Korean J. Crystallography
Vol. 14, No. 1, pp.13~15, 2003

Three Kinds of Reflections with Phase Angle 0 or π In Triclinic, Monoclinic and Orthorhombic Systems

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Triclinic, Monoclinic 및 Orthorhombic Systems에서 Phase Angle 0 또는 π를 갖는 3種類의 Reflections

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Abstract

For all primitive centric space groups in the triclinic, monoclinic and orthorhombic systems, either phase 0 or π can be allocated to three different kinds of reflections in order to specify the origin at one of the eight centers of symmetry, and the same holds for all primitive acentric space groups belonging to the point group *222*. If these phased reflections are used as a basic set, more and more phased reflections with better accuracy could emerge in the process of direct methods.

1. Introduction

Up to the early nineteen sixties, the principal method of structure determination was by interpretation of the Patterson function. Since then, the phase problems of X-ray crystallography have been solved mainly by the so-called "Direct Methods". The application of the direct methods requires a set of reflections with phases.

Fortunately, up to three known phases can be obtained by the definition of the unit cell origin.[1)]

2. Theory

The structure factor is given as follows:

$$F(hkl) = \sum_{j=1}^{n} f_j \exp[2\pi\ i(hx_j + ky_j + \ z_j) = A + i\ B$$

For centric space groups, only the real part of the structure factor remains since the imaginary part B = 0.

$$A(hkl) = \sum_{j=1}^{n/2} 2f_j \cos 2\pi\ i(hx_j + ky_j + lz_j)$$

Therefore the phases of A(*hkl*) are either 0 or π.

In the typical centric space group $P\bar{1}$, there are eight inversion centers: 0 0 0, 1/2 0 0, 0 1/2 0, 0 0 1/2, 1/2 1/2 0, 1/2 0 1/2, 0 1/2 1/2, 1/2 1/2 1/2, and they are not identical because the structural surroundings around each of these points are different, in contrast to centers of symmetry related by unit cell translations. Therefore the choice of origin at a center of symmetry can be made in eight different ways.

In order to see how the phase shifts according to different center of symmetry, a point x + 1/2, y + 1/2, z + 1/2 is substituted into the structure factor

$$A(hkl) = \sum_{j=1}^{n/2} 2f_j \cos[2\pi(hx_j + h/2 + ky_j + k/2 + lz_j + l/2)]$$

$$= \sum_{j=1}^{n/2} 2f_j \cos[2(hx_j+ky_j+lz_j)+ (h+k+l)]$$

$$= \sum_{j=1}^{n/2} (-1)^{h+k+l}\ 2f_j \cos[2\pi(hx_j + ky_j + lz_j)$$

From this equation, the relations between the origin shifts and the phase shifts of eight different re-

Table 1. Phase shift in $P\bar{1}$ (E = even, O = odd)

No	Origin shift	Phase Shift for Reflection (h k l) Parity							
		EEE	OEE	EOE	EEO	OOE	OEO	EOO	OOO
1	0, 0, 0	0	0	0	0	0	0	0	0
2	1/2, 0, 0	0	π	0	0	π	π	0	π
3	0, 1/2, 0	0	0	π	0	π	0	π	π
4	0, 0, 1/2	0	0	0	π	0	π	π	π
5	1/2, 1/2, 0	0	π	π	0	0	π	π	0
6	1/2, 0, 1/2	0	π	0	π	π	0	π	0
7	0, 1/2, 1/2	0	0	π	π	π	π	0	0
8	1/2, 1/2, 1/2	0	π	π	π	0	0	0	π

flection parities are obtained as in the Table 1.

2.1. The 21 primitive space groups of Laue groups $\bar{1}$, *2/m*, *mmm*

All space groups belonging to Laue groups $\bar{1}$, *2/m*, *mmm* satisfy the conditions shown in Table 1.

If, for example, an EEO reflection such as (021) is defined as being 0, this reduces the possible number of origins to four 1, 2, 3, 5. The phases of all the EEO reflections are now fixed as 0 and no further choices can be made from that set. Next the phase of an OEE reflection such as (102) may be set 0. This narrows the choice to origins 1 and 3. One of the parities EOE, OOE, EOO, OOO can be finally chosen as an origin determination. So if an EOE reflection such as (210) is fixed as 0, the coordinate 0 0 0 is defined as an origin and all the reflections of the parities EEO, OEE and EOE have phase 0.

