THE TREATMENT OF PSEUDO-SYMMETRIES - A SPECIAL FEATURE OF THE PROGRAM SYSTEM SAPI-85

Fan Hai-fu

Institute of Physics, Chinese Academy of Sciences, Beijing, China

One of the important features of the program system SAPI-85 is the automatic search and treatment of pseudo-symmetries. In this paper, the theoretical background is described and examples are given.

PSEUDO-SYMMETRY AND PHASE AMBIGUITY

According to Fan and Zheng (1982), structure determination using Patterson or direct methods may result in some kind of ambiguity if the structure possesses either pseudo-translational symmetry or pseudo-centrosymmetry.

1. Translational phase ambiguity due to pseudo-translational symmetry

If in a crystal structure there exists a pseudo-translation vector $t = T/n$, where T is the shortest lattice vector parallel to t and n is an integer, then the structure factor can be written approximately as below

$$F(H) \sim \sum_{j=1}^{N/n} f(j)\exp[i2\pi H.r(j)]\{1+\exp(i2\pi H.t)+\exp(i2\pi H.2t)+\ldots$$

$$\ldots+\exp[i2\pi H.(n-1)t]\}. \qquad (1)$$

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

$$S = [\exp(i2\pi H.nt)-1]/[\exp(i2\pi H.t)-1] = \begin{cases} n, & \text{if } H.t = \text{integer} \\ 0, & \text{if } H.t \neq \text{integer} \end{cases}$$

Notice that H.nt = H.T = integer . Hence, all reflections with H.t ≠ integer will be systematically very weak showing an effect of pseudo-systematic extinction. The phase of these 'weak' reflections will be very difficult to determine by conventional methods. This leads to the so-called translational phase ambiguity.

2. Enantiomorphous phase ambiguity due to pseudo-centrosymmetry

Non-centrosymmetric structures can reveal pseudo-centrosymmetry if they contain some dominating heavy atoms in a centrosymmetric arrangement. In this case either Patterson or the conventional direct methods often results in a pseudo-centrosymmetric image, in which the true structure and its enantiomorph are superimposed. Thus in the reciprocal space there will exist two equally

possible phases for each reflection leading to the so-called enantiomorphous phase ambiguity. The phase doublets can be expressed as:

$\varphi(H) = \varphi'(H) +- |\Delta\varphi(H)|$, where $\varphi'(H) = 2\pi H.r(o)$, r(o) is the positional vector of the pseudo-inverse centre in the unit cell. If the origin of the unit cell is fixed at the pseudo-inverse centre, we can obtain from the resulting pseudo-centrosymmetric image the real part A(H) and the absolute value of the imaginary part B(H) for each structure factor (Fan and Zheng, 1978). Hence the enantiomorphous phase ambiguity is in fact a sign ambiguity on the imaginary part of the structure factors.

THE MODIFIED SAYRE EQUATIONS

1. Modified Sayre equation for structures containing heavy atoms in known positions (Fan, 1965a)

For a squared structure $\rho^2(r)$, the structure factor $F^{sq}(H)$ can be written as

$$F^{sq}(H) = (1/V) \sum_{H'} F(H') F(H-H') \qquad (2)$$

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

$$F^{sq}(H) = \sum_{j=1}^{N} f^{sq}(j) \exp[i2\pi H.r(j)] \qquad (3)$$

where $f^{sq}(j)$ is the atomic scattering factor of the j^{th} atom. let the subscript u denotes atoms from the unknown part of the structure, while p denotes the heavy atoms in known positions. (3) becomes

$$F^{sq}(H) = \sum_{u} f^{sq}(u) \exp[i2\pi H.r(u)] + \sum_{p} f^{sq}(p) \exp[i2\pi H.r(p)]. \qquad (4)$$

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

$$F^{sq}(H) =$$

$$[f^{sq}(u)/f(u)]\sum_{u} f(u)\exp[i2\pi H.r(u)]+[f^{sq}(u)/f(u)]\sum_{p} f(p)\exp[i2\pi H.r(p)]+$$

$$\sum_{p}[f^{sq}(p)/f(p)]f(p)\exp[i2\pi H.r(p)]-[f^{sq}(u)/f(u)]\sum_{p} f(p)\exp[i2\pi H.r(p)].$$

