

Pseudo extra reflection conditions

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The extra reflection conditions as given in Volume A of *International Tables for Crystallography* may not be rigorously fulfilled if the thermal vibrations and positional or static disorder of the atoms are not isotropic. Although small in most cases, the intensities of reflections violating the extra reflection conditions can become measurable for large thermal and positional anisotropy. It would be useful to have an inventory of these 'pseudo extra reflection conditions' for all space groups in the early stage of structure investigation. The subject is demonstrated with the aid of four significant examples and the possibility of predicting without calculation the status of the largest part of the extra reflection conditions is discussed.

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1. Introduction: the pseudo extra reflection conditions

Some time ago, Popa & Willis (2004) gave an explanation and a generalization to any space group of an effect systematically observed over a long period of time in the diffraction patterns of the β phase of U_4O_9 : the atoms sit in general positions but the pattern obeys the reflection conditions of special sites. The structure of this compound was further refined by Cooper & Willis (2004) from single-crystal neutron data in accordance with the Popa & Willis (2004) procedure. In the actual paper the opposite effect is discussed: although all atoms sit in a special position the diffraction pattern may not obey the extra reflection conditions (ERCs) specific to this site.

The reflection conditions as given in Volume A of *International Tables for Crystallography* (2006) were derived presuming not only identical scattering amplitudes for the equivalent atoms but also identical Debye–Waller factors (DWFs). The last presumption is valid only if the thermal vibrations and positional disorder are isotropic. If not, only the lengths of the principal axes of the atomic displacement ellipsoids are the same, not their orientations. Consequently, DWFs for equivalent atoms are different and if these atoms are in special positions the associated ERCs may not be fulfilled.¹

Although, to the best of my knowledge, this effect has not been explicitly documented until now, it is probably accounted for when anisotropic atomic displacement parameters are refined in the structure-refinement programs. Nevertheless, in the early stage of structure model searching, it would be useful to know if a given ERC is rigorously fulfilled for any atomic displacement distribution or if it is only a 'pseudo extra reflection condition' (PERC). This statement is endorsed, for example, by the following comment from the article by Hahn & Looijenga-Vos (2006): 'if the special position is occupied by

atoms whose scattering power is high in comparison with the other atoms in the structure, reflections violating the extra condition will be weak'. Obviously, there is a unique explanation of such weak reflections if the extra condition is rigorously fulfilled: those 'other atoms' from the cited fragment. If the extra condition is not rigorously fulfilled, an ambiguous situation occurs: all atoms sit in the corresponding special position and have anisotropic atomic displacements (at least part of them), or there are also atoms of low scattering power sitting in other places.

2. Calculation of DWFs

To see if an ERC is rigorously fulfilled, the corresponding structure factor should be calculated including anisotropic DWFs. Accounting for the specifics of the problem, analytical expressions for DWFs obtained by not too tedious algebra are required.

For the general position the DWFs are described by six atomic displacement parameters forming a symmetrical second-rank tensor. For the special positions some constraints are imposed on these tensors by site symmetry. There are two traditional methods to deal with tensor derivation and reduction: the 'matrix method' (see *e.g.* Authier, 2006) and the 'direct-inspection method' (Fumi, 1952*a,b*).

In the matrix method the DWF tensor of an equivalent point in the general position is found from those of the first equivalent point (representative) by applying the specific transformation of the second-rank tensor at the rotation part of the symmetry operations defining this equivalent point. The tensor reduction is performed by solving a homogenous system of linear equations resulting from the invariance of the DWF tensor to the symmetry operations of the special site (Kuhs, 2006; Levy, 1956; Peterse & Palm, 1966). The constraints derived by this method can be found in Table 8.3.1.1 from Prince *et al.* (2006) for any space group. Although

¹ Hereafter one presumes harmonic thermal vibrations and Gaussian distribution for the static disorder.

appropriate for computer programming, the matrix method is too lengthy for our purpose.

The direct-inspection method proposed by Fumi (1952*a*) is a very simple one and is based on a fundamental property of tensors: the tensor elements transform under a change of basis like the product of vector components. To find the DWF tensor of an equivalent point in the general position starting from a representative it is enough to see how the coordinates are changed under the symmetry operation (rotation part) defining this equivalent point. The reduction is performed by setting invariance conditions of the DWF tensor to the symmetry operations of the special site.

