

MS.30.3

Acta Cryst. (2011) A67, C78**Diffuse scattering from molecular crystals**D. J. Goossens, *Research School of Chemistry, Australian National University, Canberra(Australia)*. E-mail: goossens@rsc.anu.edu.au

Diffuse scattering probes the local ordering in a crystal, whereas Bragg peaks are descriptive of the average long-range ordering. Short-range order can be thought of as local departures from that long-range average. The population of local configurations can be explored by modelling the three-dimensional (3-d) distribution of diffuse scattering. Local configurations are not constrained by the average crystallographic symmetry so one way of modelling diffuse scattering is by modelling a structure containing some disorder (or short-range order) and then calculating its diffuse scattering. The structure must contain enough atoms/molecules to give a statistically valid model of the populations of local configurations.

It is possible to collect three-dimensional (3-d) volumes of diffuse scattering with X-rays or neutrons [1], [2] and reconstruct large volumes of reciprocal space. Increases in computing power allow such data to be modelled in detail, even for complex systems such as molecular crystals, in which the molecules possess both external degrees of freedom (position and attitude of the molecule) and internal (molecular conformation) [3].

Thus paper describes the modelling of the local ordering in molecular crystals including *para*-terphenyl and ferroelectric triglycine sulphate. This includes a discussion of the different approaches to the analyses and the types of information available, and a brief outline of the software that has been developed to tackle such problems.

[1] E.J. Chan, *et al.*, *Acta Crystallogr.* **2010**, B66 696-707. [2] R.E. Whitfield, *et al.*, *Metallurgical and Materials Transactions A*, **2011**, in press. [3] D.J. Goossens, *et al.*, *Metallurgical and Materials Transactions A*, **42**, **2011** 23-31.

Keywords: diffuse scattering, Monte-Carlo, molecular crystals

MS.30.4

Acta Cryst. (2011) A67, C78**A new model of correlated disorder in relaxor ferroelectrics**Dmitry Chernyshov,^a Alexi Bosak,^b Sergey Vakhrushev,^c Michael Krisch,^b ^aSwiss-Norwegian Beam Lines, BP 220, 38043 Grenoble Cedex, (France). ^bEuropean Synchrotron Radiation Facility, BP 220, 38043 Grenoble Cedex, (France). ^cIoffe Physico-Technical Institute, St. Petersburg, 194021, (Russia). E-mail: dmitry.chernyshov@esrf.fr

Relaxor ferroelectrics are known since more than fifty years and have attracted significant interest because of their numerous unusual properties and a variety of applications¹; they also show pronounced diffuse scattering directly linked to relaxor physics. One of the most widely used concepts dealing with characteristic diffuse scattering is the model of polar nanoregions (PNR) in relaxors, first proposed in 1983².

The model is based on the existence of small regions (down to few unit cells in some dimensions) of local polarization, with the polarization parallel to specific high-symmetry directions. It is commonly accepted that the strong neutron- and x-ray diffuse scattering in the vicinity of Bragg reflections is a signature of PNRs³. We present new diffuse scattering maps for $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{-PbTiO}_3$ (PMN-PT), a prototypical ferroelectric relaxor. We show that the widely used concept of polar nanoregions as individual static entities is incompatible with the available body of experimental diffuse scattering results.

We propose a simple phenomenological model that not only reproduce observed diffuse scattering in great details but also is coherent with the unusual dielectric properties⁴. Our model assumes a specific, slowly changing, displacement pattern of the lead ion, which is indirectly controlled by the low-energy acoustic phonons of the system. The model qualitatively explains the temperature, pressure, and electric field dependence of diffuse neutron- and x-ray scattering, as well as the existence of hierarchy in the relaxation times of these materials.

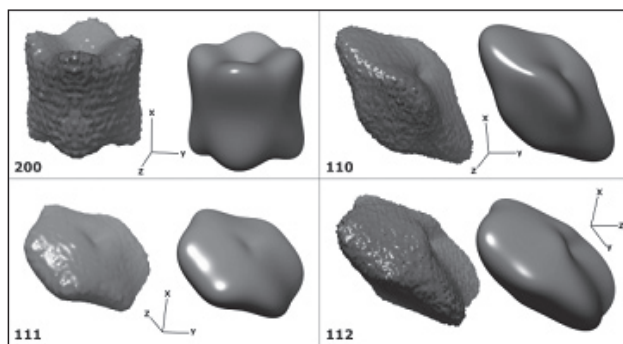


FIGURE. Comparison of experimental (PMN-PT) and model isosurfaces of diffuse scattering intensity in the proximity of various Bragg nodes.