(5)

Let $1/a(u) * f^{sq}(u)/f(u)$ and $1/a(p) = f^{sq}(p)/f(p)$, we obtain

$$F^{sq}(H) = [1/a(u)]\{ \sum_u f(u)\exp[i2\pi H.r(u)] + \sum_p f(p)\exp[i2\pi H.r(p)] \}$$

$$+ \sum_p [1/a(p) - 1/a(u)]\, f(p)\exp[i2\pi H.r(p)]$$

$$= [1/a(u)]F(H) + \sum_p [1/a(p) - 1/a(u)]\, F(H,p) \quad , \qquad (6)$$

where $F(H,p)$ is the contribution from the p^{th} heavy atom. Substituting (6) into (2) it finally follows that

$$F(H) = [a(u)/V] \sum_{H'} F(H')\, F(H-H') - \sum_p [a(u)/a(p) - 1]\, F(H,p) \; . \qquad (7)$$

This is the modified Sayre equation, which has no limitation on the atomic species in the known part of the structure. With (7) the heavy-atom phases can be extended and refined by direct methods.

2. Modified Sayre equation dealing with pseudo-translational symmetry due to the special arrangement of heavy atoms in known positions

In this case the heavy atoms will have no contribution to some class of reflections (systematically weak reflections). For this kind of reflections (7) reduces to

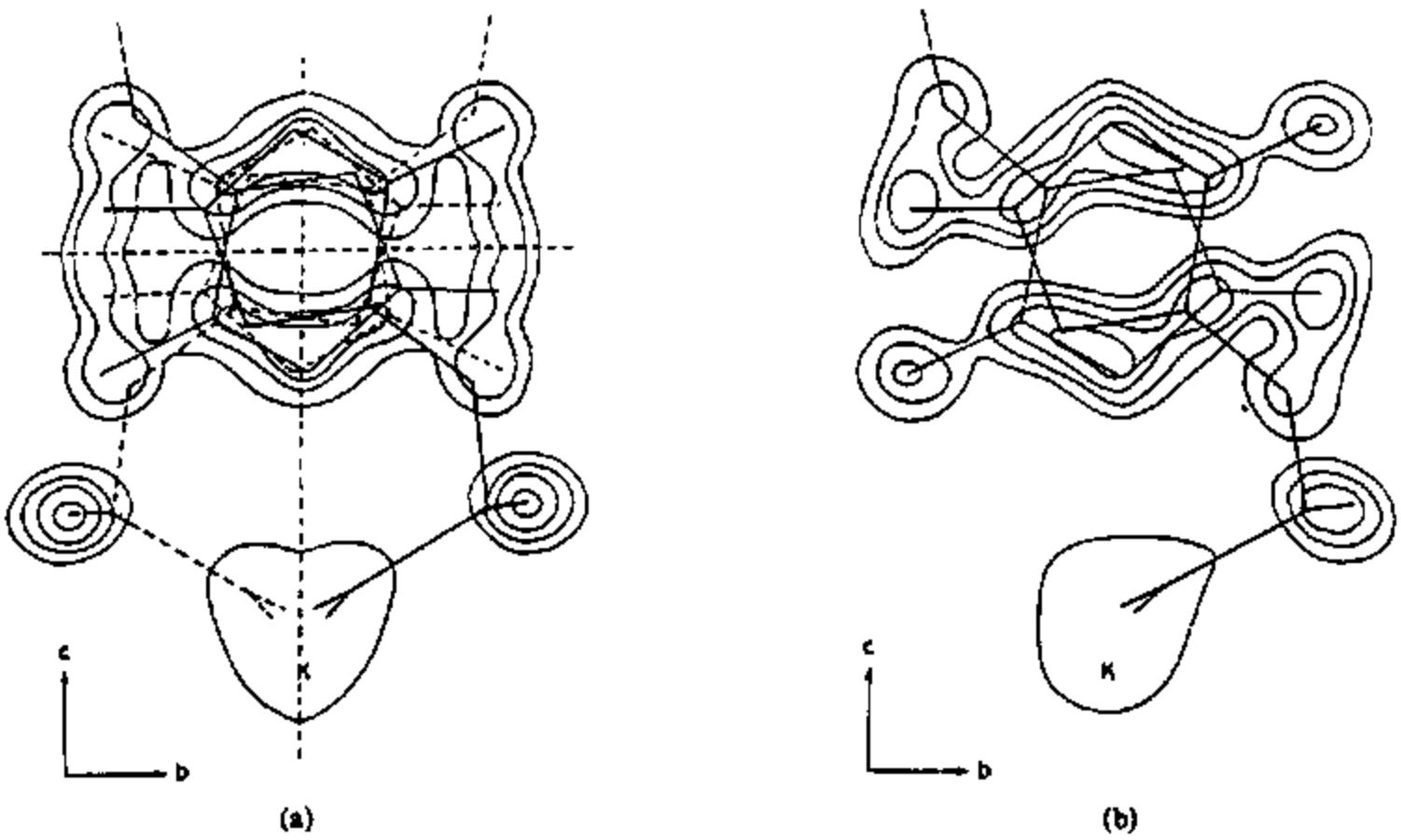
$$F^{o}(H) = [a(u)/V] \sum_{H'} F^{o}(H')\, F(H-H') \quad , \qquad (8)$$