The Fumi (1952*a*) direct-inspection method can only be applied to crystal classes in which the coordinates do not transform into linear combinations of themselves under the symmetry operations, which excludes the trigonal and hexagonal classes. Later Fumi (1952*b*) extended the direct-inspection method to these classes with the price of losing the simplicity.

In the present paper, a direct-inspection method was used to calculate DWFs for a special site which is similar in terms of simplicity to those of Fumi (1952*a*) but not identical. The key of the method is the invariance of the DWFs to the symmetry of the special site. The DWFs for the equivalent points in general positions are directly calculated from the coordinates of these points found in the Wyckoff table; the invariance is imposed by direct inspection of the isomorphism between these coordinates and those of the equivalent points in the special site. In the actual variant the DWF tensor element transformations as products of vector components and their invariance to rotations appear to be consequences of the calculations, not starting points in the DWF determination as in the Fumi (1952*a*) variant. The algorithm of the actual variant is described in the following.

Firstly, the DWFs for the general positions were calculated as described by Popa & Willis (2004). These DWFs are $\exp(-W_{(i)})$, with $W_{(i)} = 2\pi^2 \langle (\mathbf{H}\mathbf{u}_{(i)})^2 \rangle$ and where $\mathbf{u}_{(i)}$ is the atomic displacement vector of the equivalent point (*i*), $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is the reciprocal-lattice vector and $\langle \dots \rangle$ represents the thermal and static disorder averages. If the displacement vector of the representative in a general position in terms of the unit-cell vectors is $\mathbf{u}_{(1)} = u_x\mathbf{a} + u_y\mathbf{b} + u_z\mathbf{c}$, then the displacement vectors of all the equivalent points are obtained if u_x, u_y, u_z replaces x, y, z in the list of coordinates of general positions of the corresponding *symmorphic* group. Replacing these displacement vectors in $W_{(i)}$ gives the quadratic forms² in the variables h, k, l for equivalent points in general positions, all constructed with six coefficients β_{mn} defined as follows: $\beta_{11} = 2\pi^2 \langle u_x^2 \rangle$, $\beta_{22} = 2\pi^2 \langle u_y^2 \rangle$, $\beta_{33} = 2\pi^2 \langle u_z^2 \rangle$, $\beta_{12} = 2\pi^2 \langle u_x u_y \rangle$, $\beta_{13} = 2\pi^2 \langle u_x u_z \rangle$ and $\beta_{23} = 2\pi^2 \langle u_y u_z \rangle$. Now considering a special position, the atomic displacement quadratic forms of equivalent points can be denoted by $W_{[ij]}$ (label in square brackets) to distinguish them from those of

general positions. If the coordinates of the first equivalent point of the special position are replaced into the set of coordinates of general positions, coordinates of all the equivalent points of the special position are obtained, each being obtained r times, r being the ratio between the multiplicities of the general and special positions. If m is the ratio between the multiplicity of the special position and the centring multiplier (1, 2, 3 or 4), then there are $(r-1)m$ equalities involving $W_{(i)}$ allowing the constraints of β_{mn} and then $W_{[ij]}$ to be determined (redundantly in most cases).

3. Checking the ERCs for the special positions 4*b* and 8*c* in the group $\bar{I}42d$ (No. 122)

According to *International Tables for Crystallography* Volume A (2006), pp. 428–429, in the space group $\bar{I}42d$ the special positions 4*b* of site symmetry $\bar{4}$.. and 8*c* of site symmetry 2.. both have the ERC $hkl : l = 2n + 1$ or $2h + l = 4n$, but only for the first site is the condition fulfilled if the atomic displacement is anisotropic.

The DWFs are first calculated for equivalent points in the general position 16*e*, following the procedure described in the previous section. The DWFs are the same for the first and second sets of coordinates. The coordinates in the first set are

$$(1) \ x, y, z \quad (2) \ \bar{x}, \bar{y}, z \quad (3) \ y, \bar{x}, \bar{z} \quad (4) \ \bar{y}, x, \bar{z} \quad (5) \ \bar{x} + \frac{1}{2}, y, \bar{z} + \frac{3}{4} \\ (6) \ x + \frac{1}{2}, \bar{y}, \bar{z} + \frac{3}{4} \quad (7) \ \bar{y} + \frac{1}{2}, \bar{x}, z + \frac{3}{4} \quad (8) \ y + \frac{1}{2}, x, z + \frac{3}{4}. \quad (1)$$

