Short Communications

Direct structure determination in *P*1 and other non-centrosymmetric symmorphic space groups. By H. Schenk,

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In non-centrosymmetric symmorphic space groups the correct phase set need not be the one with the best Σ_2 consistency. A new criterion

$$P1C = \sum_h \sum_k \frac{(|U_h| - |U_k|)^2}{(1 - |U_{h+k}|)(1 - |U_{h-k}|)} |\pi - (\varphi_{h+k} + \varphi_{h-k} - 2\varphi_h)|$$

is shown to be more powerful in specifying the correct phase set.

Introduction

In direct phase determinations the Σ_2 relation,

$$\varphi_h = \frac{\sum_k |E_h E_k E_{h-k}| (\varphi_k + \varphi_{h-k})}{\sum_k |E_h E_k E_{h-k}|}, \quad (1)$$

is most commonly used. In general the set of phases which is most consistent with the Σ_2 relation corresponds to the correct structure. However, in symmorphic space groups (*i.e.* space groups not containing glide planes or screw axes) the most consistent Σ_2 solution is the trivial one with all phases $\varphi_h = 0$.

Recently we described a direct method for solving structures in centrosymmetric symmorphic space groups (Schenk & De Jong, 1973). In this method the Σ_2 relation is only used for generating symbolic signs, whilst the correct Σ_2 solution is found by means of the criterion:

$$HKC = \sum_h \sum_k \frac{(|U_h| - |U_k|)^2}{(1 - |U_{h+k}|)(1 - |U_{h-k}|)} S(h+k) S(h-k). \quad (2)$$

This criterion is consistent with the Harker–Kasper inequalities for $\bar{1}$.

In this paper an analogous method for non-centrosymmetric symmorphic space groups is proposed. As in the centrosymmetric groups the Σ_2 consistency cannot be used to determine the correct solution and it can be expected that a new criterion related to (2) will be more successful.

Criterion for non-centrosymmetric symmorphic space groups

From the Harker–Kasper inequalities for $\bar{1}$ it follows that if

$$|U_h|, |U_{h-k}|, |U_{h+k}| \text{ are large, } |U_k| = 0$$

and

$$|U_h|^2 > (1 - |U_{h+k}|)(1 - |U_{h-k}|),$$

then the sign relation

$$S(h+k)S(h-k) = -1 \quad (3)$$

must hold (*e.g.* Woolfson, 1961).

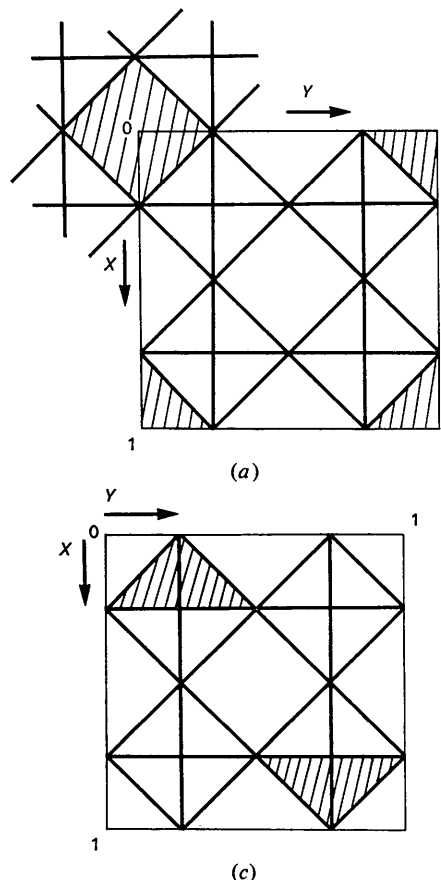This relation can be interpreted geometrically. An example: in Fig. 1, Fourier components of the reflexions