where $F^{o}(H)$ denotes the structure factors in which the heavy-atom contribution equals zero (systematically 'weak' reflections). (8) can be used to derive the phases of 'weak' reflections from the 'strong' ones. This has been verified with the structure of SHAS, $C_5 H_6 O_5 N_3 K$ (Fan Hai-fu, 1975).

The structure belongs to space group $P\,2_1\,2_1\,2_1$ with $a=7.51$, $b=9.95$, $c=10.98$ A and $Z=4$. The arrangement of the heavy atoms, K, possesses a subperiodicity of translation, $t=(a+b+c)/2$. 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. However using (8) and assuming that the phases of F(H-H') are dominated by the heavy atoms, the phases of $F^{o}(H)$ can be easily derived. Fig.1a shows the Fourier projection along the 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 b and c axes respectively , which are due to the pseudo-translational symmetry 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.

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



3. Modified Sayre equation for superstructures

Pseudo-translational symmetry may be also due to the special arrangement of all the atoms in the unit cell, their positions can only be known exactly after the whole structure has been solved. This is the case in dealing with superstructures. In this case we need another type of modified Sayre equation (Fan, He, Qian and Liu, 1978. See also Fan, Yao, Main and Woolfson, 1983).

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 have

$$\rho(r) = \rho(r,\mathrm{sub}) + \Delta\rho(r) \quad . \tag{9}$$

By squaring both sides of (9) and negleting the term $\Delta\rho^2(r)$, it follows that

$$\rho^2(r) = \rho^2(r,sub) + 2\rho(r,sub)\Delta\rho(r) \quad , \tag{10}$$

from which, by Fourier transformation, one finds

$$F^{sq}(H) = F^{sq}(H,sub) + (2/V)\sum_{H'} F(H',sub)\,\Delta F(H-H') \quad . \tag{11}$$

On the other hand, by Fourier transforming (9), we have

$$F(H) = F(H,sub) + \Delta F(H) \quad . \tag{12}$$

Now consider a reciprocal vector H, if it dose not fall on a grid point of the reciprocal lattice of the subcell strucutre then it must correspond to a 'weak' (superstructure) reflection. In this case, both $F^{sq}(H,sub)$ and $F(H,sub)$ equal zero. Then from (11) and (12), we obtain

$$F^{sq}(H,wk) = (2/V)\sum_{H'} F(H',sub)\,F(H-H',wk) \quad , \tag{13}$$

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

$$F^{sq}(H,wk) \sim (f^{sq}/f)\sum_{j=1}^{N} f\,\exp[i2\pi H.r(j)] = (1/a)\,F(H,wk) \tag{14}$$