The *symmorphic* group is $\bar{I}42m$ (No. 121), consequently the atomic displacement quadratic forms of the equivalent points in general positions are

$$W_{(1)} = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl \\ W_{(2)} = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl \\ W_{(3)} = \beta_{22}h^2 + \beta_{11}k^2 + \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{23}hl + 2\beta_{13}kl \\ W_{(4)} = \beta_{22}h^2 + \beta_{11}k^2 + \beta_{33}l^2 - 2\beta_{12}hk + 2\beta_{23}hl - 2\beta_{13}kl \\ W_{(5)} = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 - 2\beta_{12}hk + 2\beta_{13}hl - 2\beta_{23}kl \\ W_{(6)} = \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl + 2\beta_{23}kl \\ W_{(7)} = \beta_{22}h^2 + \beta_{11}k^2 + \beta_{33}l^2 + 2\beta_{12}hk - 2\beta_{23}hl - 2\beta_{13}kl \\ W_{(8)} = \beta_{22}h^2 + \beta_{11}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{23}hl + 2\beta_{13}kl. \quad (2)$$

3.1. Special position 4*b*, site symmetry $\bar{4}$.

The coordinates of equivalent points are

$$[1] \ 0, 0, 0 \quad [2] \ \frac{1}{2}, 0, \frac{3}{4}.$$

Replacing [1] (0, 0, 0) in the set of coordinates [equation (1)] gives

$$(1) = (2) = (3) = (4) = (0, 0, 0) = [1]; \\ (5) = (6) = (7) = (8) = \left(\frac{1}{2}, 0, \frac{3}{4}\right) = [2].$$

Consequently the following relations should be fulfilled by the quadratic forms [equation (2)]

² In the paper by Popa & Willis (2004), page 320, right column, unlabelled equation, the correct left side is W_6 not W_{10} . The error occurred because the list of coordinates (ten) was rearranged in a later version of the manuscript, but the unlabelled equation was not updated.

Table 1

Square modules of the structure factors for the special site 8c of the space group $I42d$ calculated with $\beta_{11} = 0.04$, $\beta_{22} = 0.005$, $\beta_{33} = 0.01$, $\beta_{12} = 0.014$ for $z = 0.1$.

The unique set of reflections was generated with the unit-cell parameters $a_0 = 4.125$, $c_0 = 5.125$ Å arbitrarily chosen.

<i>h</i>	<i>k</i>	<i>l</i>	$ F_{hkl} ^2$	<i>h</i>	<i>k</i>	<i>l</i>	$ F_{hkl} ^2$
1	0	1	19.1362	4	1	1	14.6055
2	0	0	53.7197	2	2	4	21.6299
1	1	2	5.1984	4	0	2	2.0931
2	1	1	17.7942	3	2	3	1.1972
2	0	2	0.2191	4	2	0	28.5719
1	0	3	2.1850	3	1	4	0.2061
2	2	0	45.2137	3	3	2	4.2143
3	0	1	11.0302	2	1	5	15.5901
3	1	0	0.0057	4	2	2	1.0271
0	0	4	30.4173	4	1	3	4.2518
2	1	3	2.8242	3	0	5	13.2691
3	1	2	3.9399	1	1	6	18.6568
3	2	1	10.6152	4	3	1	9.2464
2	0	4	25.5314	5	0	1	3.9428
3	0	3	0.4704	5	1	0	0.0733
4	0	0	33.6590	4	0	4	15.9971
1	0	5	18.5606	2	0	6	0.0441

$$W_{(1)} = W_{(2)} = W_{(3)} = W_{(4)} = W_{[1]};$$

$$W_{(5)} = W_{(6)} = W_{(7)} = W_{(8)} = W_{[2]}.$$

From the first equalities set $\beta_{22} = \beta_{11}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$ are obtained, and the same from the second set. As expected these constraints are identical to those from Table 8.3.1.1 of Prince *et al.* (2006). With these constraints there is a unique atomic displacement quadratic form for all equivalent points, namely

$$W_{[1]} = W_{[2]} = W = \beta_{11}(h^2 + k^2) + \beta_{33}l^2.$$

Consequently, in the expression of the structure factor for the special position 4b the unique DWF can be factorized, and then the ERC is rigorously fulfilled in this case, although the atomic displacements are anisotropic.

