Acta Crystallographica Section A
Foundations of Crystallography
ISSN 0108-7673

Received 3 February 2008
Accepted 6 May 2008

Intensity statistics of Friedel opposites

U. Shmueli,[a]* M. Schiltz[b] and H. D. Flack[c]

[a]School of Chemistry, Tel Aviv University, 69978 Tel Aviv, Israel, [b]Laboratoire de Cristallographie, École Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland, and [c]Laboratoire de Cristallographie, University of Geneva, Switzerland. Correspondence e-mail: ushmueli@post.tau.ac.il

A previous analysis of the average intensity and mean-square intensity difference of Friedel opposites, confined to the space group $P1$ [Flack & Shmueli (2007). *Acta Cryst.* A**63**, 257–265], is here extended to all the non-centrosymmetric space groups. The present analysis presumes purely non-centrosymmetric content of the unit cell. An important result of this study is that the average intensity and mean-square intensity difference of Friedel opposites have the same values for all the non-centrosymmetric space groups as those previously obtained for the triclinic space group $P1$. The ratios of average intensity and root-mean-square intensity difference to their triclinic equivalents were derived and exemplified for general as well as for special reflections. For the latter, enhancements were obtained which are shown to be due to those of average intensity and not to a mechanism related to Friedel opposites being explicitly considered.

1. Introduction

A detailed analysis of the mean-square Friedel intensity difference was carried out by Flack & Shmueli (2007) for the simplest triclinic space group $P1$, while assuming the presence of a centrosymmetric substructure. Although this rigorous approach to the problem is useful for structures that conform to the symmetry examined, it was by no means obvious that the results are applicable to, or have a bearing on, symmetries other than $P1$. On the contrary, the mean-square Friedel intensity difference depends on the low moments of intensity and these are known to be space-group dependent (*e.g.* Wilson, 1978). We have therefore decided to simplify the treatment by omitting the presence of centrosymmetric and other symmetric substructures, and eventually carry out the analysis for all the non-centrosymmetric space groups. The concise version of trigonometric structure factors (Shmueli, 2001) was found very useful in the early stages of this analysis. So the average intensity and mean-square intensity difference of Friedel opposites was found to be the same for all non-centrosymmetric space groups, presuming a purely non-centrosymmetric content of the unit cell and general reflections only. We have also derived the ratios of these quantities to the corresponding ones for $P1$ for general reflections as well as for special reflections in all the space groups. These ratios furnish the intensity average multiples of interest. Applications of the results obtained in this study will be reported elsewhere (Flack & Bernardinelli, 2008).

2. Preliminaries

Let g be the number of asymmetric units in the unit cell, G be a lattice centering factor equal to 1, 2, 3 or 4 for P-type, A-, B-, C- or I-type, $R_{\rm hex}$-type or F-type lattices, respectively, N be the number of atoms in the unit cell, N/g be the number of atoms in the asymmetric unit, and let all the atoms be spherical, have only isotropic displacement parameters and be located in general positions, there being no centrosymmetric or any other symmetric substructure. Let $(\mathbf{P}_i, \mathbf{t}_i)$ be the space-group operator generating the ith asymmetric unit from the reference unit (that generated by the identity operator). The structure factor is given by

$$F(\mathbf{h}) = \sum_{j=1}^{N/g}(f_j + if_j'')\sum_{i=1}^{g}\exp[2\pi i\mathbf{h}^T(\mathbf{P}_i\mathbf{r}_j + \mathbf{t}_i)] \equiv \sum_{j=1}^{N/g}(f_j + if_j'')(A_j + iB_j), \quad (1)$$

where

$$A_j = \sum_{i=1}^{g}\cos[2\pi\mathbf{h}^T(\mathbf{P}_i\mathbf{r}_j + \mathbf{t}_i)]$$

and

$$B_j = \sum_{i=1}^{g}\sin[2\pi\mathbf{h}^T(\mathbf{P}_i\mathbf{r}_j + \mathbf{t}_i)],$$

where A_j and B_j are respectively the real and imaginary parts of the trigonometric structure factor (hereafter t.s.f.) for the jth atom of the asymmetric unit.

If we expand equation (1), the structure factor for any space group is given by

$$F(\mathbf{h}) = \sum_{j=1}^{N/g} f_j A_j + i\sum_{j=1}^{N/g} f_j'' A_j + i\sum_{j=1}^{N/g} f_j B_j - \sum_{j=1}^{N/g} f_j'' B_j$$

and introducing the abbreviations

$$\sigma = \sum_{j=1}^{N/g} f_j A_j, \quad \sigma'' = \sum_{j=1}^{N/g} f_j'' A_j,$$
$$\xi = \sum_{j=1}^{N/g} f_j B_j, \quad \xi'' = \sum_{j=1}^{N/g} f_j'' B_j,$$

we can write

$$F(\mathbf{h}) = \sigma + i\sigma'' + i\xi - \xi''.$$

Since ξ and ξ'' change sign when $\mathbf{h}$ changes sign, we have

$$F(-\mathbf{h}) = \sigma + i\sigma'' - i\xi + \xi''$$

and hence the mean reduced intensity of Friedel opposites is

$$\begin{aligned} A_v &= \tfrac{1}{2}(|F(\mathbf{h})|^2 + |F(-\mathbf{h})|^2) \\ &= \tfrac{1}{2}[(\sigma - \xi'')^2 + (\sigma'' + \xi)^2] + \tfrac{1}{2}[(\sigma + \xi'')^2 + (\sigma'' - \xi)^2] \\ &= \sigma^2 + \sigma''^2 + \xi^2 + \xi''^2, \end{aligned}$$

and its average is

$$\begin{aligned} \langle A_v\rangle &= \langle\sigma^2\rangle + \langle\sigma''^2\rangle + \langle\xi^2\rangle + \langle\xi''^2\rangle \\ &= \left\langle \sum_{j=1}^{N/g}\sum_{k=1}^{N/g} f_j f_k A_j A_k \right\rangle + \left\langle \sum_{j=1}^{N/g}\sum_{k=1}^{N/g} f_j'' f_k'' A_j A_k \right\rangle \\ &\quad + \left\langle \sum_{j=1}^{N/g}\sum_{k=1}^{N/g} f_j f_k B_j B_k \right\rangle + \left\langle \sum_{j=1}^{N/g}\sum_{k=1}^{N/g} f_j'' f_k'' B_j B_k \right\rangle \\ &= \sum_{j=1}^{N/g}\sum_{k=1}^{N/g} [(f_j f_k + f_j'' f_k'')(\langle A_j A_k\rangle + \langle B_j B_k\rangle)]. \end{aligned} \quad (2)$$

The intensity difference between Friedel opposites is

$$\begin{aligned} D &= |F(\mathbf{h})|^2 - |F(-\mathbf{h})|^2 \\ &= (\sigma - \xi'')^2 + (\sigma'' + \xi)^2 - (\sigma + \xi'')^2 - (\sigma'' - \xi)^2 \\ &= -4\sigma\xi'' + 4\sigma''\xi \\ &= 4(\sigma''\xi - \sigma\xi'') \end{aligned}$$

and the mean-square intensity difference is

$$\langle D^2\rangle = 16(\langle\sigma''^2\xi^2\rangle - 2\langle\sigma\sigma''\xi\xi''\rangle + \langle\sigma^2\xi''^2\rangle).$$

