Vol 12 No 3, March 2003
1009-1963/2003/12(03)/0310-05
Chinese Physics

Solving a superstructure from two-wavelength x-ray powder diffraction data – a simulation*

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(Received 2 December 2002)

Two different kinds of phase ambiguities are intrinsic in two-wavelength x-ray powder diffraction from acentric crystal structures having pseudo-translation symmetry. In a test calculation we have solved the problem for the first time by two different phasing procedures developed originally in single-crystal structure analysis. They are the direct method of breaking enantiomorphous phase ambiguity in protein crystallography and that of breaking translational phase ambiguity for superstructures. An artificial structure was used in the test, which is based on atomic coordinates of the known structure, SHAS ($C_5H_6O_5N_3K$), with the atom K replaced by Rb. The arrangement of Rb atoms possesses a subperiodicity of $t = (a + b + c)/2$. Two-wavelength synchrotron x-ray powder diffraction data were simulated with λ_1=0.0816nm and λ_2=0.1319nm. Overlapped reflections were uniformly decomposed at the beginning and redecomposed afterward when the partial-structure information became available. The enantiomorphous phase ambiguity was resolved only for reflections with $h + k + l$ even. Phases of reflections with $h + k + l$ odd were derived by the direct method of solving superstructures. A fragment was then obtained, which led to the complete structure in five cycles of Fourier iteration.

Keywords: two-wavelength powder diffraction, superstructures, direct methods
PACC: 6110M

1. Introduction

Anomalous scattering effect can be used for *ab initio* solution of crystal structures by x-ray powder diffraction.[1,2] However, when dealing with acentric crystals, the problem of phase ambiguity will be intrinsic to two-wavelength powder diffraction data. Burger and Prandl[3] proposed the use of the maximum-entropy method to remove the problem. Gu *et al*[4] proposed an alternative method, which breaks the phase ambiguity and resolves the problem directly. They introduced direct methods of breaking phase ambiguities in protein crystallography into powder diffraction analysis. In a test with the known acentric crystal structure of leotidine bromate ($C_{14}H_{20}O_2N_2$ ·HBr), their method was able to break the phase ambiguity and finally reveal the complete structure. A more complicated case is considered in the present paper. When dealing with noncentrosymmetric structures having pseudo-translation symmetry, *ab initio* phasing of two-wavelength powder diffraction data will be difficult. Since there will be two different kinds of phase ambiguity intrinsic to the data, one is the enantiomorphous phase ambiguity and the other is the translational phase ambiguity. In the single-crystal diffraction analysis, there are already successful procedures for solving these two kinds of phase ambiguity.[5–7] However, *ab initio* phasing of powder diffraction data is much more difficult than that for single crystals owing to the serious overlapping among individual reflections. It would be interesting to see whether methods developed for single-crystal analysis could be applied as well to the powder-diffraction analysis. The main difficulty arising from powder diffraction data in comparison with single-crystal diffraction is the overlapping of individual reflections. In the present test we use a set of artificial powder diffraction data, which is simulated from a set of single-crystal diffraction data by merging together reflections with diffraction angles (theta) closer to each other than 0.02 degrees.

2. Method

2.1. Breaking enantiomorphous phase ambiguity

*Project supported by the National Natural Science Foundation of China (Grant No 19974068).
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In powder diffraction, the two reflections of a Bijvoet pair, $F(\boldsymbol{h})$ and $F(-\boldsymbol{h})$, will always overlap. Hence there will be no use of the imaginary part of anomalous scattering, $\Delta f''$. However, the real part of anomalous scattering $\Delta f'$ can be used to simulate isomorphous replacement data. This means that powder diffraction data from two wavelengths can be treated as those from a single pair of isomorphous crystals. For centrosymmetric crystals, the diffraction data from two suitable wavelengths will be sufficient to solve the phase problem. However, for non-centrosymmetric crystals, phase ambiguity will occur with reflections not in the centric zone. This leads to enantiomorphous phase ambiguity as shown in Fig.1.