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 (14) into (13), we finally obtain

$$F(H,wk) = (2a/V)\sum_{H'} F(H',sub)\,F(H-H',wk) \tag{15}$$

For a superstructure, the phases of the subcell-structure reflections can be determinated by conventional methods without much difficulties. Then with equation (15) 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 and Liu, 1978):

Freielebenite, $Pb\ Ag\ Sb\ S_3$

The structure was solved by Ito and Nowacki (1974a). It belongs to space group $P\ 2_1/a$ with $a=7.518$, $b=12.809$, $c=5.940$ Å, $\beta=92.25^{\circ}$ and $Z=4$. There are two pseudo-translation vectors in the structure, i.e. $t_1=a/2$ and $t_2=b/3$. 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 a conventional direct method. Then by using a symbolic addition procedure, the signs of 68 out of the total 94 'weak' reflections were derived from (15). These reflections were arranged in descending order of

$$W = F(H,wk) \sum_{H'} F(H',sub)\ F(H-H',wk)$$

and then 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 and Nowacki (1974b). It belongs to space group $P\ 2_1/m$ with $a=8.918$, $b=31.899$, $c=8.462$ Å, $\beta=117.79^{\circ}$ and $Z=1$. There are two pseudo-translational vectors in the structure, i.e. $t_1=a/2$ and $t_2=c/2$. 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, it can be recognized that both Freielebenite and Iordanite may actually be solved by the method described above.

Table 1
Test on 68 'weak' hk0 reflections of $Pb\ Ag\ Sb\ S_3$

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.

4. Modified Sayre equation dealing with pseudo-centrosymmetry

In this case, conventional methods often result in a pseudo-centrosymmetric solution containing both enantiomorphs. From such a solution the real part A(H) of the structure factors can be calculated and the absolute value of the imaginary part B(H) can be obtained as $|B(H)| = [F(H)^2 - A(H)^2]^{1/2}$.

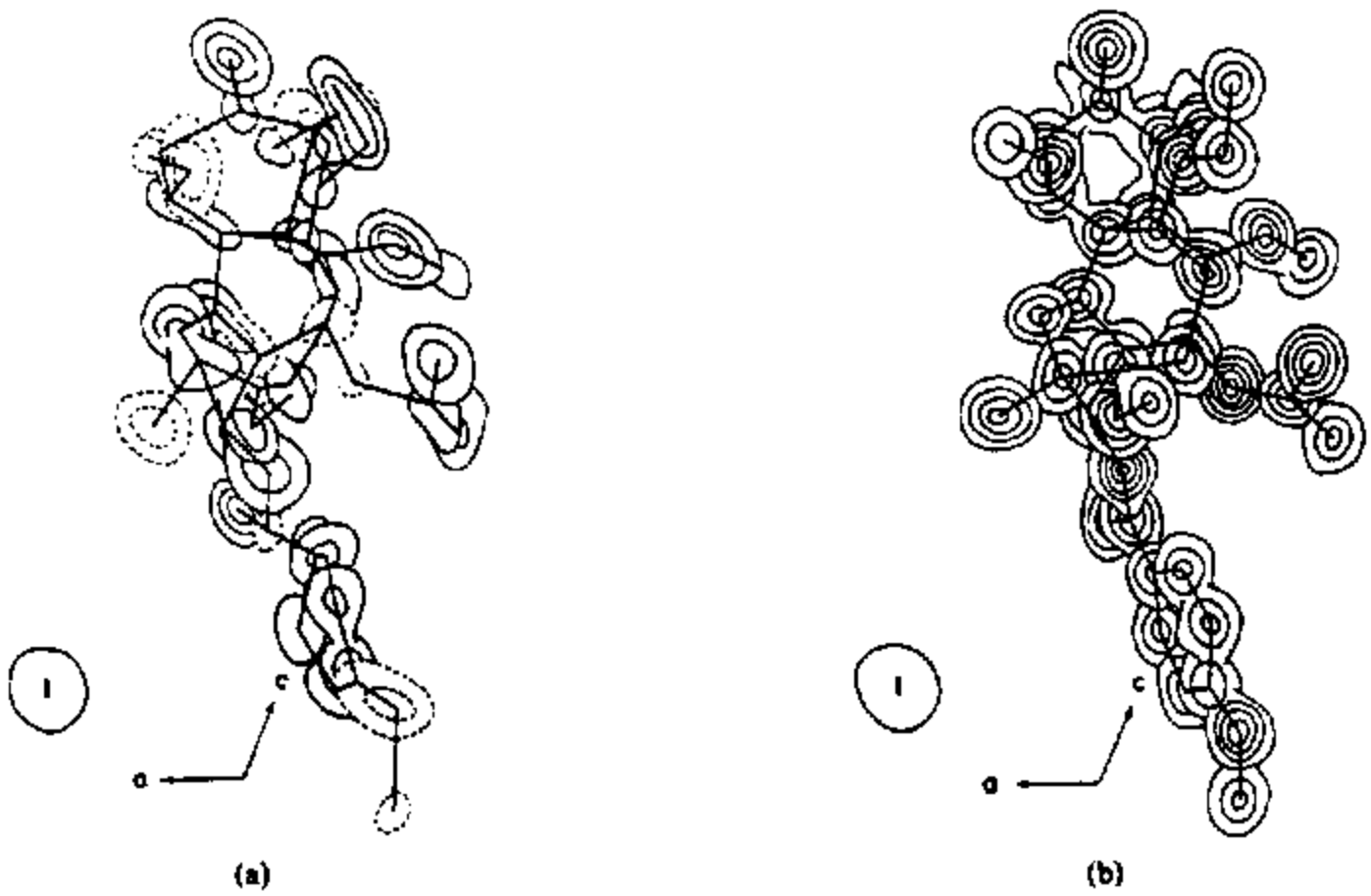
By separating the real and the imaginary parts of the structure factors in (7), one obtains the so-called component relation (Fan, 1965b)