3.2. Special position 8c, site symmetry 2..

The coordinates of equivalent points are

$$[1] 0, 0, z \quad [2] 0, 0, \bar{z} \quad [3] \frac{1}{2}, 0, \bar{z} + \frac{3}{4} \quad [4] \frac{1}{2}, 0, \bar{z} + \frac{3}{4}. \quad (3)$$

By replacing [1] 0, 0, z in the set of coordinates [equation (1)] then

$$(1) = (2) = [1], (3) = (4) = [2], (5) = (6) = [3], (7) = (8) = [4]$$

and then

$$W_{(1)} = W_{(2)} = W_{[1]}, \quad W_{(3)} = W_{(4)} = W_{[2]},$$

$$W_{(5)} = W_{(6)} = W_{[3]}, \quad W_{(7)} = W_{(8)} = W_{[4]}.$$

From the first equality $\beta_{13} = \beta_{23} = 0$ is obtained (as in Table 8.3.1.1). The remaining equalities between $W_{(i)}$'s are redundant and $W_{[k]}$'s for equivalent points in 8c are

$$W_{[1]} = a + c, \quad W_{[2]} = b - c, \quad W_{[3]} = a - c, \quad W_{[4]} = b + c, \quad (4)$$

where a, b, c are defined as follows:

$$\begin{aligned} a &= \beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2, \\ b &= \beta_{22}h^2 + \beta_{11}k^2 + \beta_{33}l^2, \\ c &= 2\beta_{12}hk. \end{aligned} \quad (5)$$

Taking into account equations (3) and (4), the structure factor for this site is given as

$$F_{hkl} = [1 + (-1)^{h+k+l}] \times \left\{ \begin{aligned} &\exp[-(a+c)]\exp(2\pi ilz) + \exp[-(b-c)]\exp(2\pi i\bar{z}) \\ &+ \exp[-(a-c)]\exp\{2\pi i[h/2 + (\bar{z} + 3/4)l]\} \\ &+ \exp[-(b+c)]\exp\{2\pi i[h/2 + (z + 3/4)l]\} \end{aligned} \right\}. \quad (6)$$

The first factor on the right of equation (6) is due to body centring. Furthermore, F_{hkl} and then $|F_{hkl}|^2$ can be calculated for those three cases of hkl defining the ERC: (i) $l = 2n + 1$, (ii) $l = 2m, 2h + l = 4n$ for which the reflections are allowed, and (iii) $l = 2m, 2h + l \neq 4n$ for which the reflections are forbidden.

(i) $l = 2n + 1$:

$$|F_{hkl}|^2 = 4[1 + (-1)^{h+k+l}]\exp(-2a) \times \left\{ \begin{aligned} &\cosh(2c)[1 + \exp[2(a-b)]] \\ &+ 2\exp(a-b)\cos(4\pi lz) \\ &+ (-1)^{h+(l-1)/2+1}[1 - \exp[2(a-b)]]\sin(4\pi lz) \end{aligned} \right\}. \quad (7)$$

(ii) $l = 2m, 2h + l = 4n$:

$$|F_{hkl}|^2 = 4[1 + (-1)^{h+k+l}]\exp(-2a) \times [1 + \exp(a-b)]^2[\cosh(2c) + \cos(4\pi lz)]. \quad (8)$$

(iii) $l = 2m, 2h + l \neq 4n$:

$$|F_{hkl}|^2 = 4[1 + (-1)^{h+k+l}]\exp(-2a) \times [1 - \exp(a-b)]^2[\cosh(2c) - \cos(4\pi lz)]. \quad (9)$$

From equation (5) $a - b = (\beta_{11} - \beta_{22})(h^2 - k^2)$, then from equation (9) the ERC for the 8c site is rigorously fulfilled if $\beta_{22} = \beta_{11}$, even if other anisotropy elements such as $\beta_{33} \neq \beta_{22} = \beta_{11}$ and/or $\beta_{12} \neq 0$ exist. In contrast the ERC is violated if the anisotropy $A = \beta_{11} - \beta_{22}$ is different from zero. If $|A|$ is large the peaks $l = 2m, 2h + l \neq 4n$ become measurable, as can be seen from the simulated data in Table 1. The simulation was performed starting from values of displacement parameters possible for real samples and calculating $|F_{hkl}|^2$ using equations (7), (8) or (9) for the unique set of reflections of $I42d$ generated with some values of lattice parameters. According to the ERC 8c the peaks in bold should be forbidden, but they are not. Despite being of weak intensity, these peaks are comparative with many allowed peaks presumed to be measurable. The ERC for the 8c site is then in fact a 'PERC'.

