

## 1. INTRODUCTION TO SPACE-GROUP SYMMETRY

## 1.6.3. Theoretical background of reflection conditions

BY U. SHMUELI

We shall now examine the effect of the space-group symmetry on the structure-factor function. These effects are of importance in the determination of crystal symmetry. If  $(\mathbf{W}, \mathbf{w})$  is the matrix–column pair of a representative symmetry operation of the space group of the crystal, then, by definition

$$\rho(\mathbf{x}) = \rho(\mathbf{W}\mathbf{x} + \mathbf{w}), \quad (1.6.3.1)$$

where  $\rho(\mathbf{x})$  is the value of the electron-density function at the point with coordinates  $\mathbf{x}$ ,  $\mathbf{W}$  is a matrix of proper or improper rotation and  $\mathbf{w}$  is a translation part (*cf.* Section 1.2.2.1). It is known that the electron-density function at the point  $\mathbf{x}$  is given by

$$\rho(\mathbf{x}) = \frac{1}{V} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h}\mathbf{x}), \quad (1.6.3.2)$$

where, in this and the following equations,  $\mathbf{h}$  is the row matrix  $(h \ k \ l)$  and  $\mathbf{x}$  is a column matrix containing  $x$ ,  $y$  and  $z$  in the first, second and third rows, respectively. Of course,  $\mathbf{h}\mathbf{x}$  is simply equivalent to  $hx + ky + lz$ . If we substitute (1.6.3.2), with  $\mathbf{x}$  replaced by  $(\mathbf{W}\mathbf{x} + \mathbf{w})$  in (1.6.3.1) we obtain, after some calculation,

$$F(\mathbf{h}\mathbf{W}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}\mathbf{w}). \quad (1.6.3.3)$$

Equation (1.6.3.3) is the fundamental relation between symmetry-related reflections (*e.g.* Waser, 1955; Wells, 1965; and Chapter 1.4 in Volume B). If we write  $F(\mathbf{h}) = |F(\mathbf{h})| \exp[i\varphi(\mathbf{h})]$ , equation (1.6.3.3) leads to the following relationships:

$$|F(\mathbf{h}\mathbf{W})| = |F(\mathbf{h})| \quad (1.6.3.4)$$

and

$$\varphi(\mathbf{h}\mathbf{W}) = \varphi(\mathbf{h}) - 2\pi \mathbf{h}\mathbf{w}. \quad (1.6.3.5)$$

Equation (1.6.3.4) indicates the equality of the intensities of truly symmetry-related reflections, while equation (1.6.3.5) relates the phases of the corresponding structure factors. The latter equation is of major importance in direct methods of phase determination [*e.g.* Chapter 2.2 in Volume B (Giacovazzo, 2008)].

We can now approach the problem of systematically absent reflections, which are alternatively called the conditions for possible reflections.

The reflection  $\mathbf{h}$  is *general* if its indices remain unchanged *only* under the identity operation of the point group of the diffraction pattern. *I.e.*, if  $\mathbf{W}$  is the matrix of the identity operation of the point group, the relation  $\mathbf{h}\mathbf{W} = \mathbf{h}$  holds true. So, if the reflection  $\mathbf{h}$  is general, we must have  $\mathbf{W} \equiv \mathbf{I}$ , where  $\mathbf{I}$  is the identity matrix and, obviously,  $\mathbf{h}\mathbf{I} = \mathbf{h}$ . The operation  $(\mathbf{I}, \mathbf{w})$  can be a space-group symmetry operation only if  $\mathbf{w}$  is a lattice vector. Let us denote it by  $\mathbf{w}_L$ . Equation (1.6.3.3) then reduces to

$$F(\mathbf{h}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}\mathbf{w}_L) \quad (1.6.3.6)$$

and  $F(\mathbf{h})$  can be nonzero only if  $\exp(-2\pi i \mathbf{h}\mathbf{w}_L) = 1$ . This, in turn, is possible only if  $\mathbf{h}\mathbf{w}_L$  is an integer and leads to conditions depending on the lattice type. For example, if the components of  $\mathbf{w}_L$  are all integers, which is the case for a *P*-type lattice, the above condition is fulfilled for all  $\mathbf{h}$  – the lattice type does not impose any restrictions. If the lattice is of type *I*, there are two lattice points in the unit cell, at say 0, 0, 0 and 1/2, 1/2, 1/2. The first of these does not lead to any restrictions on possible reflections. The

