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The Program *SAPI* and its Applications. III. Determination of Structures having Pseudo-Translational Symmetry

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Abstract

Optimization has been made of the program *SAPI* for automatic solution of structures having pseudo-translational symmetry. This includes: (1) floating default cutoff of *E*'s; (2) automatic and user-adjustable balance between the number of systematically strong reflections and that of the systematically weak ones; (3) *R* factors for reflection subsets corresponding to the 'strong' group and the 'weak' groups. Examples on solving structures with pseudo-translational symmetry are discussed in detail. They include known as well as unknown structures and centrosymmetric as well as non-centrosymmetric structures, all of which can be solved starting from a default run of *SAPI*.

Introduction

Pseudo-translational symmetry often occurs in minerals and some important inorganic as well as organic crystals. Structures having pseudo-translational symmetry give rise to complicated positional ambiguity in real space or phase ambiguity in reciprocal space. Hence structure analysis of such kinds of crystals remains a difficult problem. The first example of applying direct methods to remove the phase ambiguity arising from pseudo-translational symmetry was given by Fan Hai-fu (1975). Since then the method has been greatly improved (Fan Hai-fu, He Luo, Qian Jin-zi & Liu Shi-xiang, 1978; Fan Hai-fu, Yao Jia-xing, Main & Woolfson, 1983) and finally incorporated into the program *SAPI* (Fan Hai-fu, 1986). For automatic discrimination of pseudo-translational symmetry and automatic grouping of the reflections accordingly, an additional subroutine *AUTOGP* is provided in *SAPI* (Fan Hai-fu, Yao Jia-xing & Qian Jin-zi, 1988). This enables structures having pseudo-translational symmetry, such as superstructures, to be solved in a fully automatic way. Apart from the above, optimization has also been made in *SAPI* to strengthen the power of dealing with structures having pseudo-translational symmetry. In this paper some treatments for the optimization are discussed and examples of practical applications are given.

Default cutoff of *E*'s

In most direct-methods programs the default minimum value of normalized structure factors, *E*'s, accepted for phase derivation is set to about 1·2. However, for structures having pseudo-translational symmetry, especially for superstructures, the total number of reflections will sometimes be much smaller than usual. In this case the number of *E*'s accepted for phase derivation may not be enough to ensure a reliable result. In order to overcome this difficulty, the default minimum value of *E*'s in *SAPI* is made automatically adjustable. The value 1·2 is used first; however it will be automatically changed by the program to 0·9 whenever the total number of input reflections is smaller than 500.

Balance between 'strong' and 'weak' reflections

One special feature of structures having pseudo-translational symmetry is that the reflections can be classified into two categories, one systematically strong and the other systematically weak. In our method, these two categories of reflections are normalized separately before they are selected for phase determination. This makes the resultant *E*'s of systematically weak reflections as large as those of systematically strong ones so as to ensure that enough 'weak' reflections take part in phase derivation. However, owing to inaccuracy of the scaling factor and/or other reasons, in the selected set of *E*'s the ratio between the number of 'strong' reflections and that of the 'weak' ones will sometimes differ from that in the original set of diffraction data. Experience has shown that better results can be obtained by keeping the ratio in the selected set of *E*'s roughly equal to the original one. This is automatically done by the program. On the other hand it is also possible

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Table 1. *Atomic positions of freieslebenite*

(*a*) Results of Ito (1973)

	Average position			True position			Shift		
	X	*Y*	*Z*	*X*	*Y*	*Z*	d*X*	d*Y*	d*Z*
Pb	0·375	0·417	0·250	0·350	0·415	0·253	−0·025	−0·002	+0·003
Ag	0·375	0·750	0·250	0·378	0·760	0·212	+0·003	+0·010	−0·038
Sb	0·375	0·083	0·250	0·365	0·087	0·272	−0·010	+0·004	+0·022
S1	0·125	0·250	0·250	0·138	0·219	0·346	+0·013	−0·031	+0·096
S2	0·125	0·583	0·250	0·135	0·622	0·131	+0·010	+0·039	−0·119
S3	0·125	0·917	0·250	0·148	0·942	0·266	+0·023	+0·025	+0·016

(*b*) Results from a default run of *SAPI*

			Position			Shift		
Peak	Height		*X*	*Y*	*Z*	d*X*	d*Y*	d*Z*
1	4134	Pb	0·358	0·416	0·256	−0·017	−0·001	+0·006
2	3502	Ag	0·390	0·752	0·216	+0·015	+0·002	−0·034
3	2957	Sb	0·366	0·084	0·284	−0·009	+0·001	+0·034
6	1161	S1	0·132	0·213	0·362	+0·007	−0·037	+0·112
5	1196	S2	0·131	0·621	0·139	+0·006	+0·038	−0·111
4	1247	S3	0·145	0·944	0·257	+0·020	+0·027	+0·007

