SHORT COMMUNICATIONS

Acta Cryst. (1995). A**51**, 198–201

Rotation of spherical harmonics. Erratum.

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Abstract

An error in equations (3*b*) and (3*c*) of Su & Coppens [*Acta Cryst.* (1994). A**50**, 636–643] is corrected. The correct equations are

$$\alpha = \begin{cases} \arccos(R_{31}/\sin\beta) & \text{if } R_{32}/\sin\beta \geq 0 \\ 2\pi - \arccos(R_{31}/\sin\beta) & \text{if } R_{32}/\sin\beta < 0 \end{cases}, \quad (3b)$$

$$\gamma = \begin{cases} \arccos(-R_{13}/\sin\beta) & \text{if } R_{23}/\sin\beta \geq 0 \\ 2\pi - \arccos(-R_{13}/\sin\beta) & \text{if } R_{23}/\sin\beta < 0 \end{cases}. \quad (3c)$$

All relevant information is given in the *Abstract*.

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Friedel's law and non-centrosymmetric space groups.

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Abstract

It is shown that, in projections of non-centrosymmetric space groups having symmetry *p*3*m*1 or *p*31*m*, loci exist along which Friedel's law is obeyed even in the presence of n-beam interactions and phenomenological absorption. This theoretical prediction is verified by means of convergent-beam electron diffraction experiments on $Li_2ZnTi_3O_8$.

1. Introduction

Amongst the symmetry elements, the centre of inversion is well known to play a special role in electron scattering by crystals. For instance, where the kinematical description is a useful approximation, only the Laue groups can be determined unequivocally. Effects due to n-beam scattering in general are required to resolve this problem (Goodman & Lehmpfuhl, 1968). The analysis of non-centrosymmetric diffraction patterns, however, still presents particular difficulties. For certain non-centrosymmetric space groups, a simplification that can be utilized in initial interpretation is that, in the seven-beam approximation, zone-axis patterns reduce to an equivalent two-beam form (Moodie & Whitfield, 1994). It is now shown that, for specific space groups, loci exist along which Friedel's law is obeyed even in the presence of n-beam interactions. These serve to direct attention to specific areas in convergent-beam diffraction patterns where the failure of Friedel's law can be interpreted in structural terms.

Friedel's law states that the intensities of diffracted beams related by a centre of inversion are equal, that is, that $I(\mathbf{g}) = I(\bar{\mathbf{g}})$. When this is true, the space group of a crystal can be determined at best to within a centre of symmetry and this imposes a severe limitation on diffraction techniques.

The law is known to fail when absorption is significant or when dynamical scattering is strong. Bijvolet's method, of particular importance in the X-ray crystallography of organic materials, exhibits the first condition whilst convergent-beam electron diffraction is well suited to utilize the second condition.

In convergent-beam electron diffraction (CBED), loci are very important in the determination of symmetry and the departure from symmetry (Tanaka, Terauchi & Kaneyama, 1988). It is the purpose of this communication to show that the combination of symmetry elements in a number of non-centrosymmetric space groups generates loci along which, and only along which, Friedel's law holds for any thickness and for any phenomenological potential. These constitute sensitive diagnostic features for the identification of the space groups and provide a starting point for perturbative descriptions.

2. Scattering diagrams

In the multi-slice formulation of electron scattering, which is a basis-free description, a pictorial representation of the wave function can be given in terms of scattering diagrams (Moodie, 1972). Typical scattering diagrams are shown in Fig. 1.

In essence, this diagrammatic representation derives from the circumstance that the nth-order interaction can be written in the form $(i)^n \sum \ldots \sum V(g_i) \ldots V(g_{n-1}) V(g - \sum_i g_i) Z(\zeta \ldots \zeta_{n-1})$, where the $V(g_i)$ are structure amplitudes involved in the interaction and the ζ_i are the excitation errors. Each term of the series therefore consists of a function depending only on the structure multiplied by a function depending only on the geometry.

In terms of these diagrams, the breakdown of Friedel's law basically derives from the coupling of the $\pi/2$ phase change associated with each elementary scattering event within the multiple-scattering sequence with the anti-symmetric part of the structure.