$$B(H) = (2a/V) \sum_{H'} A(H')\ B(H-H') \quad . \qquad (16)$$

(16) can be used to derive the sign of the imaginary part of the structure factors and resolve the enantiomorphous ambiguity. This has been verified with the structure of ZCW , $C_{34}\ O_{11}\ N\ H_{47}$ .H I (Fan and Zheng, 1978).

The structure belongs to space group $P\ 2_1$ with a=12.58, b=14.38, c=11.00 Å, β=114.6° and Z=2. Patterson analysis resulted in 44 enantiomorphous pairs of 'atoms', of which two pairs are ghost peaks. With these 44 pairs of 'atoms', the real part and the absolute value of the imaginary part of 331 largest structure factors were calculated. The signs of the imaginary parts of the structure factors were then derived using (16). The result is shown in Fig.2.

Fig. 2. Composite Fourier maps of ZCW.
a) Enantiomorphous ambiguity resolved using the 'component relation' (The atoms unambiguously located are denoted by solid contour lines).
b) The final map.



(a) (b)

5. Phase-difference relation

Replacing $F(H)$ by $F(H)\exp[i\varphi(H)]$ and replacing $\varphi(H)$ by $\varphi'(H) + \Delta\varphi(H)$, (7) becomes

$$F(H)\exp[i\Delta\varphi(H)] = [a(u)/V] \sum_{H'} F(H')F(H-H')\exp\{i[\varphi'_3+\Delta\varphi(H')+\Delta\varphi(H-H')]\}$$

$$- \sum_{p} \{[a(u)/a(p)]-1\}\, F(H,p)\exp\{i[\varphi(H,p)-\varphi'(H)]\}, \qquad (17)$$

where $\varphi'_3 = -\varphi'(H) + \varphi'(H') + \varphi'(H-H')$.