We thus have

$$\begin{aligned} \langle D^2/16\rangle &= \sum_{j=1}^{N/g}\sum_{k=1}^{N/g}\sum_{l=1}^{N/g}\sum_{m=1}^{N/g} (f_j'' f_k'' f_l f_m - 2 f_j f_k'' f_l f_m'' + f_j f_k f_l'' f_m'') \\ &\quad \times \langle A_j A_k B_l B_m\rangle. \end{aligned} \quad (3)$$

It follows that, for any space group, $\langle A_v\rangle$ and $\langle D^2\rangle$ may be obtained by calculating $\langle A_j A_k\rangle$, $\langle B_j B_k\rangle$ and $\langle A_j A_k B_l B_m\rangle$. This can be done by using explicit or concise expressions for t.s.f.'s (Lonsdale, 1965; Shmueli, 2001) or, much more generally, as detailed in the following sections. Since in some instances the use of t.s.f.'s is mandatory, we show in Appendix *A* an example of a calculation of the averages for $P2_12_12_1$ and some related orthorhombic non-centrosymmetric space groups, from the appropriate t.s.f.'s.

As concerns the averaging process, we have followed Shmueli & Wilson (2001) using the usual fixed-index approach based on independence of atomic contributions to the structure factor, uniform distribution of the atoms throughout the unit cell and omitting systematic absences.

2.1. A relevant classification of reflections

In this paper, it will be necessary to classify reflections according to their symmetry properties under the point group of the crystal. First, the relationship between structure factors of symmetry-related reflections is

$$F(\mathbf{P}^T\mathbf{h}) = F(\mathbf{h})\exp(-2\pi i\mathbf{h}^T\mathbf{t}), \quad (4)$$

where $(\mathbf{P}, \mathbf{t})$ is a space-group operator and $\mathbf{P}$ is an operator of the underlying point group (Waser, 1955).

For a particular reflection $\mathbf{h}$, there will always be one or more point-group operators $\mathbf{P}$ that leave $\mathbf{h}$ invariant and hence satisfy $\mathbf{P}^T\mathbf{h} = \mathbf{h}$. In this case, from (4), one finds

$$F(\mathbf{h}) = F(\mathbf{h})\exp(-2\pi i\mathbf{h}^T\mathbf{t}), \quad (5)$$

$F(\mathbf{h})$ can be non-zero only if $\exp(-2\pi i\mathbf{h}^T\mathbf{t}) = 1$, which can be so only if $\mathbf{h}^T\mathbf{t}$ is an integer.

If $\mathbf{h}^T\mathbf{t}$ in (5) is not an integer, $F(\mathbf{h})$ must vanish and corresponds to a *systematically absent* reflection.

For each reflection $\mathbf{h}$, the set of all point-group operators for which $\mathbf{P}^T\mathbf{h} = \mathbf{h}$ holds is a subgroup of the point group, called the isotropy subgroup of $\mathbf{h}$, denoted by $\mathcal{G}_\mathbf{h}$ (see *e.g.* §A2 of Appendix *A* in Bricogne, 1991) (the isotropy subgroup is elsewhere called the stabilizer or little co-group). Its order is denoted by $|\mathcal{G}_\mathbf{h}|$. Since there is always at least one point-group operator which obeys $\mathbf{P}^T\mathbf{h} = \mathbf{h}$, $|\mathcal{G}_\mathbf{h}| \geq 1$. If $|\mathcal{G}_\mathbf{h}| = 1$, $\mathbf{h}$ is known as a *general* reflection and, if $|\mathcal{G}_\mathbf{h}| > 1$, then $\mathbf{h}$ is known as a *special* reflection.

A simple example and comments on the isotropy subgroup are presented in Appendix *B*.

A reflection $\mathbf{h}$ is *centric* if for some point-group operator we have $\mathbf{P}^T\mathbf{h} = -\mathbf{h}$. A reflection for which there is no point-group operator $\mathbf{P}$ giving $\mathbf{P}^T\mathbf{h} = -\mathbf{h}$ is said to be *acentric* (see *e.g.* §A2 of Appendix *A* in Bricogne, 1991).

3. $\langle A_v\rangle$ and $\langle D^2\rangle$ for acentric and centric reflections

Tables 2.1.3.1 and 2.1.3.2 of Shmueli & Wilson (2001) present intensity-distribution effects of various symmetry operations on selected rows and zones of reflections. Their Table 2.1.3.3 presents average intensity multiples arranged by point groups. Shmueli & Wilson (2001) should be consulted for an introduction and all background information to this topic. In the context of the present study, we considered it of importance to investigate and establish the relevant intensity multiples for $\langle A_v\rangle$ and $\langle D^2\rangle$ for both general and special reflections.

Table 1
Classification of the reflections for point group 222.

See the text for the definition of the symbols.

$\mathbf{h}$	$\lvert\mathcal{G}_{\mathbf{h}}\rvert$	$\mathcal{G}_{\mathbf{h}}$	Stat(sym)	Stat($\mathbf{h}$)	$\langle A_v\rangle/\Sigma$	$\sqrt{\langle D^2\rangle/\rho}$
hkl	1	1	a	g	G	G
$0kl$	1	1	c	g	G	0
$h0l$	1	1	c	g	G	0
$hk0$	1	1	c	g	G	0
$h00$	2	2	c	s	$2G$	0
$0k0$	2	2	c	s	$2G$	0
$00l$	2	2	c	s	$2G$	0

Table 2
Classification of the reflections for point group *mm*2.

See the text for the definition of the symbols.

$\mathbf{h}$	$\lvert\mathcal{G}_{\mathbf{h}}\rvert$	$\mathcal{G}_{\mathbf{h}}$	Stat(sym)	Stat($\mathbf{h}$)	$\langle A_v\rangle/\Sigma$	$\sqrt{\langle D^2\rangle/\rho}$
hkl	1	1	a	g	G	G
$0kl$	2	m	a	s	$2G$	$2G$
$h0l$	2	m	a	s	$2G$	$2G$
$hk0$	1	1	c	g	G	0
$h00$	2	m	c	s	$2G$	0
$0k0$	2	m	c	s	$2G$	0
$00l$	4	$mm2$	a	s	$4G$	$4G$

It is shown in the following subsections that the mean intensity and root-mean-square intensity differences of Friedel opposites, divided by their triclinic equivalents, are given for any possible reflection, special or general, by

$$\langle A_v\rangle/\Sigma = |\mathcal{G}_{\mathbf{h}}|G \text{ for a centric or an acentric reflection} \quad (6)$$

$$\sqrt{\langle D^2\rangle/\rho} = \begin{cases} |\mathcal{G}_{\mathbf{h}}|G & \text{for an acentric reflection} \\ 0 & \text{for a centric reflection.} \end{cases} \quad (7)$$

The equations for the triclinic equivalents Σ and ρ are given in Flack & Shmueli (2007).