When the g and $\bar{\mathbf{g}}$ reflexions coincide, that is, for the forward-scattered beam, the contribution from each diagram can be added to that from the diagram inverted in the origin and the anti-symmetric contributions cancel. This, as is well known, accounts for the centrosymmetric distribution in intensity in the central disc of a convergent-beam diffraction pattern. If higher-layer-line contributions are appreciable, that is, if diagrams out of the zone must be considered, the result still holds in three dimensions provided that the crystal possesses a plane of reflexion normal to the incident beam.

For a reflexion g, the wave function is built up from an infinity of diagrams. In a sequence of typical diagrams, labelled p, the real and imaginary parts of the nth-order products of the structure amplitudes are written ${}^{p}D_n$ and ${}^{p}E_n$. The sequence for the reflexion g is then of the form

$$\begin{aligned}
&\delta + i({}^1D_1 + i\,{}^1E_1)Z_1 + i^2 \sum_2 ({}^1D_2 + i\,{}^1E_2)Z_2 \\
&\quad + i^3 \sum_3 ({}^1D_3 + i\,{}^1E_3)Z_3 + \ldots \\
&\quad = \tfrac{1}{2}\Big[\Big(\delta - \sum_2 {}^1D_2 Z_2 + \sum_4 {}^1D_4 Z_4 - \ldots\Big) \\
&\qquad - \Big({}^1E_1 Z_1 - \sum_3 {}^1E_3 Z_3 + \sum_5 {}^1E_5 Z_5 - \ldots\Big)\Big] \\
&\qquad + \tfrac{1}{2} i\Big[\Big({}^1D_1 Z_1 - \sum_3 {}^1D_3 Z_3 + \sum_5 {}^1D_5 Z_5 - \ldots\Big) \\
&\qquad + \Big(\delta - \sum_2 {}^1E_2 Z_2 + \sum_4 {}^1E_4 Z_4 - \ldots\Big)\Big],
\end{aligned}$$

where $\sum_n$ symbolizes the sum over all the nth-order diagrams.

In general, the Z function for the reflexions g and $\bar{\mathbf{g}}$ will be equal for each specific diagram at the orientation appropriate for the testing of Friedel's law or, equivalently, at the corresponding points of the convergent-beam discs. Hence, the corresponding sequence for $\bar{\mathbf{g}}$ is

$$\begin{aligned}
&\tfrac{1}{2}\Big[\Big(\delta - \sum_2 {}^1D_2 Z_2 + \sum_4 {}^1D_4 Z_4 - \ldots\Big) \\
&\qquad + \Big({}^1E_1 Z_1 - \sum_3 {}^1E_3 Z_3 + \sum_5 {}^1E_5 Z_5 - \ldots\Big)\Big] \\
&\qquad + \tfrac{1}{2} i\Big[\Big({}^1D_1 Z_1 - \sum_3 {}^1D_3 Z_3 + \sum_5 {}^1D_5 Z_5 - \ldots\Big) \\
&\qquad - \Big(\delta - \sum_2 {}^1E_2 Z_2 + \sum_4 {}^1E_4 Z_4 - \ldots\Big)\Big].
\end{aligned}$$

Friedel's law is thus broken since the intensities of the reflexions g and $\bar{\mathbf{g}}$ will not be equal.

When the thin-phase-grating approximation is valid, or in the high-voltage limit, the Z function reduces to a factorial (Moodie, 1972; Cowley & Moodie, 1962) and the above series can be written

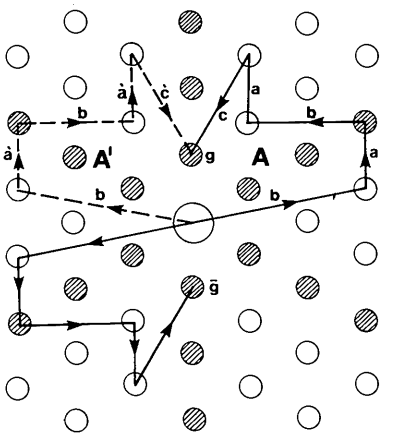
$$S_{\mathbf{g}} = (C_{\cos} - A_{\sin}) + i(C_{\sin} + A_{\cos}) \qquad (1a)$$

$$S_{\bar{\mathbf{g}}} = (C_{\cos} + A_{\sin}) + i(C_{\sin} - A_{\cos}), \qquad (1b)$$