From the imaginary part of (17), we obtain

$$\mathrm{Sin}\Delta\varphi(H) = \{[a(u)/V] \sum_{H'} F(H')F(H-H')\mathrm{Sin}[\varphi'_3+\Delta\varphi(H')+\Delta\varphi(H-H')]$$

$$- \sum_{p} [a(u)/a(p)-1]\, F(H,p)\mathrm{Sin}[\varphi(H,p)-\varphi'(H)]\}/F(H). \qquad (18)$$

This is the so-called phase-difference relation, which is equivalent to

$$B'(H) = [a(u)/V]\{\sum_{H'}[A'(H')A'(H-H')-B'(H')B'(H-H')]\mathrm{Sin}\varphi'_3 + 2\sum_{H'}A'(H')B'(H-H')\mathrm{Cos}\varphi'_3\} - \sum_{p}[a(u)/a(p)-1]F(H,p)\mathrm{Sin}[\varphi(H,p)-\varphi'(H)] \quad (19)$$

where $B'(H) = F(H)\mathrm{Sin}\Delta\varphi(H)$, $A'(H) = F(H)\mathrm{Cos}\Delta\varphi(H)$.

(19) may be regarded as the generalized component relation. (18) or (19) can be used also to solve the problem of enantiomorphous phase ambiguity arising from single-isomorphous replacement or one-wave-length anomalous scattering technique (Fan, Han, Qian and Yao, 1984).

THE PROGRAM SYSTEM SAPI-85
(Yao, Zheng, Qian, Han, Gu and Fan, 1985)

The name SAPI is an abbreviation of 'Structure Analysis Program with Intelligent control'. It may also be read inversely as 'Institute of Physics Academia Sinica'.

SAPI is based on MULTAN-80 (Main, Fiske, Hull, Lessinger, Germain, Declercq and Woolfson, 1980) and differs from which by the following:

1. The program can automatically handle structures having pseudo-translational symmetry leading directly to a correct solution in favourable cases.
2. The program can recognize pseudo-centrosymmetric solutions when dealing with non-centrosymmetric structures. In addition, the program can break the enantiomorphous ambiguity given a group of atoms, each of which comes from either one of the two enantiomorphs.
3. RANTAN procedure (Yao, 1981) is used instead of the phase permutation of MULTAN-80. In addition the RANTAN procedure has been modified to provide an intelligent control on the path of phase development according to the complexity of the structure and the early-stage result during the phase development process.
4. The program provides facilities for calculating Patterson and Minimum functions.
5. The program can output density maps as 'half-tone graphs' on a conventional lineprinter. The size and constrast of the map output can be controlled either automatically or manually.
6. The program includes a subroutine for the interpretation of space group symbols, which is a modification of the program written by Burzlaff and Hountas (1982).

The source program of SAPI-85 is available on request.

REFERENCES

Burzlaff, H. and Hountas, A. (1982) J. Appl. Cryst. 15, 464-467.
Fan Hai-fu (1965a) Acta Phys. Sin. 21, 1105-1113.
Fan Hai-fu (1965b) Acta Phys. Sin. 21, 1114-1118.
Fan Hai-fu (1975) Acta Phys. Sin. 24, 57-60.
Fan Hai-fu, Han Fu-son, Qian Jin-zi and Yao Jia-xing (1984) Acta Cryst. A40, 489-495.
Fan Hai-fu, He Luo, Qian Jin-zi and Liu Shi-xiang (1978) Acta Phys. Sin. 27, 554-558.
Fan Hai-fu, Yao Jia-xing, Main, P. and Woolfson, M.M. (1983) Acta Cryst. A39, 566-569.
Fan Hai-fu and Zheng Qi-tai (1978) Acta Phys. Sin. 27, 169-174.
Fan Hai-fu and Zheng Qi-tai (1982) Acta Phys. Sin. 31, 191-198.
Ito, T. and Nowacki, W. (1974a) Z. Krist. 139, 85-102.
Ito, T. and Nowacki, W. (1974b) Z. Krist. 139, 161-185.
Main, P., Fiske, S.J., Hull, S.E., Lessinger, L., Germain, G., Declercq, J.P. and Woolfson, M.M. (1980). MULTAN-80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England and Louvain, Belgium.
Yao Jia-xing (1981) Acta Cryst. A37, 642-644.
Yao Jia-xing, Zheng Chao-de, Qian Jin-zi, Han Fu-son, Gu Yuan-xin and Fan Hai-fu (1985) "SAPI-85: A Computer Program for Automatic Solution of Crystal Structures from X-ray Data" Institute of Physics, Academia Sinica, Beijing, China.