Direct Methods and their Application to Structures showing Superstructure Effects

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USE OF MODIFIED SAYRE EQUATION FOR SUPERSTRUCTURES

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I. PSEUDO-TRANSLATIONAL SYMMETRY AND PSEUDO-SYSTEMATIC EXTINCTION

For a crystal having a pseudo-translation-vector $\underset{\sim}{t} = \underset{\sim}{T}/n$, where $\underset{\sim}{T}$ is the shortest exact translation-vector in the crystal parallel to $\underset{\sim}{t}$ and n is an integer, the structure factor can be written approximately as follow (Fan & Zheng, 1982):

$$\underset{\sim}{F}_{\underset{\sim}{H}} \sim \sum_{j=1}^{N/n} f_j e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_j} \left[1 + e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{T}} + \cdots + e^{i2\pi \underset{\sim}{H}\cdot(n-1)\underset{\sim}{T}}\right] \qquad (1)$$

The sum of the series in the bracket of (1) is given by

$$S = \frac{\exp(i2\pi\, \underset{\sim}{H}.n\underset{\sim}{t}) - 1}{\exp(i2\pi\, \underset{\sim}{H}.\underset{\sim}{t}) - 1} = \begin{cases} n, & \text{when } \underset{\sim}{H}.\underset{\sim}{t} = \text{integer} \\ 0, & \text{when } \underset{\sim}{H}.\underset{\sim}{t} \neq \text{integer} \end{cases}$$

Notice that $\underset{\sim}{H}.n\underset{\sim}{t} = \underset{\sim}{H}.\underset{\sim}{T}$ = integer. Hence, all reflections with $\underset{\sim}{H}.\underset{\sim}{t} \neq$ integer will be systematically very weak leading to an effect of pseudo-systematic extinction. The phases of these 'weak' reflections will be very difficult to determine by conventional methods.

II. PHASES OF THE 'WEAK' REFLECTIONS DERIVED FROM THE 'STRONG' ONES

1. Modified Sayre equation for partially known structures

For a squared structure $\rho^2(\underset{\sim}{r})$, the structure factor of which can be written as

$$\underset{\sim}{F}^{sq}_{\underset{\sim}{H}} = \frac{1}{V} \sum_{\underset{\sim}{H}'} \underset{\sim}{F}_{\underset{\sim}{H}'} \underset{\sim}{F}_{\underset{\sim}{H}-\underset{\sim}{H}'} \,. \qquad (2)$$

If the atoms in $\rho(\underset{\sim}{r})$ do not overlap each other, then $\underset{\sim}{F}^{sq}_{\underset{\sim}{H}}$ can be expressed by the positional vector $\underset{\sim}{r}_j$ of the atoms in $\rho(\underset{\sim}{r})$, i.e.

$$\underset{\sim}{F}^{sq}_{\underset{\sim}{H}} = \sum_{j=1}^{N} f_j^{sq} e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_j} \,, \qquad (3)$$

where f_j^{sq} is the atomic scattering factor of the jth squared atom. Let the subscripts u and p denote the unknown and the known part of the structure respectively, then (3) becomes

$$\underset{\sim}{F}^{sq}_{\underset{\sim}{H}} = \sum_{u} f_u^{sq} e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_u} + \sum_{p} f_p^{sq} e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_p} \,. \qquad (4)$$

Assuming that the unknown part of the structure is composed of identical atoms, we can write

$$\underset{\sim}{F}_{\underset{\sim}{H}}^{sq}=(f_u^{sq}/f_u)\sum_u f_u e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_u}+(f_u^{sq}/f_u)\sum_p f_p e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_p}-\sum_p (f_u^{sq}/f_u) f_p e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_p}+\sum_p (f_p^{sq}/f_p) f_p e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_p}$$

