B values are lower, making it easier to refine a structure. Second, at low temperatures the data extends to a higher resolution thus increasing the ratio of the number of observations to parameters, leading to a higher accuracy in refined parameters. The tests of the method also indicate that the accuracy of the refinement is largely limited by the accuracy of the data available. Therefore, we also recommend that the data be collected on the fewest possible number of crystals and over the shortest possible time, thus leading to a more consistent data set.

I am very grateful to Drs Richard Garwin and David Sayre for introducing me to the wonderful world of structure determination using X-ray crystallography. I also thank them for continued guidance, encouragement, and many useful suggestions. Thanks are also due to Drs Karl Hardman and Neil Isaacs for many fruitful discussions and suggestions. Professor Dorothy Hodgkin of Oxford University and Dr Guy Dodson of York University provided the moral support and the data for insulin refinement. Dr. A. J. Geddes of the University of Leeds provided the data on barium beavuricin complex, Dr T. Takano of Cambridge University provided the data on myoglobin, and Dr R. B. Von Dreele of the University of Arizona provided the data on 6-acetyldolatriol.

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Correlation between Third Cumulants in the Refinement of Noncentrosymmetric Structures

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It is shown that correlation between the third-cumulant coefficients in noncentrosymmetric structures restricts the number of coefficients which can be refined. In the space group $P1$ all ten coefficients of one atom have to be kept fixed.

With the accurate neutron diffraction data that is now becoming available, it is possible to refine third- (and even fourth) cumulant coefficients. This note is concerned with the restriction on the number of refinable third-cumulant coefficients, arising from correlation between those coefficients in noncentrosymmetric structures. The symmetry restrictions on cumulants for atoms at special positions are tabulated in *International Tables for X-ray Crystallography* (1974) (*IT*) and by Birss (1964) (who works in a Cartesian coordinate system).

The structure factor equation including third cumulants is of the form

$$F(\mathbf{H}) = \sum_{\kappa=1}^{n} f_\kappa \exp(2\pi i x_i h_i - b_{ij} h_i h_j - i c_{ijk} h_i h_j h_k), \quad (1)$$

where $\mathbf{H}$ is the diffraction vector, and h_i ($i = 1, 2, 3$) are the Miller indices. If the third-cumulant coefficients c_{ijk}

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are set to zero, x_i refers to the fractional coordinates of the mean position of the κth atom in the unit cell and b_{ij} is identical with the usual anisotropic temperature-factor coefficients. The repeated-index summation convention is assumed in writing (1) and so, because x_i, b_{ij} and c_{ijk} are invariant to pair-wise interchange of the indices, there are three x_i terms, six b_{ij} terms and ten c_{ijk} terms for each atom κ in the unit cell. By including c_{ijk} in the structure-factor equation, allowance is made for the skewness of the probability-density function of the vibrating atom: this skewness can arise from anharmonic motion or from librational motion (Willis & Pryor, 1975).

In the refinement of hexamethylenetetramine, Duckworth, Willis & Pawley (1970) found an interdependence between the third cumulants, c_{123}, of the three atoms (C, N and H) in the asymmetric unit. They pointed out that (i) the symmetry transformations of the space group $I\bar{4}3m$ lead to the same value of c_{123} for all symmetry-related atoms, and (ii) changing c_{ijk} for all atoms in a unit cell by the same amount, Γ_{ijk}, has the effect of multiplying each structure amplitude by a phase factor $\exp(-i\Gamma_{ijk}h_ih_jh_k)$ but does not alter its magnitude.

The phenomenon is not restricted to this space group but is common to most noncentrosymmetric space groups. In the space group $P1$ the statements (i) and (ii) hold for all ten third cumulants so that, for a least-squares refinement in that space group, ten cumulants (one for each index combination) have to be fixed at arbitrary values in close analogy to the positional parameters that have to be fixed to define the origin. In fact, similar arguments will hold for all odd-order cumulants.

In a centrosymmetric space group no such arbitrariness can exist, in fact all ten third cumulants change sign under the transformation by a centre of symmetry.

Other symmetries put restrictions on some of the ten terms. Consider a structure with a twofold axis along **b**. This transformation will lead to a change of sign for c_{111}, c_{113}, c_{122}, c_{133}, c_{223}, and c_{333}. This means that conditions (i) and (ii) do not hold for these six terms and they can therefore be refined normally for all atoms except those situated on the twofold axis. For an atom at this special position these six terms are zero, which is what is tabulated in *IT* or by Birss (1964). For the remaining four terms there are no restrictions imposed by the twofold axis and one of each of these has to be fixed in the refinement unless fixed by some other symmetry.

A 2_1 axis gives the same changes of sign as the corresponding twofold axis and thereby the same six terms can be refined normally. Similarly, a glide plane will, just as a mirror plane, give sign changes for four terms, which can then be refined normally.

The easiest way to find which values are bound by symmetry probably is to look in the tables mentioned (*IT* or Birss, 1964) for the restrictions imposed by the point group corresponding to the actual space group. A zero in the tables corresponds to a cumulant for which a zero level is defined by symmetry and which can therefore be refined normally.

