

## MS73.29.4

Acta Cryst. (2005). A61, C94

**Dual-function Molecular Crystal with  $[\text{Fe}^{\text{III}}(\text{C}_2\text{O}_4)\text{Cl}_2]^-$  Chain Anion**

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Looking for new dual-functional molecular crystal is an emergency task to molecular electronics. Two-dimensional honeycomb  $\text{Cr}^{\text{III}}\text{Mn}^{\text{II}}(\text{C}_2\text{O}_4)^{3-}$  anion as a building block succeeded on built up ferromagnetic conductors, so as zero-dimensional  $\text{FeCl}_4^-$  anion to field-induced-organic superconductor with  $\pi$ -d interaction between donor and anion. It will be interesting to explore uniform one-dimensional anion with metal atom coordinated with  $(\text{C}_2\text{O}_4)^{2-}$  and  $\text{Cl}^-$ . Several novel salts with one-dimensional  $[\text{Fe}(\text{C}_2\text{O}_4)\text{Cl}_2]^-$  anion were synthesized, one iron atom bonds to two Cl atoms and four oxygen atoms of two oxalato groups in cis-mode. Depending on the counter-cation from  $\text{A}^+$ ,  $\text{R}_4\text{N}^+$  and TTF series molecules, a uniform binding-arch or zigzag anion chain is found in the crystal. So dual-functional molecular crystal with magnetism property from paramagnetic, antiferromagnetic to ferromagnetic, conductivity from insulator, semiconductor, metal in charge-transfer complex and fast-ion conductor are constructed.

[1] Coronado E., Galan-Mascariros J.R., Gomez-Garcia C.J., Laukhin V.N., *Nature*, 2001, **408**, 447. [2] Uij S., Shinagawa H., Terashima T., Yakabe T., Terai Y., Tokumoto M., Kobayashi A., Tanaka H., Kobayashi H., *Nature*, 2001, **410**, 908.

**Keywords:** crystal structure and properties, charge-transfer complex, iron compounds

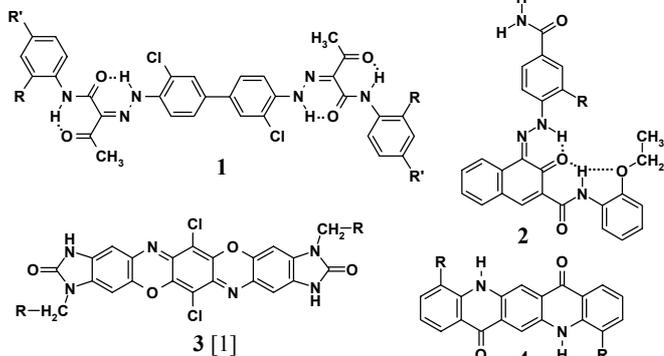
## MS73.29.5

Acta Cryst. (2005). A61, C94

**Crystal Engineering on Organic Pigments**

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The crystal structures of compounds **1-3** were determined from scratch by X-ray powder diffraction. Structure-property relationships were determined. Lattice energy calculations showed, how the crystal structures of **1-4** should be changed to improve the properties of the pigments (colour strength (**1**), weather fastness (**2**), density (**3**), and colour (**4**)). The corresponding new compounds or solid solutions were synthesized, and the improvements were proven experimentally. Some of the new pigments will be produced industrially.



R, R' = H, CH<sub>3</sub>, OCH<sub>3</sub>, F, Cl, Br, ...

[1] Schmidt M.U., Ermrlich M., Dinnebier R.E., *Acta Cryst.*, 2005, **B61**, 37.