Let $1/a_u = f_u^{sq}/f_u$, $1/a_p = f_p^{sq}/f_p$,

we obtain

$$\underset{\sim}{F}_{\underset{\sim}{H}}^{sq} = \frac{1}{a_u}\left[\sum_u f_u e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_u}+\sum_p f_p e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_p}\right]+\sum_p\left(\frac{1}{a_p}-\frac{1}{a_u}\right) f_p e^{i2\pi \underset{\sim}{H}\cdot\underset{\sim}{r}_p}$$

$$= \frac{1}{a_u}\underset{\sim}{F}_{\underset{\sim}{H}} + \sum_p\left(\frac{1}{a_p}-\frac{1}{a_u}\right)\underset{\sim}{F}_{\underset{\sim}{H},p} \quad , \tag{5}$$

where $\underset{\sim}{F}_{\underset{\sim}{H},p}$ denotes the contribution of the known part to the structure factor $\underset{\sim}{F}_{\underset{\sim}{H}}$. Substituting (5) into (2) it finally follows that

$$\underset{\sim}{F}_{\underset{\sim}{H}} = \frac{a_u}{V}\sum_{\underset{\sim}{H}'}\underset{\sim}{F}_{\underset{\sim}{H}'}\underset{\sim}{F}_{\underset{\sim}{H}-\underset{\sim}{H}'} - \sum_p\left(\frac{a_u}{a_p}-1\right)\underset{\sim}{F}_{\underset{\sim}{H},p} \quad . \tag{6}$$

Apart from the other applications (Fan, 1965), (6) can be used to facilitate the determination of the phases of the 'weak' reflections when some kind of pseudo-translational symmetry occurs. This is elucidated in the following example (Fan, 1975):

SHAS, $C_5H_6O_5N_3K$

The crystals belong to space group $P2_12_12_1$ with a=7.51, b=9.95, c=10.98 Å and Z=4. The arrangement of the K-atoms possesses a subperiodicity of translation $\underset{\sim}{t} = (\underset{\sim}{a}+\underset{\sim}{b}+\underset{\sim}{c})/2$. Consequently reflections with h+k+l odd are systematically 'weak'. The phases of which were proved to be difficult to determine by either Patterson or conventional direct methods.

Let $\underset{\sim}{F}_{\underset{\sim}{H}}^{o}$ and $\underset{\sim}{F}_{\underset{\sim}{H}}^{e}$ denote the structure factors with h+k+l odd and even respectively. Notice that $\underset{\sim}{F}_{\underset{\sim}{H},p}^{o} = 0$ in the present example, then according to (6) we can write

$$\underset{\sim}{F}_{\underset{\sim}{H}}^{o} = \frac{a_u}{V}\sum_{\underset{\sim}{H}'}\underset{\sim}{F}_{\underset{\sim}{H}'}^{o}\underset{\sim}{F}_{\underset{\sim}{H}-\underset{\sim}{H}'}^{e} \quad . \tag{7}$$

Assuming that the phases of $\underset{\sim}{F}_{\underset{\sim}{H}-\underset{\sim}{H}'}^{e}$ are controlled by the heavy-atoms, then the phases of $\underset{\sim}{F}_{\underset{\sim}{H}}^{o}$ can be easily derived from (7). Fig.1a shows the Fourier projection along the $\underset{\sim}{a}$ axis calculated with the heavy-atom phases only. In this projection there are two pseudo mirror planes, shown as two dotted lines parallel to the $\underset{\sim}{b}$ and $\underset{\sim}{c}$ axes repectively, which are originated from the pseudo-translational symmetry $\underset{\sim}{t}$. Fig.1b shows the Fourier projection calculated using heavy-atom phases for the 'strong' reflections and direct method phases for the 'weak' ones. In this projection, the pseudo-symmetry has been effectively eliminated and the true structure is revealed clearly.

2. Modified Sayre equation for superstructures

A superstructure can be described by superimposing a difference structure on to a subcell-structure, in which the atoms are related exactly by the pseudo-translational symmetry. We write

$$\rho(\underset{\sim}{r}) = \rho_{sub}(\underset{\sim}{r}) + \Delta\rho(\underset{\sim}{r}) \quad . \tag{8}$$

By squaring both sides of (8) and neglecting the term $\Delta\rho^2(\underset{\sim}{r})$, it follows that

$$\rho^2(\underset{\sim}{r}) = \rho^2_{sub}(\underset{\sim}{r}) + 2\rho_{sub}(\underset{\sim}{r})\Delta\rho(\underset{\sim}{r}) \quad , \tag{9}$$

from which, by Fourier transformation, one finds

$$\underset{\sim}{F}^{sq}_{\underset{\sim}{H}} = \underset{\sim}{F}^{sq}_{\underset{\sim}{H}\,sub} + \frac{2}{V}\sum_{\underset{\sim}{H'}} \underset{\sim}{F}_{\underset{\sim}{H'}sub}\,\Delta\underset{\sim}{F}_{\underset{\sim}{H}-\underset{\sim}{H'}} \quad . \tag{10}$$

