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Title: Recognizing and Modeling Problems in Nonroutine X-Ray Crystal Structures

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Crystal engineers and supramolecular chemists are interested in design, creation, and control of the structure of the solid state. In addition to ionic, covalent, and coordination bonds, the so-called nonbonding interactions and weak interactions such as hydrogen bonding and π-π interactions, play a crucial role in determining the three dimensional structures of large molecules and aggregates. The design of engineered cocrystalline organic solids requires control over molecular packing. Nearly all cocrystals, almost by definition exhibit supramolecular structures including examples of one-, two-, and three-dimensional types. Most of the resulting structures are well-behaved using standard refinement techniques. Contemporary estimates are that 90-95% of structures are completely routine. However, many of the remaining structures exhibit phenomena which pose particular challenges during structure solution and refinement. Included in these phenomena are pseudo symmetry, disorder, twinning, structure modulation, stacking faults, or other interesting phenomena for which dimensionality greater than three is required for the mathematical description of the extended order and thus for which the standard structure solution/refinement packages are not well optimized.

The effect of pseudo symmetry on the diffraction pattern is to induce systematic dependence of the intensities as a function of *h*, *k*, and *l*, often manifested as a systematic pattern of weak and strong reflections. In disorder the orientations of some part of the scattering material differs from unit cell to unit cell. Disorder is not always random, for example whole molecules or planes or columns may be disordered by a symmetry operation of the crystal or by operations that would be symmetry related for a parent structure of higher symmetry. Problems with the refinement of the structure of twinned crystals occur when twin related reflections are neither clearly separated nor completely overlapped. When diffraction patterns are completely overlapped problems are worst if there is an equal amount of each twin component. The diffraction intensities of a twinned crystal must be carefully analyzed in order to separate the contributions from the different individual orientations forming the twin. Modulation waves can be either commensurate or incommensurate, *i.e.*, a small number of wavelengths of the modulation wave does not necessarily correspond to a simple translation of the overall structure. Modulated structures can often be thought to be the consequence of the interaction of two (or more) coexisting substructures. Substructures need not have identical repeat distances for all three dimensions of a crystal. Modulated structures almost have a higher symmetry, and application on a local scale of the pseudo symmetry operations gives rise to faults in the structure.

Indexed reflections of a diffraction pattern see the results of these defects averaged over sites in the crystal. A meaningful parameterization of the effects of these defects is required to obtain reliable values for other parameters. Stacking faults can occur which allow substructures to have alternative origins or orientations. Often this causes effects that can be modelled by changing the scale of reflection intensities or differences in reflection intensities for particular classes of reflections, but not necessarily for all classes of reflections. An approximate structure solution can identify the possibility of a stacking fault, and appropriate modeling can then be used to establish the ratio of the components. Refinement, including definition of atoms with refinable local coordinates relative to refinable orthonormal axial systems, refinable thermal groups, and use of constraints and restraints to control refinement of a structure containing poorly defined groups of disorder overlapped atoms, have subsequently been incorporated into standard routine refinement packages. Other aspects such as the ability to conveniently refine multiply twinned crystals or groups of atoms within larger refinable groups of atoms, essential in the refinement of the multiple twinned-disordered structures, as well as refinable TL (libration) and TLX (libration with refinable origin) thermal groups, which in addition to providing more rational models of the atomic displacements, also decrease the total number of refinable variables thereby improving the refinement, are available only in specialized programs or must be programmed by the user. Ways to recognize the nature of the problem in a given structure and several of the specialized modeling techniques will be described.