As an example, we show in Tables 1 and 2 the values of the expressions in (6) and (7) in terms of G, the lattice centering factor, for the general and special reflections in all the non-centrosymmetric orthorhombic space groups. Since, however, only the point-group operators are of importance in this context, it is sufficient to consider only the two relevant point groups.

Each table contains the average intensity multiples for general and special reflections in space groups based on the point group in the table caption; G is the lattice-centering factor and here can be 1, 2 or 4; $\mathcal{G}_{\mathbf{h}}$ is the Hermann–Mauguin symbol of the isotropy subgroup corresponding to each set of reflections in the leftmost column; Stat(sym) is a or c if the set of reflections is acentric or centric and Stat($\mathbf{h}$) is g or s if the set of reflections is general or special, respectively.

From Tables 1 and 2, one can find the values of the averages for any non-centrosymmetric orthorhombic space group. For example, the values of the averages for the $00l$ reflection in Table 2 are 4, 8 and 16 for the space groups $Pna2_1$, $Ccc2$ and $Fdd2$, respectively.

It is in order to mention at this point that we have also undertaken an explicit tabulation of $\langle A_v\rangle/\Sigma$ and $(\langle D^2\rangle/\rho)^{1/2}$ for all low non-centrosymmetric space groups, presented in Table 3 in the supplementary material.[1] Our results are entirely compatible with those of Shmueli & Wilson (2001). Applications are presented in Flack & Bernardinelli (2008).

3.1. Derivation of $\langle A_v\rangle$ and $\langle D^2\rangle$ for general and special acentric reflections

To evaluate all the averages in equations (2) and (3), we first consider the second-order terms in A and B, *i.e.* A_jA_k, B_jB_k and A_jB_k. It follows from the assumed independence of atomic contributions to the structure factor that, for $j \neq k$, $\langle A_jA_k\rangle = \langle A_j\rangle\langle A_k\rangle = 0$ since the averages of cosine and sine vanish. Likewise, for $j \neq k$, $\langle B_jB_k\rangle = \langle A_jB_k\rangle = 0$. This leaves $\langle A_j^2\rangle$, $\langle B_j^2\rangle$ and $\langle A_jB_j\rangle$ to be examined.

If one expands A_j and B_j, given in equation (1), one finds

$$\begin{aligned} A_j &= \sum_{i=1}^{g} \cos[2\pi\mathbf{h}^T(\mathbf{P}_i\mathbf{r}_j + \mathbf{t}_i)] \\ &= \sum_{i=1}^{g}[\cos(2\pi\mathbf{h}^T\mathbf{P}_i\mathbf{r}_j)\cos(2\pi\mathbf{h}^T\mathbf{t}_i) - \sin(2\pi\mathbf{h}^T\mathbf{P}_i\mathbf{r}_j)\sin(2\pi\mathbf{h}^T\mathbf{t}_i)] \\ &= \sum_{i=1}^{g}[C_i\cos(2\pi\mathbf{h}^T\mathbf{P}_i\mathbf{r}_j) - S_i\sin(2\pi\mathbf{h}^T\mathbf{P}_i\mathbf{r}_j)] \end{aligned} \quad (8)$$

and

$$\begin{aligned} B_j &= \sum_{i=1}^{g} \sin[2\pi\mathbf{h}^T(\mathbf{P}_i\mathbf{r}_j + \mathbf{t}_i)] \\ &= \sum_{i=1}^{g}[\sin(2\pi\mathbf{h}^T\mathbf{P}_i\mathbf{r}_j)\cos(2\pi\mathbf{h}^T\mathbf{t}_i) + \cos(2\pi\mathbf{h}^T\mathbf{P}_i\mathbf{r}_j)\sin(2\pi\mathbf{h}^T\mathbf{t}_i)] \\ &= \sum_{i=1}^{g}[C_i\sin(2\pi\mathbf{h}^T\mathbf{P}_i\mathbf{r}_j) + S_i\cos(2\pi\mathbf{h}^T\mathbf{P}_i\mathbf{r}_j)], \end{aligned} \quad (9)$$

where

$$C_i = \cos(2\pi\mathbf{h}^T\mathbf{t}_i) \quad \text{and} \quad S_i = \sin(2\pi\mathbf{h}^T\mathbf{t}_i). \quad (10)$$

Let us start by evaluating $\langle A_j^2\rangle$.

$$\begin{aligned} A_j^2 = \sum_{m=1}^{g}\sum_{n=1}^{g}[&C_mC_n\cos(2\pi\mathbf{h}^T\mathbf{P}_m\mathbf{r}_j)\cos(2\pi\mathbf{h}^T\mathbf{P}_n\mathbf{r}_j) \\ &+ S_mS_n\sin(2\pi\mathbf{h}^T\mathbf{P}_m\mathbf{r}_j)\sin(2\pi\mathbf{h}^T\mathbf{P}_n\mathbf{r}_j) \\ &- C_mS_n\cos(2\pi\mathbf{h}^T\mathbf{P}_m\mathbf{r}_j)\sin(2\pi\mathbf{h}^T\mathbf{P}_n\mathbf{r}_j) \\ &- S_mC_n\sin(2\pi\mathbf{h}^T\mathbf{P}_m\mathbf{r}_j)\cos(2\pi\mathbf{h}^T\mathbf{P}_n\mathbf{r}_j)]. \end{aligned} \quad (11)$$

When one averages the double summation (11), the third and fourth terms, which contain products of sine and cosine functions, vanish. Further, since all the atoms are assumed to be in general positions and be uniformly distributed throughout the unit cell, the averages

$$\langle\cos(2\pi\mathbf{h}^T\mathbf{P}_m\mathbf{r}_j)\cos(2\pi\mathbf{h}^T\mathbf{P}_n\mathbf{r}_j)\rangle$$
$$\text{and} \quad \langle\sin(2\pi\mathbf{h}^T\mathbf{P}_m\mathbf{r}_j)\sin(2\pi\mathbf{h}^T\mathbf{P}_n\mathbf{r}_j)\rangle \quad (12)$$

vanish unless

$$\mathbf{h}^T\mathbf{P}_m\mathbf{r}_j = \mathbf{h}^T\mathbf{P}_n\mathbf{r}_j, \quad (13)$$

[1] Table 3 is available from the IUCr electronic archives (Reference: SH5073). Services for accessing these archives are described at the back of the journal.

in which case each of the averages in (12) evaluates to 1/2. Condition (13) can be rewritten as

$$(\mathbf{P}_m^T\mathbf{h})^T\mathbf{r}_j = (\mathbf{P}_n^T\mathbf{h})^T\mathbf{r}_j. \tag{14}$$

We shall now consider four cases.