For point group 222 we find a non-zero entry only for c_{123} and for a crystal belonging to this point group one c_{123} will have to be kept at an arbitrary value.

For point group $\bar{4}m2$ we find two non-zero entries, namely $c_{113} = -c_{223}$. This means that one of the c_{113}'s or of the c_{223}'s has to be given an arbitary value. That only one is arbitrary can be seen from the fact that the diagonal twofold axis relates c_{113} of one atom to c_{223} of one of the equivalent atoms. It is also consistent with 222 being a subgroup of $\bar{4}m2$.

A similar case was met in the refinement of tellurium (Larsen, Hazell, Pawley & Mackenzie, 1978). The space group is $P3_121$ with tellurium on a twofold axis at $x, 0, \frac{1}{3}$. The program used for the refinement works in an orthogonal system with its a' and c' axes coinciding with the conventional a and c.

The special position $2\|x$ has the following non-zero cumulants: c_{111}, c_{122}, c_{123}, and c_{133}. The point group 32 corresponding to space group $P3_121$ would place further restrictions on the cumulants. We refer to Table 4 by Birss where we find for the orientation $3\|z$, $2\|y$ the condition $c_{112} = -c_{222}$, all other terms 0. We have to interchange x and y so we have the condition $c_{122} = -c_{111}$ for point group 32 in the orientation we use. For the refinement this meant that c_{123} and c_{133} could be refined normally but a singular matrix resulted unless either c_{111} or c_{122} was kept fixed. If one was increased, the other decreased by the same amount.

If we had referred to the usual hexagonal coordinates and used Table 5.5C in IT, the twofold axis would have given six non-zero, interrelated components: c_{111}, $c_{112} = c_{122}$, $c_{113} = c_{123}$, c_{133}. The point group has non-zero entries only for $c_{112} = c_{122}$ and this is therefore the arbitary parameter.

Our conclusion is that if one refines third cumulants for a noncentrosymmetric structure, it is necessary to keep fixed a parameter corresponding to each unique, non-zero entry in IT, Table 5.5C, for the point group.

It could of course be argued, just as in the case of arbitrary coordinates, that it would be more reasonable to fix the sum of c_{ijk} for all atoms rather than fixing c_{ijk} for a particular atom, but in many least-squares programs this would be more troublesome.

It should be noted that the third cumulants are arbitrary only as far as the crystallographic refinement goes. For a physical interpretation such as curvilinear motion, the third cumulants will have well-defined values, not necessarily zero. This is demonstrated in the refinement of hexamethylenetetramine.

For a noncentrosymmetric structure the phases but not the numerical values of all structure factors change if we alter certain cumulants by arbitrary amounts. This means that the shapes of peaks on a Fourier map can be changed in an arbitrary way. In the case of the tellurium structure mentioned above, the peaks in the Fourier map were changed from round to triangular shape in this way.

This is another reason, apart from that given by Coppens (1974), why electron density maps for noncentrosymmetric structures may not be meaningful.

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L'Association des Familles de Wyckoff dans les Changements de Repère Conventionnel des Groupes Spatiaux et les Passages aux Sous-groupes Spatiaux*

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This paper is the continuation of another paper devoted to the systematic derivation of space subgroups and changes in standard setting of space groups. In the present paper, the correspondence of the sets of equivalent positions in such transitions is examined. Any set W_G of general positions of the space group G splits up into $i_{g/G}$ sets W_g of general positions of the space subgroup g ($i_{g/G}$ is the index of subgroup g): there is a one-to-one correspondence between the W_g sets and the complexes of g in the partition of G; the coordinates of each W_g are obtained, as a function of coordinates of W_G, from generating the symmetry operation of the corresponding complex. Miscellaneous examples of splitting of the W_G set are investigated in the transitions: $I422$–$P222$, $Fddd$–Bb, $P\bar{1}$–$P\bar{1}$, $I23$–$F23$, $P6_222$–$P222$. Any set W_G^P of special positions of G is the result of the superposition of general positions on particular points of point symmetry P. Such superpositions arise in the connected sets of g; there are three ways of grouping the positions in these sets: superposition in one set which turns into one special set W_g^p, superposition of several general sets which become one general set W_g, and mixed inner–outer superposition which leads to one special set of positions W_g^p, their point groups being any subgroup p of P. These properties are illustrated by example of the transition $P6_222$–$P222$ (10 types of special sets W_G^P). In the changes in standard setting in a given space group, each general or special set is connected with only one set; if the change of setting is associated with any symmetry operation of the space group, each set of positions is applied to itself.

Dans un mémoire précédent (Billiet, Sayari & Zarrouk, 1978), nous avons développé une méthode qui traite la dérivation systématique des changements de repère cristallographique; il s'agit des passages qui conduisent d'un repère conventionnel d'un groupe spatial donné G à n'importe quel repère conventionnel d'un sous-groupe spatial quelconque g du groupe G; le passage d'un repère conventionnel à un autre repère conventionnel du même groupe spatial n'est qu'un cas particulier où g se confond avec G.

Il convient de compléter cette étude par l'association des familles de Wyckoff dans de tels changements de repère cristallographique. L'intérêt expérimental est immédiat car l'on est alors en mesure de proposer des

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