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Prototype Structures and Structure Factor Algebra as an Aid to the Refinement of Problem structures

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Many structures are problematic in that, although they are well organised in one or two dimensions, alternative relationships are possible between adjacent columns or layers. This allows the possibility of polytypes, stacking faults and twinning. A prototype structure is an ideally ordered structure from which a model of the observed intensities can be constructed and refined, assuming definable (or refinable) relationships (**R**,**t**) between blocks of structure. Coherence between blocks in the evaluation of a structure factor only requires that the operator **R** operating on a reciprocal lattice vector **h** of the prototype, creates another such lattice vector **h'** = **Rh**. Structure factor algebra uses refinable population and twinning parameters to combine the structure factors of equivalent or pseudo equivalent reflections of the prototype structure. This may change the symmetry of the diffraction pattern from that of the ordered prototype structure.
A common situation is when the prototype structure can be related to an idealised 1:1 disordered parent structure of higher symmetry. Alternative orderings may then be possible and symmetry operations destroyed upon ordering the parent structure can be used to identify possible polytypes and twin-disorder scenarios. Examples from recently studied structures using my program RAELS will illustrate the principals.

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Structure Determination without Fourier Inversion: a New Concept

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Assume a one-dimensional crystal structure (or structure projection) of m equal and independent point atoms $j = 1, ..., m$ with coordinates x_j, $0 < x_j < 1$ or $< ½$ (for the centrosymmetric case). Take an orthonormal parameter space of dimension m, $\mathbf{P}^m[0, 1]^m$, or $\mathbf{P}^m[0, ½]^m$, respectively, and, due to the atom permutability, its asymmetric part $\mathbf{A}^m$ (or half of $\mathbf{A}^m$ after origin definition of centrosymmetric structures). Describe in it the structure by a vector $\boldsymbol{x} = (x_1, ..., x_m)$ with components to be determined [1]. Rank any set of n diffraction amplitudes $g(h_i)$, $i = 1, ..., n$, $g(h) = |\sum_j \cos 2\Pi h x_j|$, observed on relative scale, in descending order of g (for simplicity, all amplitudes assumed to be different, $i = 1$ denoting the strongest amplitude g). - Then, from the sequence of the amplitudes alone, i.e. from the sequence of the corresponding h_i, defining n-1 independent inequalities of the type $g(h_i) > g(h_{i+1})$, one obtains in $\mathbf{A}^m$ deductively either one, or a finite number p of discrete, confined m-dimensional solution region(s) summarized as $\mathbf{L}_n$. Each of them is enveloped by a (hopefully) sufficient number of (m-1)-dimensional ''isosurfaces'' defined by $g(h_{i+1})/g(h_i) \leqslant 1$ on ''absolute scale'' and can be considered as a possible approximate solution for $\boldsymbol{x}+\Delta\boldsymbol{x}$ [2]. This principal result holds even for $n < m$, though the $|\Delta\boldsymbol{x}|$ may become impractically large, at least in some of the directions j, for too small n/m. Vice versa of course, $|\Delta\boldsymbol{x}|$, averaged over j, usually decreases with increasing n: $|\mathbf{L}_{n+1}| \leqslant |\mathbf{L}_n|$, and also $p_{n+1} \leqslant p_n$. For n not too large, $\langle|\Delta\boldsymbol{x}|\rangle$ was obtained smaller than found for the corresponding spatial resolution of a scattering density map computed by Fourier inversion using the same n reflections with correctly signed $g(h)$. - For $p > 1$, one of the p structure models is the correct one. If two or more models remain stable with increasing n, homometric solutions must be expected whereas a single model, $p = 1$, gives proof of a *unique solution* within $|\Delta\boldsymbol{x}|$. - Alternatively, a similar result can also be obtained by comparing each (or some) of n amplitudes $g(h)$ with their average, thus employing up to n inequalities, also on ''absolute scale''. (Their corresponding isosurfaces appear less complicated than those mentioned above.) Using optimal contrast in the $g(h)$, rather small solution regions may emerge from well selected data. - Ideas for obtaining two- and three-dimensional structures are briefly addressed in [3]. - The proposed talk shall provide algorithms used for examples to be presented and discuss practical aspects of this method as well as its limitations, advantages and shortcomings.

[1] Fischer et al., Z. Kristallogr. 220 (2005) 643-656
[2] Kirfel et al., Z. Kristallogr., submitted (2005)
[3] Zimmermann et al., Abstracts DGK meeting (2005) 122