(*c*) Results of Fan Hai-fu *et al.* (1983)

			Position			Shift		
Peak	Height		*X*	*Y*	*Z*	d*X*	d*Y*	d*Z*
1	3266	Pb	0·363	0·413	0·261	−0·012	−0·004	+0·011
2	3264	Ag	0·387	0·751	0·220	+0·012	+0·001	−0·030
3	3148	Sb	0·366	0·087	0·266	−0·009	+0·004	+0·016
5	791	S1	0·137	0·221	0·345	+0·012	−0·029	+0·095
6	684	S2	0·123	0·621	0·141	−0·002	+0·038	−0·109
4	870	S3	0·149	0·952	0·266	+0·024	+0·035	+0·016

for the user to specify an arbitrary ratio if this is considered to be necessary.

R factors for reflection subsets

Unlike for ordinary structures, the reliability of a structure model with pseudo-translational symmetry cannot be evaluated by one overall *R* factor,

$$R=\sum \| F_{\rm obs}|-|F_{\rm cal}\|/\sum |F_{\rm obs}|,$$

since it will be dominated by the 'strong' reflections, which are mainly contributed from the subcell (average) structure and consequently bear almost no information about the difference between the true structure and the average structure. Hence in the program *SAPI*, *R* factors for the 'strong' group and the 'weak' groups are provided separately in addition to the overall *R* factor.

Practical examples

Example 1. *Freieslebenite* (*Ito & Nowacki*, 1974)

Formula: $\mathrm{PbAgSbS_3}$; space group: $P2_1/a$; unit-cell parameters: $a=7{\cdot}518$, $b=12{\cdot}809$, $c=5{\cdot}940$ Å, $\beta=92{\cdot}25°$; $Z=4$.

This is a typical superstructure and had been a test structure of the 'key shift method' (Ito, 1973). There are two pseudo-translation vectors $\mathbf{t}_1=\mathbf{a}/2$ and $\mathbf{t}_2=\mathbf{b}/3$ in the unit cell. The asymmetric unit contains only six atoms. However, Patterson or conventional direct methods led only to an average structure. The true structure differs from the average one by small

Table 2. *R factors of freieslebenite*

(*a*) Results from a default run of *SAPI*

Overall *R* factor = 31·20%

R factors for individual index groups

Group	*R* factor
1	23·77
2	37·38
3	25·68
4	41·33
5	44·60
6	28·78

(*b*) Results after one cycle of Fourier calculation based on (*a*)

Overall *R* factor = 18·70%

R factors for individual index groups

Group	*R* factor
1	8·30
2	25·49
3	27·32
4	22·94
5	27·35
6	21·66

Index relationships of the reflection groups

Group	Index relationships
1	$H=2N$ $K=3N$
2	$H=2N$ $K=3N+1$
3	$H=2N$ $K=3N+2$
4	$H=2N+1$ $K=3N$
5	$H=2N+1$ $K=3N+1$
6	$H=2N+1$ $K=3N+2$

Table 3. *Atomic positions of hwangheite*

(*a*) Results from a default run of *SAPI*

			Position			Shift		
Peak	Height		*X*	*Y*	*Z*	d*X*	d*Y*	d*Z*
1	4994	Ce1	0·000	0·000	0·258	0·000	0·000	+0·008
2	4946	Ce2	0·000	0·000	0·749	0·000	0·000	−0·001
3	4330	Ba1	0·000	0·000	0·000	0·000	0·000	0·000
4	4101	Ba2	0·000	0·000	0·506	0·000	0·000	+0·006
11	726	F1	0·000	0·000	0·318			
9	775	F2	0·000	0·000	0·688			
10	762	O1	0·275	0·146	0·132			
12	708	O2	0·275	0·147	0·388			
21	577	O3	0·150	0·292	0·617			
8	789	O4	0·148	0·291	0·873			
6	820	C1	0·000	0·000	0·130			
17	615	C2	0·000	0·000	0·388			
14	658	C3	0·000	0·000	0·618			
7	818	C4	0·000	0·000	0·886			

(*b*) Results from least-squares refinement by Qian Jin-zi *et al.* (1982)

	Position			Shift		
	X	*Y*	*Z*	d*X*	d*Y*	d*Z*
Ce1	0·000	0·000	0·255	0·000	0·000	+0·005
Ce2	0·000	0·000	0·745	0·000	0·000	−0·005
Ba1	0·000	0·000	0·000	0·000	0·000	0·000
Ba2	0·000	0·000	0·501	0·000	0·000	+0·001
F1	0·000	0·000	0·317			
F2	0·000	0·000	0·685			
O1	0·294	0·150	0·127			
O2	0·298	0·149	0·395			
O3	0·139	0·286	0·608			
O4	0·148	0·290	0·872			
C1	0·000	0·000	0·127			
C2	0·000	0·000	0·394			
C3	0·000	0·000	0·609			
C4	0·000	0·000	0·874			

