MS.30.3


**Diffuse scattering from molecular crystals**

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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.


**Keywords:** diffuse scattering, Monte-Carlo, molecular crystals

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MS.30.4


**A new model of correlated disorder in relaxor ferroelectrics**

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Relaxor ferroelectrics are known since more than fifty years and have attracted significant interest because of their numerous unusual properties and a variety of applications; 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 1983.

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 PNRs. We present new diffuse scattering maps for PbMg_{1/3}Nb_{2/3}O_{3-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.

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MS.30.5


**Diffuse scattering in one dimensional “liquid-like” aperiodic composites**

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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 superspaces, 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 pattern of the associated diffuse planes are observed. At lower temperature, these crystals present unique phase ordering phase transitions, to higher dimensional crystallographic superspaces [6].


**Keywords:** relaxor ferroelectrics, diffuse scattering, perovskite structure

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Diffuse scattering iso-surfaces in do-decane-urea host-guest compound in slabs perpendicular to the channel axis and close to multiple values of the guest reciprocal parameter.

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Indenyl nickel catalysts: the effect of structure on oligomerisation reactions

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Indenyl complexes, which have the ability to undergo a facile ring slippage of the indenyl ligand from η⁶ to a η⁵ alkyl-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 arsonic or antimony donor ligands have been synthesised in the past [2]. More recently, Ni(II) complexes containing arsine and stibine donor ligands and the η⁵-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 alkyl and cyclopentadienyl ligands.

Herein, we describe a novel methodology for the synthesis of new neutral [(η-R-Ind)Ni(Ph)X] and cationic [(η-R-Ind)Ni(Ph)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(Ph)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,  , 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 MBF₃ salts (M=Ag or TI), 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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Keywords: zeolites, cation positions, adsorption