[1] D. Viehland, S.J. Jang, L.E. Cross, M. Wutting, *J. Appl. Phys.* **1990**, 68, 2916-2921. [2] G. Burns, B.A. Scott, *Solid State Comm.* **1973**, 13, 423-426 [3] G. Xu, G. Shirane, J.R.D. Copley, P.M. Gehring, *Phys. Rev. B* **2004**, 69, 064112-1 - 064112-6 [4] <http://lanl.arxiv.org/abs/1101.0490>

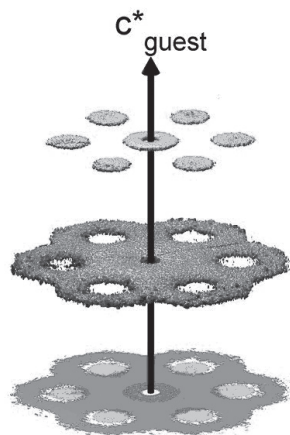
Keywords: relaxor ferroelectrics, diffuse scattering, perovskite structure

MS.30.5

Acta Cryst. (2011) A67, C78-C79**Diffuse scattering in one dimensional “liquid-like” aperiodic composites**Laurent Guérin,^a Céline Mariette,^a Bertrand Toudic,^a Philippe Rabiller,^a Claude Ecolivet,^a Mark Hollingsworth,^b ^aInstitut de Physique, Rennes, UMR 6251 CNRS Université de Rennes 1 35000 Rennes (France). ^bDepartment of Chemistry, Kansas State University, Manhattan (USA). E-mail: laurent.guerin@univ-rennes1.fr

Uniaxial aperiodic composites are made of host opened non-stoichiometric structures confining guest molecules which possess their own periodicity [1], [2], [3]. From the crystallographic point of view, translation symmetry is recovered in higher dimensional superpaces, in agreement with the existence of non-periodic Bragg peaks, indexed with more than three indices [4]. This aperiodicity generates many kinds of disorder, which may concern self-correlation functions, pair correlation functions, molecular disorder [5]. They induce a very rich diffuse scattering pattern in the reciprocal space.

Here we will focus on the shortest alkane guest molecules within urea inclusion compounds. We have recently shown that with guest heptane to dodecane molecules, these materials present a high temperature phase with one dimensional order for the guest subsystem. Very original patterns of the associated diffuse planes are observed. At lower temperature, these crystals present unique phase ordering phase transitions, to higher dimensional crystallographic superpaces [6].



Diffuse scattering iso-surfaces in dodecane-urea host-guest compound in slabs perpendicular to the channel axis and close to multiple values of the guest reciprocal parameter. (down: projected image).

[1] J.M. Hastings et al., *Phys. Rev. Lett.* **1977**, *39*, 1484. [2] R.J. Nelmes et al., *Phys. Rev. Lett., PRL* **1999**, *83*, 4081. [3] Toudic et al., *Science* **2008**, *319*, 69. [4] T. Janssen et al., *Aperiodic Crystals: From Modulated Phases to Quasicrystals*, Oxford Univ. Press **2007**. [5] T. Weber et al., *Acta Cryst. B* **2000**, *56*, 132. [6] C. Mariette et al., "Phase ordering" phase transition leading to a modulated aperiodic composite in *n*-heptane/urea, to be submitted.

Keywords: phase-ordering, inclusion compounds, aperiodic

MS.31.1

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The impact of crystallography on design of adsorption and catalytic sites in zeolites

Johan A. Martens, Steven Heyle, Christine E. A. Kirschhock, *Centre for Surface Chemistry and Catalysis, Katholieke Universiteit Leuven, Kasteelpark Arenberg 23, 3001 Leuven, (Belgium)*. E-mail: johan.martens@biw.kuleuven.be.

In this lecture two examples will be developed illustrating the essential need to combine crystallography with other diagnostic tools for designing zeolite adsorbents and catalysts.