Table 4. *R factors of hwangheite from a default run of SAPI*

(*a*) Calculated with the heavy atoms only

Overall *R* factor = 20·35%

R factors for individual index groups

Group	*R* factor
1	9·24
2	25·69
3	62·60
4	28·22

(*b*) Calculated with all the atoms found by *SAPI*

Overall *R* factor = 15·29%

R factors for individual index groups

Group	*R* factor
1	6·89
2	18·71
3	44·63
4	19·73

Index relationships of the reflection groups

Group	Index relationships
1	$L=4N$
2	$L=4N+1$
3	$L=4N+2$
4	$L=4N+3$

shifts of atomic positions with respect to those of the average structure. The original results on solving the complete structure by Ito (1973) are listed in Table 1(*a*). A default run of *SAPI* indicated that the structure possesses pseudo-translational symmetry. The reflections were classified automatically by the program into six index groups and normalized separately. Phase derivation resulted in an *E* map with peaks shown in Table 1(*b*). The top six peaks correspond to the six independent atoms with position shifts consistent with those in Table 1(*a*). For comparison with our previous method, the results of Fan Hai-fu *et al.* (1983) are listed in Table 1(*c*). As can be seen the present result is obviously better, since all the shifts are in the correct direction, while the previous result contains one shift in the wrong direction. Structure-factor calculation according to the positions shown in Table 1(*b*) resulted in a list of *R* factors shown in Table 2(*a*). One cycle of Fourier calculation reduced the *R* factors to those shown in Table 2(*b*). The reasonable value of *R* factors shows that the complete structure has been correctly solved.

Example 2. *Hwangheite* (*Qian Jin-zi, Fu Ping-qiu, Kong You-hua & Gong Guo-hong,* 1982)

Formula: $\mathrm{BaCeF(CO_3)_2}$; space group: $R3$; unit-cell parameters: $a=5{\cdot}070$, $c=38{\cdot}408$ Å; $Z=6$.

This is a superstructure with 14 independent atoms in the asymmetric unit. The two independent Ba atoms have their sites close to $(0, 0, 0)$ and $(0, 0, 1/2)$, while the two Ce atoms are close to $(0, 0, 1/4)$ and $(0, 0, 3/4)$. Hence there is a pseudo-translation vector t = c/4 in the unit cell. Patterson or conventional direct methods failed to give the true structure, since they could not find the positional shifts of Ba and Ce atoms correctly. A Fourier map phased with the average positions of Ba and Ce atoms yields eight rather than two independent F atoms and six instead of three O atoms for each CO_3 group. This makes the structure analysis much more difficult. However, a default run of *SAPI* automatically solved all these problems. The reflections were classified automatically into four index groups and normalized separately. The phase derivation procedure resulted in an *E* map, of which the largest four peaks correspond to the four heavy atoms with correct positional shifts. Among the 17 next largest peaks, ten correspond to the light atoms and others correspond to pseudo-translation images of some light atoms or diffraction ripples of the heavy atoms. Among the above peaks, those corresponding to true atoms are evidently larger than peaks of the corresponding pseudo-atoms. Hence there will be no difficulty in assigning a true atom to a proper peak and then rejecting the other peaks which belong to the corresponding pseudo-atoms. The result so obtained is given in Table 3(*a*) in comparison with the result of least-squares refinement by Qian Jin-zi *et al.* (1982) (Table 3*b*). As can be seen the two sets of results are consistent with each other. *R* factors calculated according to the direct-method result are given in Table 4. It turns out that just a default run of *SAPI* is able to reveal the complete superstructure. On the other hand, while the previous procedure (Fan Hai-fu *et al.*, 1983) yielded a similar result, it was not obtained by a default run of the program.

Example 3. *PTS*6 (*Lechter, Fan Hai-fu, Ke Heng-ming & Mak*, 1987)

Formula: $C_{27}H_{31}NO_9$; space group: $P2_1/c$; unit-cell parameters: $a = 24{\cdot}420$, $b = 8{\cdot}363$, $c = 24{\cdot}747$ Å, $\beta = 90{\cdot}22°$; $Z = 8$.

This is an unknown structure solved originally by *SAPI*. The structure contains a pseudo-translation vector $\mathbf{t} = \mathbf{a}/2 + \mathbf{c}/2$, which relates two independent molecules in the asymmetric unit. Consequently, reflections with index $h + l = 2N + 1$ are systematically much weaker than those with index $h + l = 2N$. Conventional direct methods failed to solve the structure. However a default run of *SAPI* revealed on the *E* map two fragments which contain 69 of the 74 independent atoms. One cycle of Fourier calculation led to the complete structure (Fig. 1).