3.1.1. Case 1: general reflections, *P*-type lattice. Condition (14) now reduces to

$$\mathbf{P}_m = \mathbf{P}_n. \tag{15}$$

Since the space group is based on a *P*-type lattice ($G = 1$), condition (15) is satisfied if $m = n$. Each of these nonvanishing terms thus evaluates to

$$\begin{aligned}\tfrac{1}{2}(C_mC_n + S_mS_n) &= \tfrac{1}{2}[\cos(2\pi\mathbf{h}^T\mathbf{t}_m)\cos(2\pi\mathbf{h}^T\mathbf{t}_n) \\ &\quad + \sin(2\pi\mathbf{h}^T\mathbf{t}_m)\sin(2\pi\mathbf{h}^T\mathbf{t}_n)] \\ &= \tfrac{1}{2}\cos[2\pi\mathbf{h}^T(\mathbf{t}_m - \mathbf{t}_n)]. \end{aligned}\tag{16}$$

Since, however, $m = n$, $\cos[2\pi\mathbf{h}^T(\mathbf{t}_m - \mathbf{t}_n)] = 1$ and we thus find

$$\langle A_j^2\rangle = \tfrac{1}{2}g \tag{17}$$

and similarly

$$\langle B_j^2\rangle = \tfrac{1}{2}g. \tag{18}$$

3.1.2. Case 2: general reflections, centered lattice (1< *G* ≤ 4). If we reconsider equation (15), in this case m may be different from n: indeed, if $\mathbf{t}_r$ is a centering translation then the centering operator applied to a space-group operator results in adding $\mathbf{t}_r$ to its translational part, the rotational part remaining unchanged:

$$(\mathbf{I},\mathbf{t}_r)(\mathbf{P}_m,\mathbf{t}_m) = (\mathbf{P}_m,\mathbf{t}_m + \mathbf{t}_r) \equiv (\mathbf{P}_n,\mathbf{t}_n) \tag{19}$$

and the number of centering translations associated with a certain rotational part of a space-group operator is just $G - 1$ (note that, for $G = 1$, $\mathbf{t}_r = \mathbf{0}$). Summing up, for each value of m in the non-vanishing terms of (11) there are G values of n satisfying (15) and there are therefore in the double summation in (11) gG non-vanishing terms.

Each of these non-vanishing terms thus evaluates to equation (16). It is seen from (19) that for centered lattices the difference $\mathbf{t}_m - \mathbf{t}_n$ is a centering translation and it equals $\mathbf{0}$ if $G = 1$. The value of $\cos[2\pi\mathbf{h}^T(\mathbf{t}_m - \mathbf{t}_n)]$ is thus 1 for possible reflections and −1 for systematic lattice absences from crystals belonging to lattice types other than *P*. However, as pointed out above, systematic absences are excluded from the averaging process.

We thus find

$$\langle A_j^2\rangle = \tfrac{1}{2}gG \tag{20}$$

and, following the same argument as above,

$$\langle B_j^2\rangle = \tfrac{1}{2}gG. \tag{21}$$

3.1.3. Case 3: special reflections, *P*-type lattice. Condition (14) reduces in this case to

$$\mathbf{P}_m^T\mathbf{h} = \mathbf{P}_n^T\mathbf{h}. \tag{22}$$

Since the space group is based on a *P*-type lattice, condition (22) is satisfied only if both $\mathbf{P}_m^T$ and $\mathbf{P}_n^T$ are in $\mathcal{G}_\mathbf{h}$. In that case, for each value of m in the double summation of (11), there will be exactly $|\mathcal{G}_\mathbf{h}|$ values of n satisfying condition (22). If we use (10), each of these non-vanishing terms evaluates as given in (16). Since, however, $\mathbf{h}^T\mathbf{t}$ must be an integer for reflections that are not systematically absent, $\cos[2\pi\mathbf{h}^T(\mathbf{t}_m - \mathbf{t}_n)]$ equals 1 and we find

$$\langle A_j^2\rangle = \tfrac{1}{2}g|\mathcal{G}_\mathbf{h}| \tag{23}$$

and, following similar reasoning,

$$\langle B_j^2\rangle = \tfrac{1}{2}g|\mathcal{G}_\mathbf{h}|. \tag{24}$$

3.1.4. Case 4: special reflections, centered lattice (1 < *G* ≤ 4). If the space group is based on a centered lattice, condition (22) is satisfied as before if both $\mathbf{P}_m^T$ and $\mathbf{P}_n^T$ are in $\mathcal{G}_\mathbf{h}$. However, for a given m and n which satisfy (22), there will be $G - 1$ further terms in the second summation which are related to n by pure lattice-centering operations. Thus, for each value of m, there will then be exactly $G|\mathcal{G}_\mathbf{h}|$ values of n satisfying condition (22) and, since there are g values of m, we finally obtain

$$\langle A_j^2\rangle = \tfrac{1}{2}gG|\mathcal{G}_\mathbf{h}| \tag{25}$$

and, in a similar manner,

$$\langle B_j^2\rangle = \tfrac{1}{2}gG|\mathcal{G}_\mathbf{h}|. \tag{26}$$

Equations (25) and (26) are the most general form for $\langle A_j^2\rangle$ and $\langle B_j^2\rangle$. They apply in all cases as for a *P*-type lattice $G = 1$ and for a general reflection $|\mathcal{G}_\mathbf{h}| = 1$.

3.2. Derivation of ⟨A_v⟩ and ⟨D^2⟩ for general and special acentric reflections (continued)

To evaluate $\langle A_jB_j\rangle$, we again follow the same line of argument as for $\langle A_j^2\rangle$. However, corresponding to equation (16), owing to differences in the trigonometric expansions, one finds for the non-vanishing terms

$$\begin{aligned}\tfrac{1}{2}(C_mS_n - S_mC_n) &= \tfrac{1}{2}[\cos(2\pi\mathbf{h}^T\mathbf{t}_m)\sin(2\pi\mathbf{h}^T\mathbf{t}_n) \\ &\quad - \sin(2\pi\mathbf{h}^T\mathbf{t}_m)\cos(2\pi\mathbf{h}^T\mathbf{t}_n)] \\ &= \tfrac{1}{2}\sin[2\pi\mathbf{h}^T(\mathbf{t}_n - \mathbf{t}_m)]. \end{aligned}\tag{27}$$

Since, however, this difference vector $\mathbf{t}_n - \mathbf{t}_m$ is a zero vector or a centering translation, then for possible reflections the argument of the sine function is an integer multiple of π and the sine function then vanishes. It follows that

$$\langle A_jB_j\rangle = 0. \tag{28}$$

The next stage in the analysis is to consider relevant terms of fourth order in A and B, *i.e.* $A_jA_kB_lB_m$, needed for the evaluation of $\langle D^2\rangle$ in equation (3). Once again it follows from the assumed independence of the atomic contributions to the structure factor that, if any one of the four indices j, k, l, m is different from all the others, the mean value of the fourth-order term will be zero, *e.g.* for $j \neq k$, $j \neq l$ and $j \neq m$, $\langle A_j A_k B_l B_m \rangle = \langle A_j \rangle \langle A_k B_l B_m \rangle = 0$. As a consequence, only the following terms with paired equal indices need further consideration:

