INFORMATION LOSS FROM POLYTYPIC DISORDER

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Stacking faults in structures built from identical layers are important twinning mechanisms. Occurring in sufficient concentration, they also produce rods of diffuse scattering. A well-known example is the (111)-twinning in the cubic closest sphere packing, …ABC|BAC… Another example is the monoclinic structure of piperazine hexahydrate [1] where polytypic fourfold twinning results in a tetragonal diffraction picture with extraordinary absence rules. Such twinning may lead to important ambiguities, as shown by the following two examples.

The polytypic structure of the metastable orange phase of HgI_2 [2] is built from layers of corner-linked super-tetrahedra Hg_4I_{10}, layer symmetry *pm*2. Successive layers may be stacked in two ways that result in identical interlayer contacts. The two corresponding periodic Maximum Degree of Order (MDO) structures are both tetragonal: $I4_1/amd$ with a 4-layer repeat (f) and $P4_2/nmc$ with a two-layer repeat (t). It turns out that a structure composed of extended domains …ffff…tttt… with average volume ratio 1:1 is indistinguishable from an orthorhombic alternating stacking …ftftft… twinned through stacking faults …tftf|ftft… , independently of the average domain size and the number of stacking faults.

The polytypic structure of tris(bicyclo[2.2.1]hexeno)benzene [3] shows layers with symmetry $p3_1m$. The two MDO-structures have symmetries $C2/c$ (1) and $P6_122/P6_522$ (2); corresponding repeat distances are 4 and 6 layers, respectively. Highly disordered crystals, and ordered crystals with structure MDO-1 have been observed [4]. Interestingly, 6-fold equal-volume twins of MDO-1 give exactly the same diffraction pictures, including diffuse scattering, as left-right twins of MDO-2 for any number of stacking faults.

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IDENTIFICATION OF IDEALIZED PARENT STRUCTURE SYMMETRY TO RATIONALIZE THE REFINEMENT OF PSEUDO SYMMETRIC CRYSTAL STRUCTURES

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Many problems in crystal structure refinement can be analyzed using a modulation wave approach. Pseudo symmetry operations are used to create a parent structure of higher symmetry. An ideal structure is then described as a sum of components of different symmetries, each a subgroup of the parent symmetry. Each component has the symmetry of the ideal structure as a subgroup. The diffraction pattern is then described in terms of the Fourier Transforms of these symmetrised components. Problems often arise when the diffraction pattern is dominated by the FT of the parent symmetry component, creating difficulties in determining the finer details of the crystal being studied, i.e. The symmetry, content, scale and global phase of modulation waves and the correlations between the fts of these modulation waves. Twinning and stacking faults are likely complications, especially when intrinsic symmetry elements of ordered columns, layers or substructures are destroyed when these components pack together. A pseudo symmetry element of a substructure may act on the remaining structure, causing it to move and create a different orientation of the original structure. Disorder can either increase or decrease the symmetry of a crystal. The distinction between twinning and disorder is not always clear and both can disguise systematic absences for an untwinned ordered version of the structure. Polytypic behavior is possible. Often false refinement minima exist and a modulated structure approach allows systematic identification of alternative starting models. A number of examples will be described including sensible refinement strategies. Constrained refinement is sometimes essential.

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QUANTITATIVE ANALYSIS OF PLANAR FAULTING

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Some type of crystals can be described by the stacking in one direction of identical atomic layers that are perfectly periodic in the layer plane. In this crystals heavy disorder in the stacking is a common feature. A direct solution of the diffraction pattern obtained from such crystals has been reported [1, 2]. The formalism does not make any of the usual simplifying assumptions of previous treatments. The reported solution was focused mainly in powder diffraction. We have now found the formalism is extensible to single crystals. The interference function is then seen to be a Fourier series of linear functions of the so called Delta-pair correlation functions $Ps(\Delta)$. $Ps(\Delta)$ gives the probability of finding two layers, Delta layers apart, laterally displaced one with respect to the other s times a minimum displacement vector. $Ps(\Delta)$ can be obtained directly from the diffraction pattern by Fourier transform. When we apply the formalism to RE_2Co_{17} (RE: rare earth) samples, we found out that for heavy rare earth elements, Lu, hexagonal order with few stacking faults could be seen, the intermediate rare earth (Gd, Tb, Dy) showed a mixture of hexagonal an rhombohedral order with faulting complexes. We could obtain the $Ps(\Delta)$ function for all the rare earth analyzed which allows a full determination of the faulting complexes.

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IN SITU OBSERVATION OF UNSTABLE MOLECULES BY X-RAY ANALYSIS

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Many organic reactions proceed by multi-step processes in which intermediate molecular species are involved in the conversion from one molecule to another. Such intermediate molecules, in general, are so unstable that the structure analysis has been considered to be very difficult. However, the recent X-ray technique makes it possible to trap the unstable species produced by photo irradiation in the crystalline lattice and to analyze the structures at low temperatures. We already reported the structure of a triplet carbene when the crystal of an diazo compound was irradiated with UV light at 80 K.

Another example is nitrene, which is produced by photo irradiation from phenylazide compounds as follows; $Ph(X)-N_3 = [Ph(X)-N:] + N_2$ Among the crystals of ten phenylazide compounds with different X groups, the 2-azidebiphenyl crystal showed the change of cell dimensions keeping the crystallinity when it was irradiated with UVlight at 80 K for 5 hours. The structure after irradiation clearly showed the phenylnitrene and a nitrogen molecule.

For the crystal of 2-nitrophenylazide, the analyzed structure at 80 K was not an phenylnitrene but a benzofuroxan molecule. This suggested that the nitrene should be made from 2-nitrophenylazide at the intermediate stage. The IR spectra at 15 K clearly showed the nitrene. The IR spectra of the nitrene changed to those of the benzofuroxane over 50 K. The ESR spectra at 15 K indicated that the produced nitrene is triplet. These results suggest the nitrene formation mechanism at the intermediate stage.

Keywords: NITRENE STRUCTURE CRYO TRAP