On the other hand, by Fourier transforming (8), we have

$$\underset{\sim}{F}_{\underset{\sim}{H}} = \underset{\sim}{F}_{\underset{\sim}{H}\,sub} + \Delta\underset{\sim}{F}_{\underset{\sim}{H}} \tag{11}$$

Consider a reciprocal vector $\underset{\sim}{H}$, if it does not fall on a grid point of the reciprocal lattice of the subcell-structure then it must correspond to a 'weak' (Superstructure) reflection. In this case both $\underset{\sim}{F}^{sq}_{\underset{\sim}{H}\,sub}$ and $\underset{\sim}{F}_{\underset{\sim}{H}\,sub}$ equal zero. Then from (10) and (11), we obtain

$$\underset{\sim}{F}^{sq}_{\underset{\sim}{H}\,wk} = \frac{2}{V}\sum_{\underset{\sim}{H'}} \underset{\sim}{F}_{\underset{\sim}{H'}sub}\,\underset{\sim}{F}_{\underset{\sim}{H}-\underset{\sim}{H'}\,wk} \quad , \tag{12}$$

where the subscript wk denotes the 'weak' reflection. Assuming that the crystal consists of nearly identical atoms or that the contribution of the heavy-atoms to the superstructure reflections are either nearly zero or approximately as weak as those of the light-atoms, we have

$$\underset{\sim}{F}^{sq}_{\underset{\sim}{H}\,wk} \sim \frac{f^{sq}}{f}\sum_{j=1}^{N} f\, e^{i2\pi\underset{\sim}{H}\cdot\underset{\sim}{r}_j} = \frac{1}{a}\underset{\sim}{F}_{\underset{\sim}{H}\,wk} \tag{13}$$

where f is the averaged atomic scattering factor, f^{sq} is the averaged scattering factor of the squared atoms and $a = f/f^{sq}$. Substituting (13) into (12), we finally obtain

$$\underset{\sim}{F}_{\underset{\sim}{H}\,wk} = \frac{2a}{V}\sum_{\underset{\sim}{H'}} \underset{\sim}{F}_{\underset{\sim}{H'}sub}\,\underset{\sim}{F}_{\underset{\sim}{H}-\underset{\sim}{H'}\,wk} \tag{14}$$

For a superstructure, the phases of the subcell-structure reflections can be determined by conventional methods without much difficulties. Then with equation (14) the phases of the 'weak' (superstructure) reflections can be derived by making use of the phases of the subcell-structure reflections. The method has been verified using two typical superstructures (Fan, He, Qian & Liu, 1978):

Freielebenite, $PbAgSbS_3$

The structure was solved by Ito & Nowacki (1974a). It belongs to space group $P2_1/a$ with a=7.518, b=12.809, c=5.940 Å, β=92.25° and Z=4. There are two pseudo-translation-vectors in the structure, i.e. $\underset{\sim}{t}_1 = \underset{\sim}{a}/2$ and $\underset{\sim}{t}_2 = \underset{\sim}{b}/3$. 105 reflections of the hk0 zone were used in the test. The phases (signs) of 11 'strong' reflections with h = 2n and k = 3n were first derived by conventional direct method Then by using a symbolic addition procedure, the signs of 68 out of the total 94 'weak' reflections were derived from (14). These reflections were arraneged in descending order of $w = |\underset{\sim}{F}_{\underset{\sim}{H}}|_{wk}\sum_{\underset{\sim}{H'}} |\underset{\sim}{F}_{\underset{\sim}{H'}sub}\underset{\sim}{F}_{\underset{\sim}{H}-\underset{\sim}{H'}\,wk}|$

and cumulated into 4 groups, which contain reflections with w greater than the averaged value of w times 0.3, 0.2, 0.1 and 0.0 respectively. The result is shown in Table 1.