However all centered space groups can not be applied to Table 1 due to their reflection conditions. In other words, only applicable parity groups in *A*-centered space group are OEE, EOO, OOO; in *B*-centered one EOE, OEO, OOO; *C*-centered one EEO, OOE, OOO; *I*-centered one EOO; OEO, OOE, and *F*-centered one only OOO. Therefore the reflection parity groups remained are too few to be applicable to Table 1.

2.2. The 4 primitive space groups of the point group *222*

The four primitive acentric four space groups, *P222* (16), $P222_1$ (17), $P2_12_12$ (18), $P2_12_12_1$ (19), derived from noncentric point group *222* have three different kinds of reflections, whose phases are either 0 or just like in the centric space groups.[2] Their phases can be fixed by means of Table 1 and at the same time the origin is defined as follows.

Because of the reason mentioned in 2.1, the centered space groups derived from the point group *222* are excluded here too.

2.2.1. *P222* (16)

Reflections having phase of 0 or π and their applicable parities:

(*0kl*): EOE; EEO; EOO
(*h0l*): EEO; OEE; OEO
(*hk0*): EOE; OEE; OOE

If a phase of an EEO reflection with $h = 0$ such as (021) is defined as being 0, this reduces the possible number of origins to four 1, 2, 3, 5. The phases of all the EEO reflections with $h = 0$ are now fixed as 0 and no further choices can be made from that set.

Next a phase of an OEE reflection with $k = 0$ such as (102) may be set 0. This narrows the choice to origins 1 and 3.

Finally if a phase of an EOE reflection with $l = 0$ such as (210) is fixed as 0, the coordinate 0 0 0 is defined as an origin, and all the reflections of parities EEO with $h = 0$, OEE with $k = 0$ and EOE with $l = 0$ have phase 0.

2.2.2. $P222_1$ (17)

Reflections having phase of either 0 or and their applicable parities:

(*0kl*): EOE; EEO; EOO
(*h0l*) with $l = 2n$: OEE

(*hk0*): EOE; OEE; OOE

The process to fix phases of reflections is same as that for *P222*, and only (*h0l*) with $l = 2n$ is added.

2.2.3. $P2_12_12$ (18)

Reflections having phase of either 0 or and their applicable parities:

(*0kl*) with $k = 2n$: EEO
(*h0l*) with $l = 2n$: OEE
(*hk0*): EOE; OEE; OOE

The process to fix phases of reflections is same as that for *P222*, and only (*0kl*) with $k = 2n$ and (*h0l*) with $l = 2n$ are added.

2.2.4. $P2_12_12_1$ (19)

Reflections having phase of either 0 or and their applicable parities:

(*0kl*) with $k = 2n$: EEO
(*h0l*) with $l = 2n$: OEE
(*hk0*) with $h = 2n$: EOE

The process to fix phases of reflections is same as that for *P222*, and only (*0kl*) with $k = 2n$, (*h0l*) with $l = 2n$ and (*hk0*) with $h = 2n$ are added.

3. Conclusion

The following 21 space groups, $P\bar{1}$ (2), *P2/m* (10), $P2_1/m$ (11), *P2/c* (13), $P2_1/c$ (14), *Pmmm* (47), *Pnnn* (48), *Pccm* (49), *Pban* (50), *Pmma* (51), *Pnna* (52), *Pmna* (53), *Pcca* (54), *Pbam* (55), *Pccn* (56), *Pbcm* (57), *Pnnm* (58), *Pmmn* (59), *Pbcn* (60), *Pbca* (61), *Pnma* (62), are derived from Laue groups $\bar{1}$, *2/m*, *mmm*. If the phases of the reflections with parities EEO, OEE, EOE for the 21 space groups are fixed with 0, a position 0 0 0 is specified as an origin.

Similarly the 4 space groups, *P222* (16), $P222_1$ (17), $P2_12_12$ (18), $P2_12_12_1$ (19), are derived from a noncentric point group *222*. If the phases of EEO reflections with $h = 0$ and $k = 2n$, OEE reflections with $k = 0$ and $l = 2n$ and EOE reflections with $l=0$ and $h = 2n$ for the 4 space groups are fixed with phase 0, a position 0 0 0 is defined as an origin.

If these previously phased reflections are used as an input data for the direct methods,[3] better Fourier synthesis would be obtained.

References

1) Ibers, J. A. and Hamilton, W. C., International Tables for X-Ray Crystallography. The Kynoch Press, Birmingham, England, **IV**, 339-358 (1984).
2) Suh, I.-H., *Acta Cryst.*, **A54**, 254-256 (1998).
3) Sheldrick, G. M., *Acta Cryst.*, **A46**, 467-473 (1990).