

**Order and ‘disorder’, a chemist's view: what we know,
what we don’t know and what we (often wrongly!) assume.**

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In 1912 von Laue, Friedrich & Knipping first exposed a crystal to a beam of X-rays. The experiment was initially carried out in order to understand the nature of the radiation itself; instead, its real importance was the discovery of X-ray diffraction. In the same year, 1912, WL Bragg developed his famous law thereby making it possible to calculate the positions of atoms within crystals from the intensities of diffracted beams. The “diffraction” of X-rays thus changed from the status of being a physical phenomenon to that of a tool for exploring the arrangement of atoms within crystals. The extraordinary success of X-ray crystallography ever since has led to the now largely “mature” science of crystallography.

Like all successful disciplines, however, its very success inevitably led to the imposition of rigid “rules” as to what constitutes crystalline order and what doesn’t *e.g.* “.. *A unit cell of a crystal is a .. parallel-sided region .. from which the entire crystal can be built up by purely translational displacements ..*” *Shriver and Atkins, P66, 2009!! Wrong*, as demonstrated by the (eventual) widespread acceptance of aperiodic/quasicrystalline order! Likewise, the direct observation of curved graphite planes in Transmission Electron Microscope (TEM) images of carbon support films in the 1960’s was ignored because “.. lattice planes can’t curve ..”. Bye-bye the chance to discover bucky balls and bucky tubes much earlier than they were!

In this contribution, a range of other fundamentalist type structural notions will be discussed ranging from the strange use of “nodal planes” when describing the molecular orbitals of 1-D “crystalline”, periodic ring molecules such as benzene or cyclopentadienyl to the question of why there is extensive notation describing “real”, but not “reciprocal”, space to the notion that a crystal structure refined from ISIS or synchrotron data with a good *R*-factor is necessarily correct. The need to always keep thinking and to extend our ideas of what constitutes order to encompass whatever we experimentally encounter is still with us and continues to separate thoughtful structural chemists from handle-turners.

‘Ordered’ crystalline materials are often far more subtle than the straitjackets imposed by crystallographic or chemical fundamentalism. Functionally useful materials (piezoelectrics, relaxor ferroelectrics, ionic conductors, solid solutions *etc.*), for example, are often modulated and frequently inherently flexible [1-3]. A detailed understanding of the structure, both average as well as local (on the relevant length and time scales) of such materials, is essential for an understanding of their properties and of methods to optimize and manipulate them. In this contribution, the results obtained from several such systems will be described including inherently Pb-free polar functional materials and the $\text{Li}_{3x}\text{Ln}_{2/3-x}\text{TiO}_3$, $0.047 < x < 0.147$, family of Li ion conductors. The local crystal chemistry underlying the inherent structural flexibility of these materials will be discussed along with the characteristic diffraction signatures of such behaviour.

[1] R.L.Withers, *Advances in Imaging and Electron Physics* 2008, 152, 303-337.

[2] Y Guo, Y Liu, RL Withers *et al*, *Chemistry of Materials* 2011, 23, 219-228.

[3] Z Yi, Y Liu, MA Carpenter, J Schiemer and RL Withers, *Dalton Transactions* 2011, 40, 5066-5072.