(*a*) $\langle A_j A_j B_j B_j \rangle$: it is unnecessary to evaluate this average as its coefficient in equation (3) is identically zero and makes no contribution to $\langle D^2 \rangle$;

(*b*) $\langle A_j A_l B_j B_l \rangle$, $\langle A_j A_l B_l B_j \rangle$ with $j \neq l$: owing to the independence of atomic contributions to the structure factor and making use of equation (28), these terms may be written as $\langle A_j A_l B_j B_l \rangle = \langle A_j B_j \rangle \langle A_l B_l \rangle = 0$;

(*c*) $\langle A_j A_j B_l B_l \rangle$: again the independence of atomic contributions and equations (25) and (26) lead to

$$\langle A_j A_k B_l B_m \rangle = \langle A_j^2 B_l^2 \rangle = \langle A_j^2 \rangle \langle B_l^2 \rangle = (\tfrac{1}{2} g G |\mathcal{G}_{\mathbf{h}}|)^2 = \tfrac{1}{4} g^2 G^2 |\mathcal{G}_{\mathbf{h}}|^2. \quad (29)$$

If we now use equations (25) and (26) for $\langle A_j^2 \rangle + \langle B_j^2 \rangle$ with (2), we obtain

$$\langle A_v \rangle = g G |\mathcal{G}_{\mathbf{h}}| \sum_{j=1}^{N/g} (f_j^2 + f_j''^2) = G |\mathcal{G}_{\mathbf{h}}| \sum_{j=1}^{N} (f_j^2 + f_j''^2) \equiv G |\mathcal{G}_{\mathbf{h}}| \Sigma, \quad (30)$$

where Σ is the value of $\langle A_v \rangle$ obtained by Flack & Shmueli (2007) for the triclinic space group $P1$, in agreement with Wilson's statistics.

If we now substitute (29) in (3), with index combination $j = k$, $l = m$ and $j \neq l$, we obtain

$$\begin{aligned} \langle D^2 \rangle &= 4 g^2 G^2 |\mathcal{G}_{\mathbf{h}}|^2 \sum_{j=1}^{N/g} \sum_{l=1 (j \neq l)}^{N/g} (f_j''^2 f_l^2 - 2 f_j f_j'' f_l f_l'' + f_j^2 f_l''^2) \\ &= 4 G^2 |\mathcal{G}_{\mathbf{h}}|^2 \sum_{j=1}^{N} \sum_{l=1}^{N} (f_j'' f_l - f_j f_l'')^2 \quad (31) \\ &\equiv G^2 |\mathcal{G}_{\mathbf{h}}|^2 \rho, \quad (32) \end{aligned}$$

where ρ is the value of $\langle D^2 \rangle$ obtained by Flack & Shmueli (2007) for the triclinic space group $P1$. Note that the restriction $j \neq l$ was removed from (31) since $f_j'' f_l - f_j f_l'' = 0$ for $j = l$.

Hence, under the assumptions stated, the values of the average intensity [equation (30)] and mean-square intensity difference of Friedel opposites [equation (31)] are the same for all the three-dimensional non-centrosymmetric space groups. Of course, for centric reflections $D = 0$ and this derivation is valid only for non-centrosymmetric space groups.

3.3. Derivation of $\langle A_v \rangle$ for centric reflections

We recall that a reflection $\mathbf{h}$ is centric if for some point-group operator $\mathbf{P}_m$ we have $\mathbf{P}_m^T \mathbf{h} = -\mathbf{h}$. As before, the non-vanishing averages that need to be evaluated for $\langle A_j^2 \rangle$ and $\langle B_j^2 \rangle$ are

$$\langle \cos(2\pi \mathbf{h}^T \mathbf{P}_m \mathbf{r}_j) \cos(2\pi \mathbf{h}^T \mathbf{P}_n \mathbf{r}_j) \rangle \quad (33)$$

and

$$\langle \sin(2\pi \mathbf{h}^T \mathbf{P}_m \mathbf{r}_j) \sin(2\pi \mathbf{h}^T \mathbf{P}_n \mathbf{r}_j) \rangle. \quad (34)$$

These averages vanish unless

$$\mathbf{h}^T \mathbf{P}_m \mathbf{r}_j = \pm \mathbf{h}^T \mathbf{P}_n \mathbf{r}_j, \quad (35)$$

which implies that

$$\mathbf{P}_m^T \mathbf{h} = \pm \mathbf{P}_n^T \mathbf{h}. \quad (36)$$

The '+' sign on the right-hand side of (36) leads to the same expression for $\langle A_v \rangle$ as in the acentric case. In the double summation (2), there will now be additional non-vanishing terms whenever m and n satisfy

$$\mathbf{P}_m^T \mathbf{h} = -\mathbf{P}_n^T \mathbf{h}. \quad (37)$$

These additional terms evaluate to

$$\tfrac{1}{2}(C_m C_n - S_m S_n) \quad (38)$$

for $\langle A_j^2 \rangle$ and to

$$\tfrac{1}{2}(S_m S_n - C_m C_n) \quad (39)$$

for $\langle B_j^2 \rangle$, so that a full cancellation of the additional non-vanishing terms occurs. Therefore, the centric character of a reflection does not change the average intensity of Friedel opposites, which is again

$$\langle A_v \rangle = g G |\mathcal{G}_{\mathbf{h}}| \sum_{j=1}^{N/g} (f_j^2 + f_j''^2) = G |\mathcal{G}_{\mathbf{h}}| \Sigma. \quad (40)$$

However, for centric reflections, Friedel opposites are identical and therefore $D = 0$.

4. A rederivation of $\langle D^2 \rangle$ by the moment method

As pointed out in the *Introduction*, the mean-square intensity difference of Friedel opposites depends on low moments of the magnitude of the structure factor, which are known to depend on space-group symmetry. The foregoing derivations show that for $\langle D^2 \rangle$ this is not the case and we thought it to be interesting to rederive directly $\langle D^2 \rangle$ from its definition in terms of the moments by a method similar to that used by Wilson (1978). The simplest case of general reflections and a P-type lattice ($G = 1$) will be assumed since it is sufficient for the present purpose. We recall that the difference intensity of Friedel opposites is given by

$$D(\mathbf{h}) = |F(\mathbf{h})|^2 - |F(-\mathbf{h})|^2$$

and its second moment, in the fixed-index approach, is

$$\begin{aligned} \langle D^2(\mathbf{h}) \rangle &= \langle (|F(\mathbf{h})|^2 - |F(-\mathbf{h})|^2)^2 \rangle \\ &= \langle |F(\mathbf{h})|^4 \rangle - 2 \langle |F(\mathbf{h})|^2 |F(-\mathbf{h})|^2 \rangle + \langle |F(-\mathbf{h})|^4 \rangle. \quad (41) \end{aligned}$$