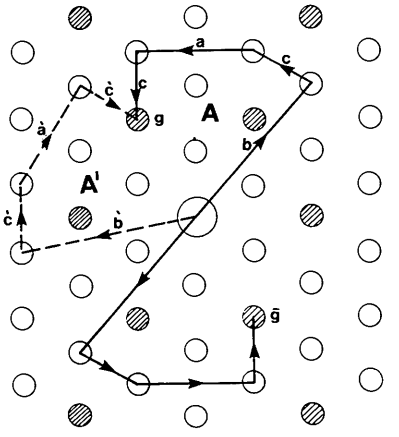
where typically $C_{\cos}$ is the cosine transform of the centrosymmetric part of the structure and $A_{\sin}$ is the sine function of the antisymmetric part of the structure (Cowley & Moodie, 1959). This effect will be particularly strong when the asymmetry arises from a non-centrosymmetric distribution of potential, for instance in the sphalerite structure with the sublattices occupied by atoms of different atomic number. Hence, in general, Friedel's law is broken in the high-voltage limit, and therefore effectively in very thin crystals.

For the forward-scattered beam, that is with g coinciding with $\bar{\mathbf{g}}$, an arbitrary sequence, $V(1)\ldots V(n)$, can be paired with its inversion in the origin (Fig. 1), the Z function at corresponding points will be equal and therefore the wave function will be centrosymmetric in reciprocal space.

Since the wave function is centrosymmetric, absorption described by a phenomenological potential can be included without destroying the inversion symmetry in the intensity

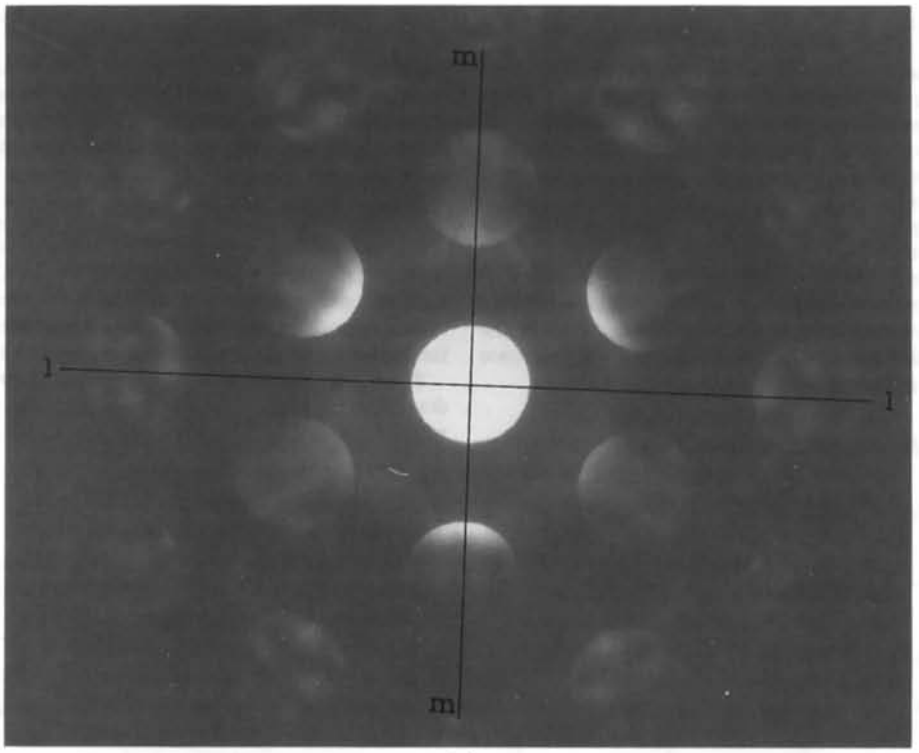


(*a*)