**Keywords:** crystal engineering, pigments, powder diffraction

## MS74 TOTAL SCATTERING AND LOCAL ORDER

Chairpersons: Despina Louca, David Keen

## MS74.29.1

Acta Cryst. (2005). A61, C94

**Static and Dynamic Pair Correlation Functions Determined by Neutron Scattering and Inelastic Correction to Total Scattering**

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The atomic pair-density function (PDF) is obtained as the Fourier-transform of the total scattering function. In case of x-ray scattering the PDF gives a snap-shot, a time averaged same-time correlation function, since the speed of light is so fast. However, the situation is more complex with neutrons, since the velocities of neutrons and atoms are comparable. On the other hand, it is easier to carry out inelastic scattering measurement with neutrons. The dynamic structure factor,  $S(\mathbf{Q}, E)$ , thus obtained, can be Fourier-transformed to give the dynamic PDF, or the frequency-resolved PDF. We show how the dynamic PDF helps to understand the nature of dielectric response of relaxor ferroelectric oxide,  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ , by direct observation of dynamic local ferroelectric polarization. The PDF obtained by powder diffraction without energy discrimination contains both static and dynamic information. For neutron scattering the dynamic part requires correction commonly known as the Placzek correction. We show how ineffective, or even damaging, this correction is, and show that the correct inelastic correction can be made within the Debye model of lattice vibration.

**Keywords:** total scattering, static and dynamic PDF, inelastic effects

## MS74.29.2

Acta Cryst. (2005). A61, C94

**The Local Structure of Ice VII Determined by Neutron Total Scattering**

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The structural characterization of the local geometry of the H-bond network in Ice VII has been a long-standing problem in ice physics. Rietveld refinements of neutron powder-diffraction data have revealed an apparently short molecular O-D bond-length [1,2] in the average structure. The assumption that the real bond-length is close to that found in the (ordered) ice VIII structure has led to the proposal of site disorder of the oxygen atom in ice VII. By converting the neutron-diffraction pattern of ice VII into a total structure factor, thereby retaining the information content of the diffuse scattering, we have been able to make a direct measurement of the molecular bond-length, demonstrating that it is indeed identical to that found in ice VIII. Additionally, we observe clear differences in the radial-distribution function from 1.5 - 2.0 Å, potentially indicating differences in the O...D separation between the two phases and, thus, H-bond geometry.

These results should have interesting implications for the interpretation of inelastic studies of the hydrogen-bond dynamics and may shed light onto the mechanism of bond centering at higher pressures.

[1] Kuhs W.F., et al., *J. Chem Phys.*, 1984, **81**, 3612. [2] Nelmes R.J., et al., *Phys. Rev. Lett.*, 1998, **81**, 2719.

**Keywords:** ice phases, neutron scattering, high pressure

## MS74.29.3

Acta Cryst. (2005). A61, C94-C95

**Medium Range Ordering of Local Polarizations in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$** 

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Local polarizations and the interaction between them play a crucial role in the relaxor behavior of relaxor ferroelectric  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN). We report the temperature evolution of the local and medium-range crystal structure of PMN from 1000K to 15K using neutron pair distribution function analysis [1]. We present evidence for both local atomic displacements (local polarization) and for medium-range ( $\sim 5 \text{ \AA} - 50 \text{ \AA}$ ) ordering, called polar nanoregions (PNRs). These medium-range correlations are modeled using rhombohedral symmetry, enabling for the first time an estimate of the temperature dependence of the volume fraction of the PNRs. We show that this fraction steadily increases from 0% to a maximum of  $\sim 30\%$  as the temperature decreases from 650K to 15K. Below  $T \sim 200\text{K}$  the volume fraction of the PNRs becomes significant, and PNRs freeze into the spin-glass-like state.

[1] Jeong I.-K., Darling T. W., Lee J. K., Proffen Th., Heffner R. H., Park J. S., Hong K. S., Dmowski W., Egami T. *Phys. Rev. Lett.*, in press.

**Keywords:** relaxor, medium-range ordering, PDF

#### MS74.29.4

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##### Getting the most from Total Scattering

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Total scattering, an extension of the powder diffraction method, is increasingly being used to study crystalline materials. The unique combination of Bragg and diffuse scattering can be used to determine both the average structure and the short-range fluctuations from this average within a single experiment. To maximise the structural information from such data three-dimensional atomic models consistent with all aspects of the data are required. Here I present a technique for producing such models based on the reverse Monte Carlo (RMC) method. The existing RMC method has been expanded to take explicit account of the Bragg intensity profile from crystalline materials [1].