Following Wilson (1978) and modifying his notation for complex scattering factors, for compatibility with other parts of this paper, we can write

$$F(\mathbf{h}) = \sum_{i=1}^{N/g} \mathrm{f}_i J_i(\mathbf{h}),$$

where $\mathrm{f}_i = f_i + if_i''$ and f_i is the real part of the scattering factor of atom i, including the real part of the resonant scattering contribution, and

$$J_i(\mathbf{h}) = \sum_{m=1}^{g} \exp[2\pi i \mathbf{h}^T(\mathbf{P_m}\mathbf{r}_i + \mathbf{t}_m)]. \quad (42)$$

The fourth moment of $|F(\mathbf{h})|$ is

$$\langle |F(\mathbf{h})|^4 \rangle = \sum_{i=1}^{N/g}\sum_{j=1}^{N/g}\sum_{k=1}^{N/g}\sum_{l=1}^{N/g} \mathrm{f}_i\mathrm{f}_j^*\mathrm{f}_k\mathrm{f}_l^* \langle J_i(\mathbf{h})J_j^*(\mathbf{h})J_k(\mathbf{h})J_l^*(\mathbf{h})\rangle. \quad (43)$$

As shown by Wilson (1978), for non-centrosymmetric structures those terms which survive on averaging have index combinations (i) $i = j = k = l$, (ii) $i = j$ and $k = l$ with $j \neq k$ and (iii) $i = l$ and $j = k$ with $i \neq k$. Hence,

$$\langle |F(\mathbf{h})|^4 \rangle = \sum_{i=1}^{N/g} |\mathrm{f}_i|^4 \langle |J_i(\mathbf{h})|^4\rangle + 2\sum_{i=1}^{N/g}\sum_{k=1(i\neq k)}^{N/g} |\mathrm{f}_i|^2|\mathrm{f}_k|^2 \langle |J_i(\mathbf{h})|^2\rangle \langle |J_k(\mathbf{h})|^2\rangle. \quad (44)$$

Following Shmueli & Weiss (1995), we can write

$$\langle |J_i(\mathbf{h})|^2\rangle = \sum_{s=1}^{g}\sum_{u=1}^{g} \langle \exp[2\pi i\mathbf{h}^T(\mathbf{P}_s - \mathbf{P}_u)\mathbf{r}_i]\rangle \exp[2\pi i \mathbf{h}^T(\mathbf{t}_s - \mathbf{t}_u)]. \quad (45)$$

The inner average in this equation vanishes unless $\mathbf{P}_s - \mathbf{P}_u$ is a zero matrix, in which case it equals unity. It therefore follows that

$$\langle |J_i(\mathbf{h})|^2\rangle = \sum_{s=1}^{g}\sum_{u=1}^{g} \delta_{su} \exp[2\pi i \mathbf{h}^T(\mathbf{t}_s - \mathbf{t}_u)] = g. \quad (46)$$

We can now rewrite the fourth moment of $|F(\mathbf{h})|$ as

$$\begin{aligned}\langle |F(\mathbf{h})|^4 \rangle &= \sum_{i=1}^{N/g} |\mathrm{f}_i|^4 \langle |J_i(\mathbf{h})|^4\rangle + 2g^2 \sum_{i=1}^{N/g}\sum_{k=1(i\neq k)}^{N/g} |\mathrm{f}_i|^2|\mathrm{f}_k|^2 \\ &= \sum_{i=1}^{N/g} |\mathrm{f}_i|^4 \langle |J_i(\mathbf{h})|^4\rangle + 2\sum_{i=1}^{N}\sum_{k=1(i\neq k)}^{N} |\mathrm{f}_i|^2|\mathrm{f}_k|^2. \end{aligned} \quad (47)$$

Hence, the fourth moment of $|F(\mathbf{h})|$ consists of a single summation which is well known to be space-group dependent (*e.g.* Wilson, 1978) and a double summation which is space-group independent. Let us consider the remaining two moments in (41). The fourth moment of $|F(-\mathbf{h})|$ is given by

$$\langle |F(-\mathbf{h})|^4 \rangle = \sum_{i=1}^{N/g}\sum_{j=1}^{N/g}\sum_{k=1}^{N/g}\sum_{l=1}^{N/g} \mathrm{f}_i\mathrm{f}_j^*\mathrm{f}_k\mathrm{f}_l^* \langle J_i(-\mathbf{h})J_j^*(-\mathbf{h})J_k(-\mathbf{h})J_l^*(-\mathbf{h})\rangle.$$

Since, from (42), $J_i(-\mathbf{h}) = J_i^*(\mathbf{h})$ and $J_i^*(-\mathbf{h}) = J_i(\mathbf{h})$, there is in practice no difference between the fourth moments of $|F(\mathbf{h})|$ and $|F(-\mathbf{h})|$. Hence,

$$\begin{aligned}&\langle |F(\mathbf{h})|^4 \rangle + \langle |F(-\mathbf{h})|^4 \rangle \\ &= 2\sum_{i=1}^{N/g} |\mathrm{f}_i|^4 \langle |J_i(\mathbf{h})|^4\rangle + 4\sum_{i=1}^{N}\sum_{k=1(i\neq k)}^{N} |\mathrm{f}_i|^2|\mathrm{f}_k|^2. \end{aligned} \quad (48)$$

We now consider the remaining mixed term: $-2\langle |F(\mathbf{h})|^2|F(-\mathbf{h})|^2\rangle$.

$$\begin{aligned}&-2\langle |F(\mathbf{h})|^2|F(-\mathbf{h})|^2\rangle \\ &= -2\sum_{i=1}^{N/g}\sum_{j=1}^{N/g}\sum_{k=1}^{N/g}\sum_{l=1}^{N/g} \mathrm{f}_i\mathrm{f}_j^*\mathrm{f}_k\mathrm{f}_l^* \langle J_i(\mathbf{h})J_j^*(\mathbf{h})J_k(-\mathbf{h})J_l^*(-\mathbf{h})\rangle \\ &= -2\sum_{i=1}^{N/g}\sum_{j=1}^{N/g}\sum_{k=1}^{N/g}\sum_{l=1}^{N/g} \mathrm{f}_i\mathrm{f}_j^*\mathrm{f}_k\mathrm{f}_l^* \langle J_i(\mathbf{h})J_j^*(\mathbf{h})J_k^*(\mathbf{h})J_l(\mathbf{h})\rangle. \end{aligned} \quad (49)$$

The index combinations of the surviving terms in the average in (49) are: (i) $i = j = k = l$, (ii) $i = j, k = l$ with $i \neq k$ and (iii) $i = k, j = l$ with $i \neq j$. Index combination (i) contributes

$$-2\sum_{i=1}^{N/g} |\mathrm{f}_i|^4 \langle |J_i(\mathbf{h})|^4\rangle \quad (50)$$

and, if we compare (50) with (48), it is seen that the summations over the space-group-dependent fourth moments of $|J_i(\mathbf{h})|$ cancel out. This is a significant result. Index combination (ii) contributes

$$-2\sum_{i=1}^{N/g}\sum_{k=1(k\neq i)}^{N/g} |\mathrm{f}_i|^2|\mathrm{f}_k|^2 \langle |J_i(\mathbf{h})|^2\rangle \langle |J_k(\mathbf{h})|^2\rangle$$

and this reduces, analogously to (47), to

$$-2\sum_{i=1}^{N}\sum_{k=1(k\neq i)}^{N} |\mathrm{f}_i|^2|\mathrm{f}_k|^2. \quad (51)$$