4. Conserved, removed or modified ERCs

When isotropic DWFs are replaced by anisotropic ones the ERCs (if they exist) can not only be conserved or removed, as was shown in the previous section, but they can also be modified, as can be seen in the following two examples.

4.1. Group $P\bar{4}3n$ (No. 218), special position 6c

According to *International Tables for Crystallography* Volume A (2006), p. 665, for this special position the site symmetry is $\bar{4}$.. and the ERC is

$$hkl : h + k + l = 2n \text{ or } h = 2n + 1, k = 4n, l = 4n + 2. \quad (10)$$

Using the procedure described previously gives $\beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23} = 0$; then the corresponding structure factor is

$$F_{hkl} = \exp(-a) \exp(i\pi h/2)(-1)^k [1 + (-1)^h] + \exp(-b) \exp(i\pi k/2)(-1)^l [1 + (-1)^k] + \exp(-c) \exp(i\pi l/2)(-1)^h [1 + (-1)^l], \quad (11)$$

where $a = \beta_{11}h^2 + \beta_{22}(k^2 + l^2)$, $b = \beta_{11}k^2 + \beta_{22}(h^2 + l^2)$ and $c = \beta_{11}l^2 + \beta_{22}(h^2 + k^2)$.

It is readily seen from equation (11) that the reflections $h, k, l = 2n + 1$ are not allowed and also that $F_{hkl} \neq 0$ for $h + k + l = 2n$. Still left to check is the combination of one odd index and two even indices:³ $h = 2n + 1, k = 2m, l = 2j$. Replacing equation (11) gives

$$|F_{hkl}| = 2 \exp(-b) |1 - (-1)^{(k+l)/2} \exp A| = 2 \exp(-b) \begin{cases} |1 - \exp A| & \text{for } k + l = 4n \\ |1 + \exp A| & \text{for } k + l = 4n + 2, \end{cases} \quad (12)$$

where $A = b - c = (\beta_{11} - \beta_{22})(k^2 - l^2)$. For the isotropic case $\beta_{11} = \beta_{22}$, then $A = 0$ and equation (12) is in agreement with the second part of ERC [equation (10)]. With anisotropic displacement parameters the first part of equation (10) is conserved, the second is removed, and then the ERC is modified, becoming $h + k + l = 2n$.

4.2. Group $Pn\bar{3}n$ (No. 222), special position 8c

According to *International Tables for Crystallography* Volume A (2006), p. 677, the site symmetry and the ERC are $\bar{3}$. and $h, k, l : h, k, l = 2n$. The constraints of the displacement parameters are $\beta_{11} = \beta_{22} = \beta_{33}$ and $\beta_{12} = \beta_{13} = \beta_{23}$, then the structure factor is

$$|F_{hkl}| = [1 + (-1)^{h+k+l}] \exp(-a - b) \times |1 + (-1)^l \exp(b - c) + (-1)^k \exp(b - d) + (-1)^h \exp(b - e)|, \quad (13)$$

where $a = \beta_{11}(h^2 + k^2 + l^2)$, $b = 2\beta_{12}(hk + hl + kl)$, $c = 2\beta_{12}(hk - hl - kl)$, $d = 2\beta_{12}(-hk + hl - kl)$ and $e = 2\beta_{12}(-hk - hl + kl)$. It can be seen from equation (13) that if

³ It is a cubic group, then h, k, l are permuted.

$\beta_{12} \neq 0$ then $|F_{hkl}| \neq 0$ not only for $h, k, l = 2n$ but also for $h = 2n + 1, k = 2n + 1$ and $l = 2n$.⁴ In other words the ERC $h, k, l = 2n$ is extended to $h + k + l = 2n$.

5. Numerical checking and prediction of PERCs

The analytical calculations developed above proved that using anisotropic DWFs may result in full or partial violation of the ERCs. Using such calculations to realize a necessary inventory of PERCs is a tedious and uneconomical enterprise. It is much more convenient to carry out numerical simulations similar to those presented above, resulting in Table 1. For this purpose any existing computer software providing a unique set of reflections together with the corresponding structure factors can be used.