Fig. 1. The lines for which the Fourier components $\cos(2\pi x, 0, 0)$, $\cos(0, 2\pi y, 0)$ $\cos(2\pi x, 2\pi y, 0)$ and $\cos(2\pi x, -2\pi y, 0)$ are zero have been drawn heavy. 100, 110 and 1$\bar{1}$0 are strong reflexions. If $S(100) = S(110) = S(1\bar{1}0) = +1$ then a concentration of electron density can be expected in the shaded part of (*a*). If $S(100) = S(1\bar{1}0) = +1$ and $S(110) = -1$, then a concentration of electron density can be expected in another part of the cell, which is shaded in (*b*).
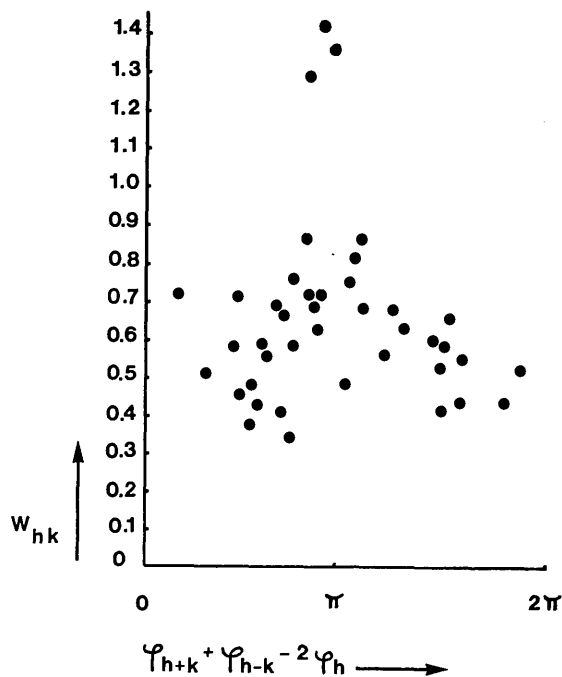
Fig. 2. The weights W_{hk} are plotted as a function of $\varphi_{h+k}+\varphi_{h-k}-2\varphi_h$ for a hypothetical structure with 10 equal atoms in a unit cell of $P1$ symmetry.

$h=100$, $h+k=110$, $h-k=1\bar{1}0$, and $k=010$ have been drawn. In Fig. 1(a) the signs of the first three reflexions are all $+1$ and in Fig. 1(b) $S(100)=S(1\bar{1}0)=+1$ and $S(110)=-1$.

If these three reflexions are all strong then on the basis of the signs a concentration of electron density can be expected in the shaded parts in both Figures. Now it is easy to see that if reflexion 010 is strong then the situation in Fig. 1(a) is the most probable one, but if 010 is weak then the situation in Fig. 1(b) is the more probable. Thus Fig. 1(a) is an illustration of the Σ_2 relation and Fig. 1(b) of relation (3).

This geometrical explanation is not restricted to centro-symmetric structures, so that a modified relation can be proposed for non-centrosymmetric structures:

$$\varphi_{h+k}+\varphi_{h-k}-2\varphi_h=\pi \qquad (4)$$

for strong structure factors h, $h+k$ and $h-k$ and weak k. For centrosymmetric phases (4) is equivalent to (3).

This suggests the following criterion for non-centrosymmetric symmorphic space groups:

$$P1C=\sum_h \sum_k \frac{(|U_h|-|U_k|)^2}{(1-|U_{h+k}|)(1-|U_{h-k}|)}$$
$$\times |\pi-(\varphi_{h+k}+\varphi_{h-k}-2\varphi_h)| \qquad (5)$$

in which $0\le\varphi_{h+k}+\varphi_{h-k}-2\varphi_h\le 2\pi$.

The maximum value of $P1C$ is found for all phases $\varphi_h=0$ and $P1C$ is expected to have a minimum value for the correct phase set. For centrosymmetric phase sets $P1C$ is equivalent to HKC.

Experimental test

The $P1C$ criterion has been tested in two artificial structures, in which the positions of the atoms were randomly generated. For a ten-atom structure the results are $P1C$ (correct phases) $=8\cdot64$ and $P1C$ (all phases $=0$) $=26\cdot64$. The weights

$$W_{hk}=\frac{(|U_h|-|U_k|)^2}{(1-|U_{h+k}|)(1-|U_{h-k}|)}$$

of all terms of $P1C$ are plotted in Fig. 2 as a function of $(\varphi_{h+k}+\varphi_{h-k}-2\varphi_h)$. This plot shows a concentration around π. For a 20-atom structure, $P1C$ (correct phases) $=5\cdot85$ and $P1C$ (all phases $=0$) $=15\cdot13$.

In our opinion the difference in $P1C$ values is large enough to discern the correct solution.

References

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Comment on *The dependence of the Debye–Waller temperature factors on the atomic masses* by C. Scheringer.

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The theorem on the independence of Debye–Waller B values on the atomic masses in the limit of high temperatures (from which it follows that the heavier atoms in a lattice do not necessarily have the smaller B values) is further discussed. It appears that the high-temperature condition prevents direct application of the theorem in its present form to molecular crystals.

Introduction

Recently Scheringer (1973), prompted by the theorem on the irrelevance of the atomic masses for Debye–Waller

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B values in the limit of high temperatures (Huiszoon & Groenewegen, 1972), has stressed the mass dependence of atomic mean-square amplitudes of vibration. Scheringer does not question the correctness of the derivation of the theorem; however, he argues that the theorem has been misinterpreted. We disagree with Scheringer and want to make some further remarks concerning Scheringer's point of view.