Index combination (iii) contributes

$$-2\sum_{i=1}^{N/g}\sum_{j=1(j\neq i)}^{N/g} \mathrm{f}_i^2\mathrm{f}_j^{*2} \langle |J_i(\mathbf{h})|^2\rangle \langle |J_j(\mathbf{h})|^2\rangle.$$

Each of the second moments of $|J|$ is equal, as before, to g – the number of asymmetric units in the unit cell. However, it must be noted that the product $\mathrm{f}_i^2\mathrm{f}_j^{*2}$ is complex and, since this contribution to $\langle D^2(\mathbf{h})\rangle$ is of necessity real, we must take the real part of this product only. Further, in order to compare this contribution with others, we shall change the dummy index j to k. The contribution of index combination (iii) is therefore written as

$$-2\sum_{i=1}^{N}\sum_{k=1(k\neq i)}^{N} \mathcal{R}(\mathrm{f}_i^2\mathrm{f}_k^{*2}). \quad (52)$$

If we combine (52), (51) and (50) with (48), (41) becomes

$$\begin{aligned}\langle D^2(\mathbf{h})\rangle &= 2\sum_{i=1}^{N}\sum_{k=1(k\neq i)}^{N} [(|\mathrm{f}_i|^2|\mathrm{f}_k|^2 - \mathcal{R}(\mathrm{f}_i^2\mathrm{f}_k^{*2})] \\ &= 2\sum_{i=1}^{N}\sum_{k=1(k\neq i)}^{N} \{(f_i^2 + f_i''^2)(f_k^2 + f_k''^2) \\ &\quad - \mathcal{R}[(f_i + if_i'')^2(f_k - if_k'')^2]\} \\ &= 4\sum_{i=1}^{N}\sum_{k=1}^{N} (f_i f_k'' - f_i'' f_k)^2, \end{aligned} \quad (53)$$

which is the same result as was obtained in the previous section for $G = 1$. Note that the restriction $i \neq k$ was removed from (53) since $f_i f_k'' - f_i'' f_k = 0$ for $i = k$.

This direct consideration of moments leads to a correct expression for $\langle D^2(\mathbf{h})\rangle$ and shows clearly that $\langle D^2(\mathbf{h})\rangle$, under the assumptions stated in this article, is space-group independent. Of course, for centric reflections $D(\mathbf{h}) = 0$ and this derivation is valid only for non-centrosymmetric space groups.

5. Concluding remarks

Specifically, we have established that there is no enhancement of the root-mean-square Friedel intensity difference of general reflections in any non-centrosymmetric space group presuming, of course, the absence of centrosymmetric or other symmetric substructures. We stress again the significant result that the space-group-dependent fourth moments of $|J_i(\mathbf{h})|$ cancel out in the evaluation of $\langle D^2\rangle$. Moreover, we have been able to show that, although certain special reflections have an increased root-mean-square Friedel intensity difference, this is due to an equivalent increase in the average intensity rather than to an effect specific to the difference intensity. More generally, the present work, taken together with those of Flack & Shmueli (2007) and Flack & Bernardinelli (2008), demonstrates the tremendous advantage to be drawn from analyzing and using the average and difference intensity of Friedel opposites rather than the intensities of reflections hkl and $\bar{h}\bar{k}\bar{l}$ taken separately. Further theoretical and practical developments of these ideas are to be expected.

APPENDIX *A*
Derivation of $\langle A_v\rangle$ and $\langle D^2\rangle$ for $P2_12_12_1$ and some related space groups

This Appendix shows a derivation of the required intensity statistics for the space group $P2_12_12_1$, starting from tabulated trigonometric structure factors (t.s.f.'s), the tabulation given by Shmueli (2001) being used. It will be seen that this derivation encompasses several related space groups as well. Table A1.4.3.4 (Shmueli, 2001) shows that the t.s.f.'s for $P2_12_12_1$ are as in the following table.

Parity	A	B
$h+k=2n$; $k+l=2n$	4ccc	−4sss
$h+k=2n$; $k+l=2n+1$	−4css	4scc
$h+k=2n+1$; $k+l=2n$	−4scs	4csc
$h+k=2n+1$; $k+l=2n+1$	−4ssc	4ccs

Or, briefly,

$$A = 4wpqr \quad \text{and} \quad B = 4WPQR,$$

where $w = \pm1$, $W = \pm1$ and each of p, q, r, P, Q, R may be a cosine (c) or sine (s) function of $2\pi hx$, $2\pi ky$ or $2\pi lz$. The relationship of the products pqr and PQR seen in the above table ($p = \mathrm{c} \leftrightarrow P = \mathrm{s}$ *etc.*) is, in fact, valid for all the space groups based on the point group 222.

If we use equation (2), we have

$$\langle A_jA_k\rangle = 16\langle w_jp_jq_jr_jw_kp_kq_kr_k\rangle$$

and a similar expression for $\langle B_jB_k\rangle$. In the averaging, we need to retain only even powers of cosine and sine, which occur only when $j = k$. We shall also allow for the independence of atomic contributions to the structure factor. Hence,

$$\begin{aligned}\langle A_jA_k\rangle &= \langle A_j^2\rangle\\ &= 16\langle p_j^2q_j^2r_j^2\rangle\\ &= 16\langle p_j^2\rangle\langle q_j^2\rangle\langle r_j^2\rangle\\ &= 2\end{aligned}$$

since $\langle \mathrm{c}^2\rangle = \langle \mathrm{s}^2\rangle = \frac{1}{2}$. Likewise, $\langle B_jB_k\rangle = \langle B_j^2\rangle = 2$. Equation (2) thus reduces to

$$\begin{aligned}\langle A_v\rangle &= 4\sum_{j=1}^{N/4}(f_j^2 + f_j''^2)\\ &= \sum_{j=1}^{N}(f_j^2 + f_j''^2)\\ &\equiv \Sigma \end{aligned} \qquad (54)$$

in agreement with Wilson's statistics.

For $\langle D^2\rangle$, the relevant average, appearing in (3), is

$$\langle A_jA_kB_lB_m\rangle = \langle 4w_jp_jq_jr_j4w_kp_kq_kr_k4W_lP_lQ_lR_l4W_mP_mQ_mR_m\rangle$$

and we need to retain even powers of cosine and sine which, in this case, limit the index combinations to (i) $j = k = l = m$ and (ii) $j = k$, $l = m$ with $j \neq l$. For combination (i), the coefficient of the average in (3) is identically equal to zero, so only combination (ii) contributes as

$$\begin{aligned}\langle A_j^2B_l^2\rangle &= 4^4\langle p_j^2q_j^2r_j^2P_l^2Q_l^2R_l^2\rangle\\ &= 256\langle p_j^2\rangle\langle q_j^2\rangle\langle r_j^2\rangle\langle P_l^2\rangle\langle Q_l^2\rangle\langle R_l^2\rangle\\ &= 4.\end{aligned}$$

Consequently, (3) reduces to

$$\begin{aligned}\langle D^2\rangle &= (4\times16)\sum_{j=1}^{N/4}\sum_{(l\neq j)=1}^{N/4}(f_j''f_l - f_jf_l'')^2\\ &= 4\sum_{j=1}^{N}\sum_{l=1}^{N}(f_j''f_l - f_jf_l'')^2.\end{aligned} \qquad (55)$$

The restriction on $l \neq j$ is, of course, now redundant, since the factor $(f_j''f_l - f_jf_l'')^2 = 0$ for $l = j$. The derivation presented in this Appendix is also valid for all the orthorhombic space groups based on the point group 222 and on a P-type lattice.