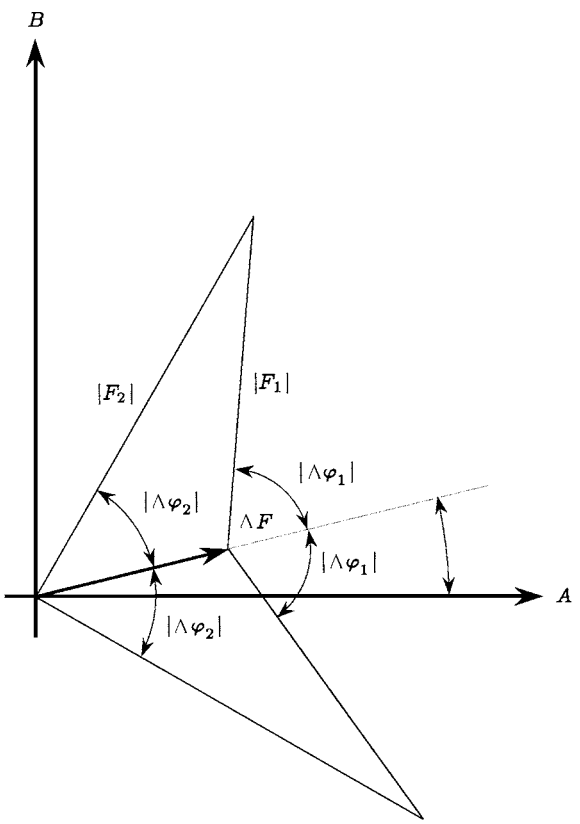

Fig.1. Enantiomorphous phase ambiguity from 2-wavelength powder diffraction. $|F_1|$ is the structure-factor amplitude corresponding to λ_1. $|F_2|$ is the structure-factor amplitude corresponding to λ_2. ΔF is the structure-factor difference between λ_2 and λ_1 for Rb atoms. φ' is the phase angle of ΔF. $\Delta\varphi_1$ is the phase difference between F_1 and ΔF. $\Delta\varphi_2$ is the phase difference between F_2 and ΔF.

The phase ambiguity for a given reciprocal vector $\boldsymbol{h}$ can be expressed as

$$\varphi = \varphi' \pm |\Delta\varphi|, \tag{1}$$

where φ' is the phase of ΔF, the vector difference between the two structure factors having the same reciprocal vector $\boldsymbol{h}$ but corresponding to two different wavelengths. According to Fig.1, we have

$$\Delta\varphi_1 = \pm\cos^{-1}(F_2^2 - F_1^2 - \Delta F^2/2F_1\Delta F) \tag{2}$$

and

$$\Delta\varphi_2 = \pm\cos^{-1}(F_2^2 - F_1^2 + \Delta f^2/2F_2\Delta F). \tag{3}$$

In order to break the phase ambiguity we need to determine the sign of $\Delta\varphi$. This is similar to the case of single isomorphous replacement in protein crystallography (see Ref.[8]). A direct method has been developed to find the sign of $\Delta\varphi$.[6] The method is implemented by the program OASIS.[9] The main point of this method is to calculate the probability for $\Delta\varphi$ to be positive:

$$\begin{aligned} P_+(\Delta\varphi_h) = &\frac{1}{2} + \frac{1}{2}\tanh\Big\{ \sin|\Delta\varphi_h| \\ &\times \Big[\sum_{h'} m_{h'} m_{h-h'} \kappa_{h,h'} \\ &\times \sin(\Phi'_3 + \Delta\varphi_{h',\mathrm{best}} + \Delta\varphi_{h-h',\mathrm{best}}) \\ &+ \chi \sin\delta_h \Big] \Big\}. \end{aligned} \tag{4}$$

For further details the reader is referred to Ref.[4] and references therein.

2.2. Breaking the translational phase ambiguity

It is well known that Fourier recycling can lead a partial structure to the complete one. However, phases of certain classes of reflections will be difficult to determine, when the partial structure possesses higher translation symmetry than that of the whole structure. That is the translational phase ambiguity, which leads to the overlapping of several structure image related by the pseudo-translation symmetry. Suppose that in the partial structure there exists a pseudo periodicity $\boldsymbol{t} = \boldsymbol{T}/n$, where $\boldsymbol{T}$ is the shortest lattice vector of the whole structure in the direction parallel to $\boldsymbol{t}$ and n is an integer. Then reflections with $\boldsymbol{h}\cdot\boldsymbol{t} \neq n$ will be systematically weak owing to no or very weak contribution from the partial structure. Phases of reflections with $\boldsymbol{h}\cdot\boldsymbol{t} = n$ can easily be obtained by making use of the known partial structure, while those with $\boldsymbol{h}\cdot\boldsymbol{t} \neq n$ are rather difficult to derive. To tackle this problem, Fan[5] has proposed the use of a modified Sayre equation

$$F_W(\boldsymbol{h}) = \frac{2\Theta}{V}\sum_{h'} F_S(\boldsymbol{h}')F_W(\boldsymbol{h}-\boldsymbol{h}'). \tag{5}$$

where $F_W(\boldsymbol{h})$ denotes the structure factor of systematically weak reflections, $F_S(\boldsymbol{h}')$ is that of systematically strong ones, Θ is an atomic form factor, V is the volume of the unit cell. Equation (5) relates phases of systematically strong reflections to those of systematically weak ones. With this equation the phases of weak reflections can be derived from those of strong ones. This method has been further improved and incorporated into the program SAPI.[10] For details the reader is referred to Ref.[7] and references therein.