Analysis of the RMC-generated atomic models gives much more detailed information than is available directly from the data. I will give several examples where this method has been used to successfully study the structure and dynamical disorder of materials including those with the perovskite structure [2], those showing negative thermal expansion and molecular crystals. I will also show examples of low-energy phonon dispersion curves obtained from the models [3].

[1] Keen D. A., et al, *J. Phys.: Cond. Matt*, 2005, **17**, S15. [2] Hui Q., et al, *J. Phys.: Cond. Matt*, 2005, **17**, S111. [3] Goodwin A. L., et al *Phys. Rev. Lett.* **93**, 075502, 2004.

**Keywords:** reverse Monte Carlo, structural simulation, neutron X-ray scattering

#### MS74.29.5

*Acta Cryst.* (2005). A61, C95

##### Characterisation of Nanoparticles

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Powder diffraction patterns of ZnO as well as CdSe/ZnS core shell nanoparticles were obtained and analysed with respect to particle size, defect density and local structure. The pair distribution function was successfully used to analyze the local structure.

The ZnO pattern was refined by the Rietveld method using a

wurtzite structure. The moderate agreement shows that the particles are of anisotropic shape and have a stacking fault density of some 20%. The nanoparticles were modelled and size, shape, stacking fault density, positional and displacement parameters fitted to the powder pattern by means of the Debye formula as well as to the respective experimental Pair Distribution Function. The two methods give similar results of some 3.5 nm parallel [100] and 2.5 nm parallel [001] in size.

The CdSe nanoparticles and CdSe/ZnS core-shell nanoparticles show diffraction patterns that qualitatively fit to a wurtzite structure. The size of 3 nm as well as stacking fault density of 25% and distortions at a surface layer degrade the powder pattern. The pattern of the CdSe/ZnS core-shell nanoparticles are widened at the high 2 $\theta$  side compared to the pure CdSe nanoparticles. The smaller metal-anion distance (Zn-X=0.235 nm, Cd-X=0.27 nm) causes a distortion of the whole particle.

**Keywords:** nanoparticle, pair distribution function, local structure

#### MS75 SURFACES

**Chairperson:** Laurence D. Marks

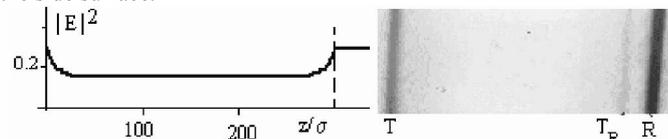
#### MS75.29.1

*Acta Cryst.* (2005). A61, C95

##### Electromagnetic Wave Tunneling Through a Barrier With Periodical Structure

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We discuss specific features of electromagnetic wave localization inside specimen with periodical structure in diffraction regime. The problem was solved by Hambartsumian's layer addition method modified for cholesteric liquid crystal layer (CLCL)[1]. Experiment for a perfect single crystal of silicon was fulfilled when x-ray beam was reflected from atomic planes (2 $\bar{2}0$ ). We reveal an interesting manifestation of electromagnetic wave tunneling through barrier with periodical structure, namely, we theoretically and experimentally showed that when electromagnetic wave propagated through the barrier in the Bragg regime the wave field in the specimen was localized near the specimen boundaries, while it was practically absent inside the sample. Using this we explained the fact (observed in experiment) that absorption and scattering inside the sample are practically absent, and that reflection takes place only from the two surface layers of the sample. Fig. 1 shows electromagnetic wave intensity distribution in CLCL in the Bragg diffraction regime (a) and x-ray sectional photograph from the two block silicon systems, when the primary beam (which is reflected from the first block and incident onto the second block) then forms three beams; R is reflected from the entrance surface, T is the transmitted beam and  $T_R$  is reflected from the side surface.



[1] Gevorgyan A.H., et al., *Opt. Spectrosc.*, 2000, **88**, 647.

**Keywords:** diffraction, tunneling, surface physics

#### MS75.29.2

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##### Holographic Methods for Surface Crystallography

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A hologram stores information about the amplitude and phase of a wave in an interference pattern with a known reference wave. The unknown wave may be recovered through a process known as reconstruction. It has been suggested that many diffraction patterns, e.g. those formed by photoelectrons, or low energy backscattered electrons may be capable of a holographic interpretation, and