It is seen from equations (54) and (55) that the average intensity and mean-square intensity of Friedel opposites obtained here are the same as those obtained for $P1$ (Flack & Shmueli, 2007) in the absence of symmetric substructures.

APPENDIX *B*
Examples and discussion of isotropy subgroups

We give an example of the use of isotropy subgroups for a structure in point group $mm2$. The operators of this point group are **I** or identity, m_x or mirror reflection in a plane perpendicular to [100], m_y or mirror reflection in a plane perpendicular to [010] and 2_z or twofold rotation about an axis parallel to [001]. The matrix representations of these operators, on the standard orthorhombic basis, are

$$\mathbf{I}:\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix},\quad m_x:\begin{pmatrix}\bar{1}&0&0\\0&1&0\\0&0&1\end{pmatrix},$$
$$m_y:\begin{pmatrix}1&0&0\\0&\bar{1}&0\\0&0&1\end{pmatrix},\quad 2_z:\begin{pmatrix}\bar{1}&0&0\\0&\bar{1}&0\\0&0&1\end{pmatrix}.$$

(*a*) For a reflection $\mathbf{h}$ with each of h, k and l not equal to zero, the identity $\mathbf{I}$ is the only operator obeying $\mathbf{P}^T\mathbf{h}=\mathbf{h}$, so $\mathcal{G}_{\mathbf{h}}=\{\mathbf{I}\}$ and $|\mathcal{G}_{\mathbf{h}}|=1$. There is no operator for which $\mathbf{P}^T\mathbf{h}=-\mathbf{h}$. So, $\mathbf{h}$ with each of h, k and $l\neq 0$ is a general acentric reflection.

(*b*) For a reflection $\mathbf{h}$ with $l=0$ and h and $k\neq 0$, *i.e.* $hk0$, $\mathbf{I}$ is the only operator obeying $\mathbf{P}^T\mathbf{h}=\mathbf{h}$, so $\mathcal{G}_{\mathbf{h}}=\{\mathbf{I}\}$ with $|\mathcal{G}_{\mathbf{h}}|=1$. Moreover, for 2_z, $\mathbf{P}^T\mathbf{h}=-\mathbf{h}$. So $hk0$ is a general centric reflection.

(*c*) For a reflection $\mathbf{h}$ with $h=0$, and k and $l\neq 0$, *i.e.* $0kl$, only $\mathbf{I}$ and m_x obey $\mathbf{P}^T\mathbf{h}=\mathbf{h}$. Hence, $\mathcal{G}_{\mathbf{h}}=\{\mathbf{I}, m_x\}$, $|\mathcal{G}_{\mathbf{h}}|=2$. There is no operator for which $\mathbf{P}^T\mathbf{h}=-\mathbf{h}$. Thus, $0kl$ is a special acentric reflection.

An isotropy subgroup can be one of the following ten non-centrosymmetric point groups: 1, 2, 3, 4, 6, *m*, *mm*2, 3*m*, 4*mm* and 6*mm*. One comes to this conclusion by noting that the relation $\mathbf{P}^T\mathbf{h}=\mathbf{h}$ defines $\mathbf{h}$ as being an eigenvector of $\mathbf{P}$ for which the eigenvalue is $+1$. If $\mathbf{P}$ is a pure rotation, it has only one eigenvalue of $+1$ with the eigenvector being parallel to the rotation axis. Consequently, all rotation operators in the isotropy subgroup must have parallel axes, excluding point groups such as 222 and 422. Reflection $m=\bar{2}$ is the only rotoinversion with eigenvalue $+1$ and it has two of them with the corresponding eigenvectors lying in the mirror plane. This allows isotropy subgroups to contain one or several m operators so long as all the mirror planes intersect in a single line which is a rotation axis of order 2, 3, 4 or 6.

Tables 1 and 2 in the text contain complete tabulations for the point groups 222 and *mm*2.

It is interesting to point out that the order of the isotropy subgroup has some connections of importance with the weighted reciprocal lattice. Thus, Table 2.1.3.3 in Volume B of *International Tables* (Shmueli & Wilson, 2001) concisely presents average intensity multiples for most special reflections in the 32 crystallographic point groups. However, these multiples seem to be nothing but the orders of the isotropy subgroups of the corresponding special reflections, albeit the multiples were obtained from other considerations. An important practical application of these average intensity multiples is the calculation of normalized structure factors of special reflections, where enhancement of average intensity must be taken into account if any accuracy is aimed at. They are there denoted by the symbol $\varepsilon_{\mathbf{h}}$ and a comprehensive table of these quantities, for all the point groups, was given by Iwasaki & Ito (1977).

To conclude, we note that more familiar definitions, but less well suited to the derivations made in the body of this paper, are, for example, (i) the magnitude of the structure factor of a centric or acentric reflection obeys respectively the centric or acentric probability distribution and (ii) a reflection is said to be centric or acentric if the phase of its structure factor is restricted or unrestricted, respectively.

References

Bricogne, G. (1991). *Acta Cryst.* A**47**, 803–829.
Flack, H. D. & Bernardinelli, G. (2008). *Acta Cryst.* A**64**, 484–493.
Flack, H. D. & Shmueli, U. (2007). *Acta Cryst.* A**63**, 257–265.
Iwasaki, H. & Ito, T. (1977). *Acta Cryst.* A**33**, 227–229.
Lonsdale, K. (1965). *International Tables for X-ray Crystallography*, Vol. I, Section 4.7. Birmingham: Kynoch Press.
Shmueli, U. (2001). *International Tables for Crystallography*, Vol. B, *Reciprocal Space*, edited by U. Shmueli, ch. 1.4. Dordrecht: Kluwer Academic Publishers.
Shmueli, U. & Weiss, G. H. (1995). *Introduction to Crystallographic Statistics*, Section 4.2. Oxford University Press.
Shmueli, U. & Wilson, A. J. C. (2001). *International Tables for Crystallography*, Vol. B, *Reciprocal Space*, edited by U. Shmueli, Sections 2.1.1–2.1.3. Dordrecht: Kluwer Academic Publishers.
Waser, J. (1955). *Acta Cryst.* **8**, 595.
Wilson, A. J. C. (1978). *Acta Cryst.* A**34**, 986–994.