Example 4. *PTS*24 (*He Cun-heng*, 1987)

Formula: $C_{18}H_{18}BrNO_3$; space group: $P2_1$; unit-cell parameters: $a = 12{\cdot}486$, $b = 10{\cdot}822$, $c = 14{\cdot}609$ Å, $\beta = 109{\cdot}12°$; $Z = 4$.

This is also an unknown structure solved originally by *SAPI*. The structure contains a pseudo-translation vector $\mathbf{t} = \mathbf{b}/2 + \mathbf{c}/2$, which relates two independent molecules in the asymmetric unit. Consequently, reflections with index $k + l = 2N + 1$ are systematically much weaker than those with index $k + l = 2N$. Again the structure resisted solution by conventional direct methods. The *E* map resulting from a default run of *SAPI* also failed to reveal the skeleton of the molecules. However five cycles of Fourier calculation starting from the top 20 peaks on the *E* map led finally to the complete structure, which consists of two independent organic molecules (Fig. 2) and three independent water molecules. Each of the organic

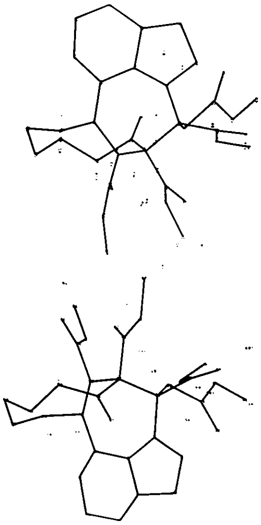

Fig. 1. Two independent molecules in the asymmetric unit of PTS6, each projected on its least-squares plane output by *SAPI*.

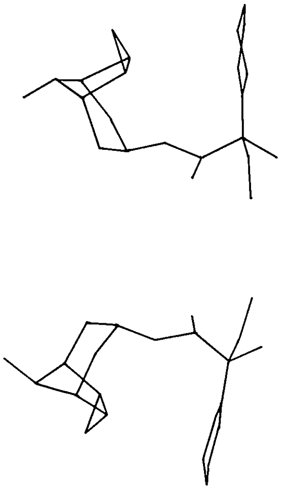

Fig. 2. Two independent molecules in the asymmetry unit of PTS24, each projected on its least-squares plane output by *SAPI*.

molecules contains one more non-hydrogen atom than the original chemical formula shows.

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Simulation and Application of the Distorted ZOLZ Patterns from Dislocations in Si*

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Abstract

The previously reported distorted zeroth-order fringes in a bright-field Tanaka pattern from a dislocated region in silicon have been computer simulated and the experimental and the many-beam calculated patterns agree well. Calculations are carried out for nine distinct cases of edge, screw and 60° dislocations in a silicon crystal. The general usefulness of the distortion of the ZOLZ pattern in determining geometrical properties of a dislocation is discussed.

1. Introduction

Carpenter & Spence (1982) reported splitting of higher-order Laue-zone (HOLZ) lines and distortion of the zeroth-order Laue-zone (ZOLZ) pattern in a convergent-beam electron diffraction (CBED) pattern from a dislocation in silicon. They also simulated the splitting of HOLZ lines by a method involving the column approximation and used the splitting of HOLZ lines to determine the Burgers vector of a dislocation. Cherns & Preston (1986) proposed a method to determine the Burgers vector of a dislocation using the splitting of a diffraction line in a defocused CBED pattern. Later, Cherns, Kiely & Preston (1988) used the sense of the displacement of the diffraction peak to deduce the sign of the Burgers vector of the dislocation and this was confirmed by kinematical calculation. Tanaka, Terauchi & Kaneyama (1988) made detailed and extensive calculations to show the influence of various dislocations on the distortion of a diffraction line crossed by a dislocation line, on the basis of isotropic elasticity. They showed that at the crossing region the line of diffraction twists and splits into $n+1$ lines, where $n=\mathbf{g}.\mathbf{b}$. The sense of the shift depends on the sign of n. They also considered the effect of the $\mathbf{g}.\mathbf{b}\times\mathbf{u}$ term when $n=0$ and demonstrated the determination of the Burgers vector of a dislocation in various cases. On the other hand, Bian (1986) reported observation of the relative shift of fringes in a bright-field ZOLZ pattern from a dislocation in Al, where, however, the Burgers vector and line direction of the dislocation (**b** and **u**) were unclear. In a systematic study of the influence of dislocations on the ZOLZ of a CBED pattern, Wen, Wang & Lu (1989) observed a similar shift of ZOLZ fringes in large-angle convergent-beam electron diffraction (LACBED; see Tanaka, Saito, Ueno & Harada, 1980) patterns near a dislocation, as well as compression and elongation of the patterns. They pointed out that this distortion of ZOLZ patterns resulted from the relative movement of two parts of the pattern separated by the shadow image of the dislocation in the direction of the Burgers vector. This

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