Besides the numerical checking a large number of PERCs can be predicted without calculation using Table 8.3.1.1 from Prince *et al.* (2006). In this table the independent elements of the DWF tensors of the equivalent positions of a given special site are found. These tensors are obtained from those of the representative position of the special site by applying the operations of the crystal point group not belonging to the site point group. The corresponding atomic displacement ellipsoids (ADEs) are identical in shape, whereas they may or may not be identical in orientation. An easy prediction of the ERC status for non-cubic groups is based only on this last condition: identical orientations mean identical DWFs, then the ERC is conserved as in *International Tables for Crystallography*.

For site symmetry $\bar{1}$ in any space group⁵ the DWF tensors have six independent elements and then the ADEs have different orientations, consequently the ERCs are removed, being in fact PERCs. The same is valid for the special sites of point groups $2, m, 2/m$ in any space group. In these cases the DWF tensors have four independent parameters and the twofold axis is a common principal axis for the ADEs but these ellipsoids have different orientations in the plane normal to this axis. On the contrary, for the special sites of point groups $4, \bar{4}, 4/m, 4mm, \bar{4}2m, 422, 4/mmm$ in the tetragonal space groups ADEs are rotation ellipsoids around the fourfold axis. These ellipsoids have identical orientations and consequently the ERCs are conserved. The same arguments and conclusions (ERCs conserved) are valid for the special sites $3, \bar{3}, 3m, 32, \bar{3}m$ and $6, \bar{6}, 6/m, 622, \bar{6}2m, 6mm, 6/mmm$ in the trigonal (hexagonal axes) and hexagonal space groups where the threefold and sixfold axis, respectively, are ADEs rotation axes. For the special sites of point groups $222, mm2, mmm$, there are three independent parameters determining the principal axes of ADEs along the three twofold axes. In the orthorhombic space groups there are no symmetry operations giving different ADE orientations, and then in these groups the ERCs are conserved. Such operations exist in tetragonal, trigonal and hexagonal space groups where the ERCs of these special sites are removed.

⁴ Note that the group is primitive so the first factor on the right side of equation (13) is not due to centring.

⁵ There are no special sites of this symmetry obeying ERCs in the triclinic and cubic groups.

For the cubic groups the prediction of ERC status from simple considerations, without any calculations, is a very difficult, rather impossible task.⁶ There are two arguments to support this statement.

(i) Although the independent elements of the DWF tensors of equivalent positions are determined only by the oriented site symmetry, the status of an ERC can be different for different cubic space groups, which is not the case inside a given non-cubic crystal system. For example, the ERC for $6d$ of symmetry $222..$ from $Pn\bar{3}$ is conserved, but it is removed for $6d$ of symmetry $222..$ from $P4_232$.

(ii) It is frequently possible to conserve the ERCs, totally or partially, even if the ADEs do not have identical orientations. For example, the ERC is conserved in $6d$ of symmetry $222..$ from $Pn\bar{3}$, although the three pairs of identical ellipsoids are oriented along the cube axes.

In $8c$ of symmetry $\bar{3}$ from $Pn\bar{3}n$ where, according to §4.2, the ERC is only partially violated, there are eight rotation ellipsoids around the four threefold axes. Note that a partial violation of the ERC may only occur in cubic space groups. Consequently, the status of ERCs in cubic groups should be checked by numerical simulation.

6. Conclusions

The ERCs as given by the *International Tables for Crystallography* were derived presuming isotropic DWFs. If anisotropic DWFs are considered, one of the following three situations occurs:

(i) the ERC is conserved as it was derived for the isotropic case;

(ii) the ERC is modified, acting on an enlarged group of Miller indices;

(iii) the ERC may be completely removed, becoming a PERC.

The supplementary diffraction peaks not predicted by the 'original' ERCs or, at least, by part of them may become measurable if the anisotropy of DWFs is not small. For the early stage of the structure investigation it is useful to have an

inventory of the real status of the extra reflection conditions for all space groups. This could be of a fundamental importance when searching for a structural model, helping to avoid possible confusions resulting in the wrong initial choice of model. The largest part of this inventory is already available from the symmetry considerations given in the previous section. The rest can be easily obtained by numerical simulations using the existing structure-refinement programs.

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⁶ Except for the special sites of monoclinic symmetries $2, m, 2/m$ already discussed.