Iordanite, $Pb_{28}As_{12}S_{46}$

The structure was solved by Ito & Nowacki (1974b). It belongs to space group $P2_1/m$ with a=8.918, b=31.899, c=8.462 Å, β=117.79° and Z=1. There are two pseudo-translation-vectors in the structure, i.e. $\underset{\sim}{t}_1 = \underset{\sim}{a}/2$ and $\underset{\sim}{t}_2 = \underset{\sim}{c}/2$. 252 reflections of the hk0 zone and 222 reflections of the 0kl zone were used in the test. They were treated in the way similar to that in the preceding example. The results are listed in Tables 2 and 3.

From the results shown above, it can be recognized that both the two tested superstructures, Freielebenite and Iordanite, may actually be solved by the method described.

III. PROGRAMS FOR SOLVING CRYSTAL STRUCTURES HAVING PSEUDO-TRANSLATIONAL SYMMETRY

The procedure described above has been improved and made automatic leading to a modified version of the MULTAN-80 (Fan, Yao, Main & Woolfson, 1983). The program has been proved, by three practical examples, to be very efficient. It can solve superstructures automatically without the necessity of knowing the subcell-structure. A new version is to be released by the end of this year, which possesses the following feathers:

1. The intensity data are searched automatically to see whether there exists any pseudo-systematic extinction. If so, the reflections are grouped according to the index relationships found by the program. Alternatively the user can also input index relationships for the classification of reflections in different groups.
2. The temperature and scaling factors are calculated for different index groups separately or the user may specify the values of these factors for different index groups independently.
3. The reflections which participate in the phase derivation are selected according to the E values calculated independently for different index groups. However, the E values actually used in the tangent refinement are those calculated according to the overall temperature and scaling factors.
4. The tangent refinement will be carried out in two steps. In the first step, only the phases of the 'strong' reflections are developed. Then in the second step, those phases previously derived and having their weight greater than a certain limit will be treated as known phases and the phases of the 'weak' reflections together with those of the remaining 'strong' ones are developed.
5. Unlike the original MULTAN-80 program, E-maps are calculated using the E values before, but not after, rescaling.

