a layered brownmillerite. Experimental data is displayed on the right, whereas the left side shows diffuse scattering calculated [2] from a computer model with random stacking faults. The scattering of the average structure (Bragg peaks) is removed from the calculated pattern.

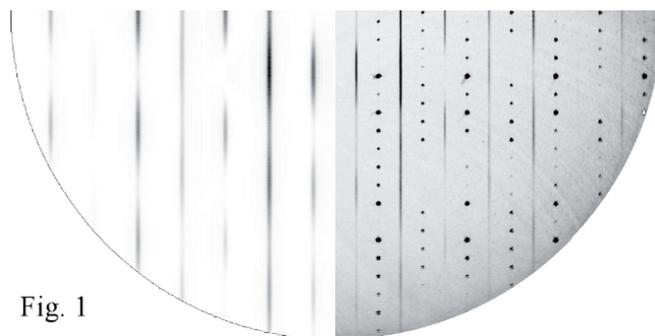


Fig. 1

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**Keywords:** diffuse, scattering, brownmillerite

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#### Hydrogen storage characteristics of melt spun $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$ nano-quasicrystalline alloys

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The present study describes the microstructural changes with respect to the quenching rate and their correlation with hydrogen storage characteristics of  $\text{Ti}_{45}\text{Zr}_{38}\text{Ni}_{17}$  quasicrystalline alloys. The ribbons of the alloy have been synthesized at different quenching rates obtained through different wheel's surface speeds (35, 40, 45 and 50