The synthetic FAU type zeolites known as zeolite X and Y are important industrial adsorbents. The cubic symmetry of the FAU zeolite crystals renders them particularly suitable for investigations of the organization of framework charge compensating cations and guest molecules using diffraction techniques and structure refinement. Adsorbates are known to alter cation positions and bring about important cation redistribution. While in early studies, cation redistribution upon adsorption and desorption were considered to be rather of secondary importance, the more recent insight is that cation migrations are essential and can even be triggered in order to facilitate regeneration of the adsorbent. In this lecture we present an example where the chemical reduction of an isolated ruthenium cation triggers a cascade of cation migrations leading to the elimination of the adsorption site.

This specific adsorbent is meant for NO_x trapping from automotive exhaust gas in lean-rich cycles. In the lean phase, NO_x is trapped while in the lean phase it needs to be desorbed and reduced to the harmless dinitrogen over a catalyst. At the typical water content of exhaust gas sodium cations and water molecules form very specific cation-water-networks extending in the channels of zeolite Y. In these networks the water ligands can reversibly be replaced by NO_x molecules. Ru³⁺ cations are preferentially located in hexagonal prisms of the zeolite structure. Switching to rich conditions leads to the reduction of these Ru³⁺ cations to Ru⁰ and disturbs the charge balance of framework and cations. It entails a migration of Na⁺ ions from the water nets back to

framework sites causing abrupt release of the trapped NO_x. Under lean conditions, the NO_x adsorption sites are restored by oxidation and repositioning of the ruthenium cation. Knowledge of site occupancies from structure refinement of the adsorbent in saturated and regenerated state enabled the design of an optimal Ru,Ba,Na-Y zeolite adsorbent composition.

In the catalysis area the hydrocracking of *n*-decane model molecule has been used systematically in our laboratory for probing zeolite pore architectures in terms of dimensionality of the pore system and pore diameter. It is particularly useful to assist the structural characterization of complicated materials such as structural intergrowths, nanozeolites and fragile materials. In the lecture some examples will be given on how such catalytic testing and crystallography go hand in hand in answering practical catalytic questions such as the actual location of active sites.

Keywords: zeolites, cation positions, adsorption

MS.31.2

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Indenyl nickel catalysts: the effect of structure on oligomerisation reactions

Clara S. B. Gomes, Leonel C. Silva, Sandra I. Costa, M. Teresa Duarte, Pedro T. Gomes, *Centro de Química Estrutural, Torre Sul, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa (Portugal)*. E-mail: clara.gomes@ist.utl.pt

Indenyl complexes, which have the ability to undergo a facile ring slippage of the indenyl ligand from η⁵ to a η³ allyl-type coordination, have shown to be active in olefin oligo-/polymerisation [1]. On the other hand, several Ni(II) complexes containing simultaneously cyclopentadienyl and neutral arsenic or antimony donor ligands have been synthesised in the past [2]. More recently, Ni(II) complexes containing arsine and stibine donor ligands and the η³-allyl moiety have been prepared and their cationic derivatives showed to be highly active catalysts for the oligomerisation of styrene [3]. Taking this into account, we decided to study complexes containing an indenyl ligand, whose behaviour lies in between those of the allyl and cyclopentadienyl ligands.

Herein, we describe a novel methodology for the synthesis of new neutral [(η-R-Ind)Ni(EPh₃)X] and cationic [(η-R-Ind)Ni(EPh₃)₂]BF₄ and [(η-R-Ind)Ni(COD)]BF₄ indenyl nickel complexes, containing neutral AsPh₃, SbPh₃ or COD (1,5-cyclooctadiene) and/or halide (X=Cl, Br, I) ligands, which were characterised by NMR, elemental analysis and, when possible, by X-ray diffraction. In these complexes, the indenyl ligand contains methyl or silyl substituents (SiMe₃). Comparative X-ray characterisation of the neutral compounds with [(η-Ind)Ni(PPh₃)Cl] [4], enabled the confirmation of the dependence of the indenyl ligand distortion upon the neutral ligand donor ability. Structural parameters, such as the *slip parameter*, Δ_{M-C}, the *hinge angle*, HA, and the *fold angle*, FA, were calculated from crystal data allowing the quantification of the indenyl slip-fold distortion. These compounds are highly active as homogeneous catalysts for the oligomerisation of styrene, at room temperature. Neutral complexes are only active when in situ halide abstraction is induced by MBF₄ salts (M=Ag or Tl), whereas the cationic ones are very active without the need of an aluminium co-catalyst. Their catalytic activity and the oligomer mass properties depend upon the nature of the substituents present in the indenyl ligand and of the donor ligand used.

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