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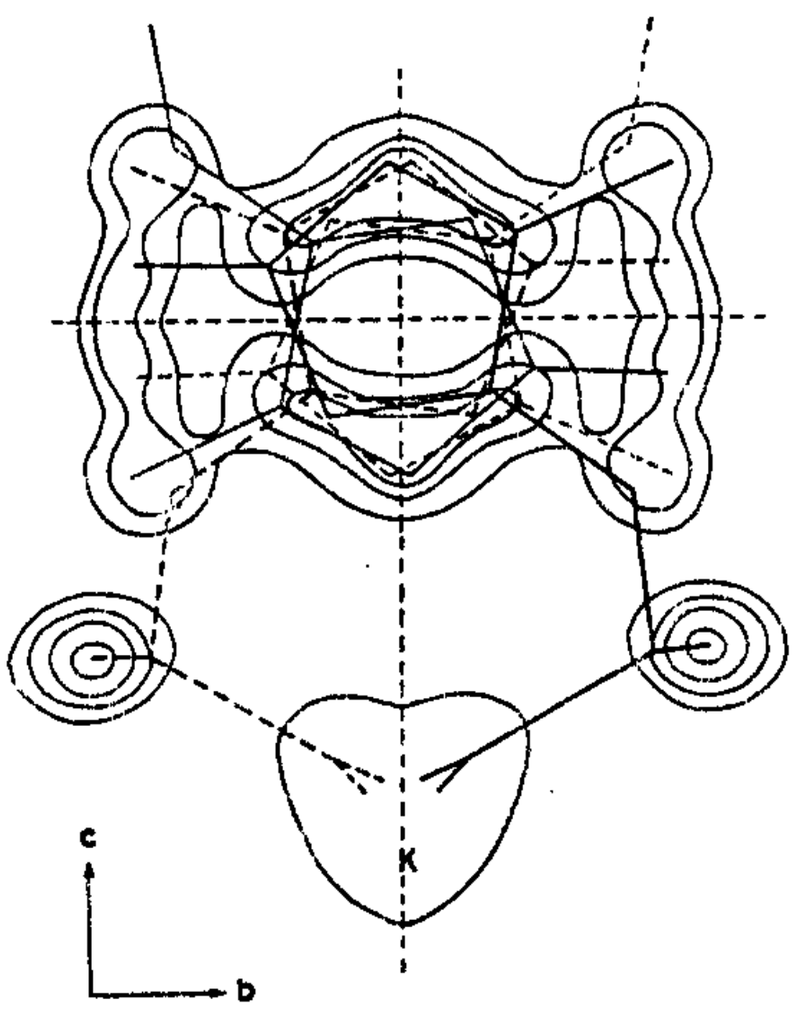
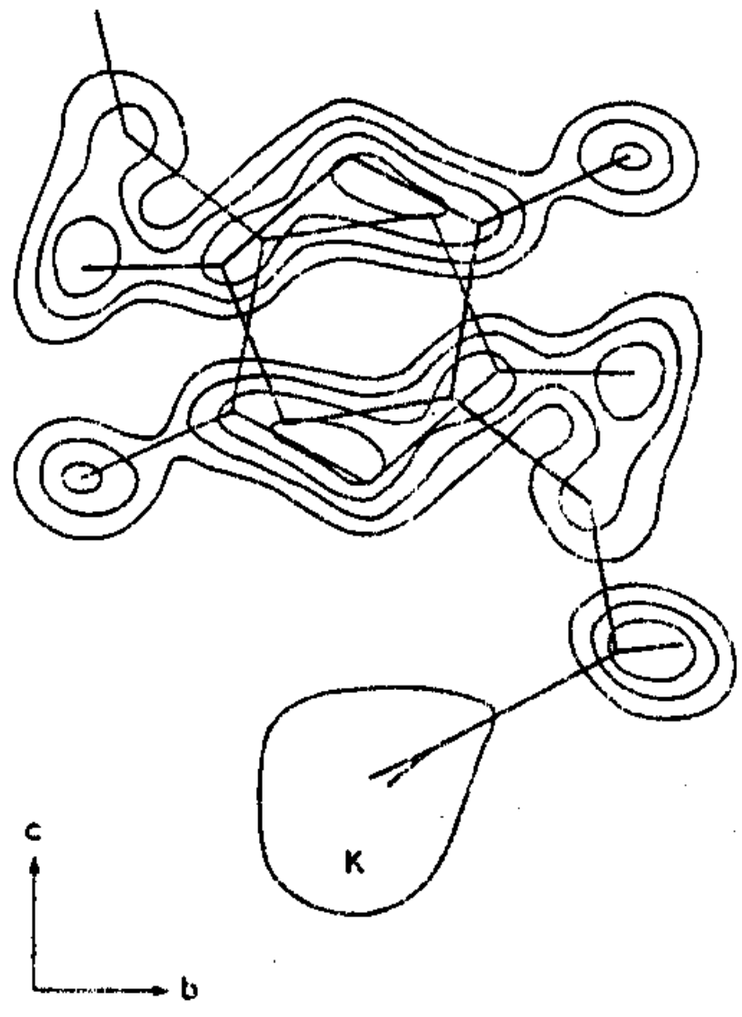
Fig. 1. Fourier projections of SHAS.
a) Calculated with the heavy-atom phases.
b) Translational ambiguity resolved using the modified Sayre equation.



(a)



(b)

Table 1
Test on 68 'weak' hk0 reflections of $PbAgSbS_3$

Gn	Wmin	Nr	%
1	.3<W>	41	100
2	.2<W>	45	97.8
3	.1<W>	59	91.5
4	.0	68	88.2

Table 2
Test on 118 'weak' hk0 reflections of $Pb_{28}As_{12}S_{46}$

Gn	Wmin	Nr	%
1	.3<W>	58	100
2	.2<W>	70	100
3	.1<W>	84	98.8
4	.0	118	89.0

Table 3
Test on 72 'weak' 0kl reflections of $Pb_{28}As_{12}S_{46}$

Gn	Wmin	Nr	%
1	.3<W>	39	94.9
2	.2<W>	46	89.1
3	.1<W>	55	85.5
4	.0	72	79.2

Gn --- Group number;
Wmin --- The minimum value of W in the group;
<W> --- The averaged W over the whole set of 'weak' reflections;
Nr --- The number of reflections in the group;
% --- The percentage of reflections with signs correctly determined.