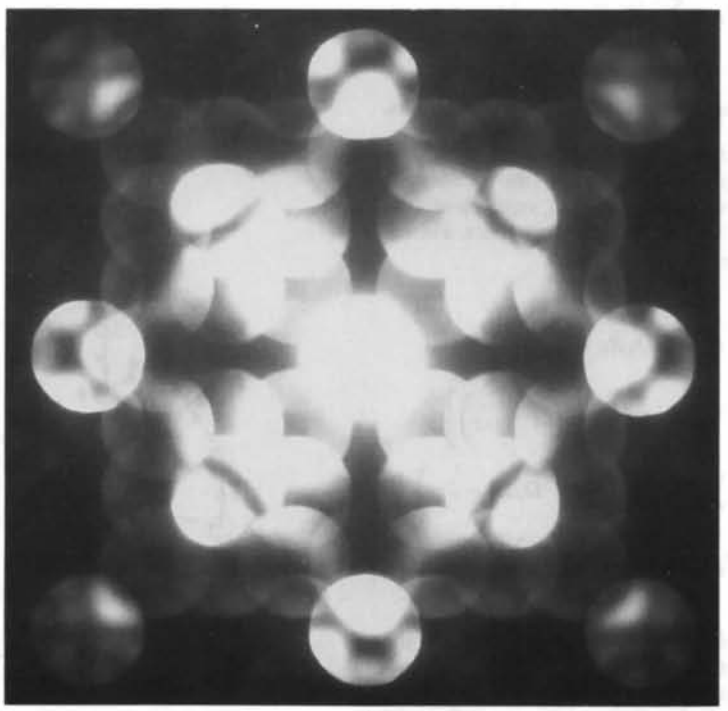


(*b*)

Fig. 1. Scattering diagrams for projections of non-centrosymmetric space groups with symmetry $p31m$ and $p3m1$. Scattering diagram A is paired with diagram A' generated by inversion in the origin followed by reflexion in a mirror plane.



(*a*)



(*b*)

Fig. 2. Convergent-beam electron diffraction patterns of $Li_2ZnTi_3O_8$ of space group no. 212, $P4_332$, illustrating the point that for a given structure two different projections can define the symmetry elements of the space group by means of loci of fundamentally different character. (*a*) Projection along [111]. Friedel's law breaks down for the first-order reflexions but holds along the loci, labelled *l*—*l*, which are at right angles to the planes of reflexion, labelled *m*—*m*. The symmetry of the projection is therefore *p*3*m*1. (*b*) Projection along [001] which is centrosymmetric. There is no breakdown of Friedel's law, but the loci of zeros associated with glide lines establishes the symmetry of this projection as *p*4*gm* (Gjønnes & Moodie, 1965).

of the forward-scattered beam, that is, of the zero-order convergent-beam disc.

In certain non-centrosymmetric space groups, there exist projections that are centrosymmetric and for these Friedel's law will hold. There is, however, another class in which specific reflexions remain real under n-beam dynamical scattering conditions. Projections of non-centrosymmetric space groups having point-group symmetry $p31m$ or $p3m1$ are now shown to be of this type. The possibility of the existence of loci in two dimensions along which Friedel's law holds then arises since the Z function for the reflexions $\mathbf{g}$ and $\bar{\mathbf{g}}$ will be equal at corresponding points of the convergent-beam discs. For point-group symmetry $p31m$ or $p3m1$ (Fig. 1), a typical scattering diagram A is paired with the diagram A' generated by inversion in the origin followed by reflexion in a mirror plane of the space group.

The sum of the contributions is then real since (i) segments of type a and a' are real; (ii) segments of type b and b' are complex conjugates because of the action of the mirror planes; and (iii) segments of type c and c' are complex conjugates because of the action of the trigonal axis or the mirror. The particular case of the diagrams associated with systematic interactions is covered by (i). These cover all possible relationships amongst the diagrams.