2.3. Phasing strategy

The powder diffraction data are first converted to a set of single-crystal-like data by uniformly splitting the overlapped reflections into their single-reflection components. The whole set of reflections is then divided, according to the pseudo-translation symmetry, into two categories, i.e. systematically strong reflections and systematically weak ones. The heavy-atom substructure is obtained using diffraction data from one of the two wavelengths by conventional direct methods with overlapped reflections uniformly decomposed. Phases of reflections belonging to the first category are derived from the two-wavelength data by the procedure described in Ref.[4]. Starting with these phases, the program SAPI[10] is used to break the translational phase ambiguity using the structure-factor magnitudes of both categories (strong and weak) from one of the two wavelengths. This leads to a Fourier map, which reveals at least a partial structure containing some of the light atoms. The originally overlapped reflections (strong and weak) are redecomposed according to the partial structure. With the redecomposed magnitudes of 'strong' and 'weak' reflections, Fourier recycling is then used to complete the structure.

3. Data

Two-wavelength x-ray powder-diffraction data were simulated using atomic coordinates from the known structure SHAS, $C_5H_6O_5N_3K$,[a)] with the atom K replaced by Rb. The model structure belongs to the space group $P2_12_12_1$ with unit-cell parameters a=0.751, b=0.995, c=1.098nm and Z=4. Coordinates of the Rb atom are x=0.0000, y=0.2500 and z=0.3909. Hence, the arrangement of heavy atoms possesses a subperiodicity of $\boldsymbol{t}=(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})/2$. Consequently, Rb atoms have no contribution to reflections with $h+k+l$ odd. In other words, reflections with $h+k+l$ even are systematically strong, while others are systematically weak. The two wavelengths used in the present simulation are λ_1=0.0816nm and λ_2=0.1319nm. Anomalous corrections (in electrons) of Rb are $\Delta f_1'$=–8.313, $\Delta f_1''$=3.786 for λ_1 and $\Delta f_2'$=–0.719, $\Delta f_2''$=1.221 for λ_2. Structure factors are calculated within the range $10^\circ < 2\theta < 125^\circ$. The half-height width of a single diffraction peak is assumed to be 0.02° (measured in diffraction angle θ). Hence, reflections are assumed to be isolated (unique), if their θ-value differs from that of the nearest neighbour more than 0.02°. Others are regarded as overlapped. There are 319 unique reflections out of the total 4711 λ_1 data and 538 unique reflections out of the total 1214 λ_2 data. We assume that experimental errors due to preferred orientation, absorption, etc, have been treated properly with available techniques. Hence, they are not considered in the simulation.

4. Test and results

4.1. Locating the heavy atom

With the total 1214 uniformly decomposed reflections of the λ_2 data, the program SAPI[10] can successfully locate the Rb atom at x=0.014, y=0.2528, and z=0.3930.

4.2. Breaking the enantiomorphous phase ambiguity

As is explained in Ref.[4] two-wavelength powder diffraction data cannot uniquely determine the phase of reflections *ab initio*. Instead, there are two possible phases for each reflection not in a centric zone. This is the enantiomorphous phase ambiguity. Since the heavy atom Rb does not give reliable indication to phases of reflections with $h+k+l$ odd, only the phase ambiguity of reflections with $h+k+l$ even was treated by the direct method.[4] Results are summarized in Table 1. As is seen, the phase ambiguity has been broken efficiently.

a) Li P F and Fan H F 1964 (Unpublished work).

Table 1. Results of breaking the enantiomorphous phase ambiguity for reflections with $h + k + l$ even.

Cycle	Average phase error	F(obs) weighted average phase error
1	33.65	26.59
2	29.12	21.85
3	28.96	21.77
Background error†	27.20	21.05

†The background error is calculated against the final structure model using $|\Delta\varphi|$ derived from uniformly decomposed reflections with correct signs of $\Delta\varphi$'s.