The wave amplitudes for reflexions $\mathbf{g}$ and $\bar{\mathbf{g}}$ are therefore equal along the six loci that are normals to the mirror lines. These connect the origin to the first-order reflexions in projections with symmetry $p31m$ and connect the origin to the second ring of reflexions in projections with symmetry $p3m1$ (see Fig. 1). Friedel's law holds along these loci even with the inclusion of phenomenological absorption. Since the loci are determined by the Z function, they should be detectable in the sense of having a finite width. For very thin crystals, when the phase-grating approximation is valid, Friedel's law will hold over the entire disc and the breakdown that derives entirely from thickness effects will in general be rather small. For the set of reflexions in the case just considered, the antisymmetric parts of (1) vanish and (1a) and (1b) reduce to

$$S_{\mathbf{g}} = S_{\bar{\mathbf{g}}} = C_{\cos} + iC_{\sin}.$$

3. Upper-layer-line contribution and convergent-beam electron diffraction

In order to obtain the result in its most general form, that is, in order to include upper-layer-line interactions, the diagrams of Fig. 1 must be drawn in three dimensions. When this is done, it can be seen that an additional symmetry element is required for cancellation of the imaginary parts of the structure amplitudes in every pair of lines in the scattering diagram. This additional element is, in fact, a mirror plane normal to the projection and containing the mirror line of the projection.

4. Experimental

Loci have already been observed for the [001] projection of silica (Moodie & Fehlmann, 1993), which has space group no. 152 ($P3_121$) and projection symmetry $p31m$.

In Fig. 2 are shown the convergent-beam electron diffraction patterns for the [001] and [111] projections of $Li_2ZnTi_3O_8$ of space group no. 212 ($P4_332$) (Joubert, Berthet & Bertaut, 1970). The [001] projection of this space group has symmetry $p4gm$ and the CBED pattern exhibits the general reflexion condition that $h00$ reflexions are forbidden for h not equal to $4n$. Friedel's law is seen to hold for all reflexions in this centrosymmetric projection. For the [111] projection of symmetry $p3m1$, there are loci along which Friedel's law holds, namely lines from the origin through the $1\bar{2}1$ and $2\bar{4}2$ reflexions. However, the first-order reflexions show a strong breakdown of Friedel's law. The departure of this structure from the centrosymmetric space group of spinel, no. 227, $Fd\bar{3}m$, essentially arises from ordering of octahedrally coordinated 12 Ti and 4 Li atoms in Wyckoff positions 12(d) and 4(b) of space group $P4_332$ The $1\bar{1}0$ and $\bar{1}10$ reflexions that arise as a consequence of the cation ordering are antiphase.

SiO_2 and $Li_2ZnTi_3O_8$ exemplify the two major structural subdivisions for non-centrosymmetric structures (Moodie, 1965). The non-centrosymmetric character depends on the positions in the former and on weights in the latter.

APPENDIX

15 non-centrosymmetric space groups have special projections with symmetry $p31m$: these include the [001] projections of the trigonal space groups 150 ($P321$), 152 ($P3_121$), 154 ($P3_221$), 157 ($P31m$), 159 ($P31c$), 160 ($R3m$), and 161 ($R3c$) and of the hexagonal space groups 189 ($P\bar{6}2m$) and 190 ($P\bar{6}c$). For these, the $\langle 001 \rangle$ lattice directions are mirror lines of the projections. For three of these space groups only, nos. 157, 160 and 189, these mirror lines are in fact mirror planes normal to the projections. The other special projections with symmetry $p31m$ are the [111] projections of cubic space groups 215 ($P\bar{4}3m$), 216 ($F\bar{4}3m$), 217 ($I\bar{4}3m$), 218 ($P\bar{4}3n$), 219 ($F\bar{4}3c$) and 220 ($I\bar{4}3d$). For three of these space groups, nos. 215, 216 and 217, the mirror lines are in fact mirror planes normal to the projections.

16 non-centrosymmetric space groups have special projections with symmetry $p3m1$: these include the [001] projections of trigonal space groups 149 ($P312$), 151 ($P3_112$), 153 ($P3_212$), 155 ($R32$), 156 ($P3m1$) and 158 ($P3c1$), and hexagonal space groups 187 ($P\bar{6}m2$) and 188 ($P\bar{6}c2$), which all have mirror lines normal to the $\langle 100 \rangle$ equivalent lattice directions. In just two of these cases is the mirror line a mirror plane normal to the projection, namely space groups 156 and 187. The other special projections with symmetry $p3m1$ are the [111] projections of cubic space groups 207 ($P432$), 208 ($P4_232$), 209 ($F432$), 210 ($F4_132$), 211 ($I432$), 212 ($P4_332$), 213 ($P4_132$) and 214 ($I4_132$). None of these cubic space groups have mirror planes normal to their [111] projections.

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