4.3. Breaking the translational phase ambiguity

The heavy-atom substructure possesses the translational symmetry $\boldsymbol{t} = (\boldsymbol{a} + \boldsymbol{b} + \boldsymbol{c})/2$, which is higher than that of the whole structure, leading to the translational phase ambiguity. To break the ambiguity, structure-factor magnitudes of 'strong' and 'weak' reflections from λ_2 together with phases of 'strong' reflections derived from the previous section were input to the program SAPI.[10] The output showed a fragment of seven light atoms in addition to the heavy atom Rb. The whole set of reflections was redecomposed according to this partial structure. This is made by forcing the ratio between structure-factor magnitudes within an overlapped reflection equal to that of the corresponding structure-factor magnitudes calculated from the partial structure. With the redecomposed reflections and phases from the partial structure, five cycles of Fourier iteration led to the complete structure (Fig.2(a)).

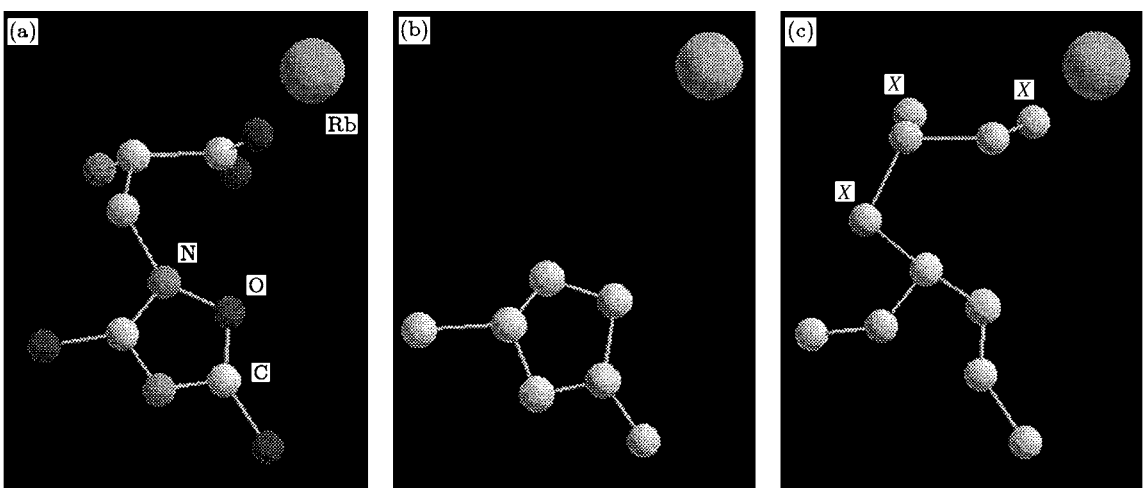

Fig.2. Results from Fourier recycling based on direct-method phasing of powder diffraction data. (a) Result from 2-wavelength powder diffraction data, complete structure obtained after 5 cycles of Fourier iteration. (b) Result from 2-wavelength powder diffraction data without breaking the translational phase ambiguity, only a fragment obtained after 8 cycles of Fourier iteration. (c) Result from one-wavelength powder diffraction data, only a fragment obtained after 10 cycles of Fourier iteration, which contains some ghost peaks (marked with an X).

5. Comparison with other phasing protocols

Our experience on single-crystal structure analysis showed that it is essential to break the translational phase ambiguity in solving structures having pseudo-translation symmetry. To confirm this in powder diffraction analysis, we have used the same input to the program SAPI[10] as that in the previous section, but disabled the function of breaking translational phase ambiguity in it. The output fragment from SAPI[10] did not lead to a complete structure after eight cycles of Fourier iteration as is in Fig.2(b). On the other hand, in the present test, it is also essential to use two-wavelength diffraction data and to break the enantiomorphous phase ambiguity. This ensures reliable starting phases of 'strong' reflections. A comparison was made with the heavy-atom method by using the λ_2 data alone. The output fragment of SAPI[10] after ten cycles of Fourier iteration leads to the result shown in Fig.2(c), which is not a complete structure and contains also some ghost peaks (marked with an X).

6. Concluding remarks

This paper points out that *ab initio* direct-method phasing is possible for powder diffraction data of superstructures. An advantage of the method is that there is no need to prepare single-crystal samples. This is important when it is difficult to obtain high-quality single crystals of sufficient size.

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