second, however, requires that  $\exp[-\pi i(h + k + l)]$  be equal to unity. Since  $\exp(\pi i n) = (-1)^n$ , where  $n$  is an integer, the possible reflections from a crystal with an *I*-type lattice must have indices such that their sum is an even integer; if the sum of the indices is an odd integer, the reflection is *systematically absent*. In this way, we examine all lattice types for conditions of possible reflections (or systematic absences) and present the results in Table 1.6.3.1.

The reflection  $\mathbf{h}$  is *special* if it remains unchanged under at least one operation of the point group of the diffraction pattern in addition to its identity operation. *I.e.*, the relation  $\mathbf{h}\mathbf{W} = \mathbf{h}$  holds true for more than one operation of the point group. We shall now assume that the reflection  $\mathbf{h}$  is special. By definition, this reflection remains invariant under more than one operation of the point group of the diffraction pattern. These operations form a subgroup of the point group of the diffraction pattern, known as the stabilizer (formerly called the *isotropy subgroup*) of the reflection  $\mathbf{h}$ , and we denote it by the symbol  $\mathcal{S}_{\mathbf{h}}$ . For each space-group symmetry operation  $(\mathbf{W}, \mathbf{w})$  where  $\mathbf{W}$  is the matrix of an element of  $\mathcal{S}_{\mathbf{h}}$  we must therefore have  $\mathbf{h}\mathbf{W} = \mathbf{h}$ . Equation (1.6.3.3) now reduces to

$$F(\mathbf{h}) = F(\mathbf{h}) \exp(-2\pi i \mathbf{h}\mathbf{w}). \quad (1.6.3.7)$$

Of course, if  $\mathbf{W}$  represents the identity operation,  $\mathbf{w}$  must be a lattice vector and the discussion summarized in Table 1.6.3.1 applies. We therefore require that  $\mathbf{W}$  is the matrix of an element of  $\mathcal{S}_{\mathbf{h}}$  other than the identity.  $F(\mathbf{h})$  can be nonzero only if the exponential factor in (1.6.3.7) equals unity. This, in turn, is possible only if  $\mathbf{h}\mathbf{w}$  is an integer.

Let us consider a monoclinic crystal with *P*-type lattice (*i.e.* with an *mP*-type Bravais lattice) and a *c*-glide reflection as an example. Assuming  $\mathbf{b}$  perpendicular to the *ac* plane, the  $(\mathbf{W}, \mathbf{w})$  representation of *c* is given by

$$c: \left[ \begin{pmatrix} 1 & 0 & 0 \\ 0 & \bar{1} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \begin{pmatrix} 0 \\ y \\ 1/2 \end{pmatrix} \right].$$

The indices of reflections that remain unchanged under the application of the mirror component of the glide-reflection operation must be *h0l*. The translation part of the *c*-glide-reflection operation has the form  $(0, y, 1/2)$ , where  $y = 0$  corresponds to the plane passing through the origin. Hence, for any value of  $y$ , the scalar product  $\mathbf{h}\mathbf{w}$  is  $l/2$  and the necessary condition for a nonzero value of an *h0l* reflection is  $l = 2n$ , where  $n$  is an integer. Intensities of *h0l* reflections with odd  $l$  will be *systematically absent*.

Table 1.6.3.2 shows the effect of some glide reflections on reflection conditions.<sup>4</sup>

Let us now assume a crystal with an *mP*-type Bravais lattice and a twofold screw axis taken as being parallel to  $\mathbf{b}$ . The  $(\mathbf{W}, \mathbf{w})$  representation of the corresponding screw rotation is given by

$$2_1: \left[ \begin{pmatrix} \bar{1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & \bar{1} \end{pmatrix}, \begin{pmatrix} x \\ 1/2 \\ z \end{pmatrix} \right].$$

The diffraction indices that remain unchanged upon the application of the rotation part of  $2_1$  must be of the form  $(0k0)$ . The translation part of the screw operation is of the form  $(x, 1/2, z)$ , where the values of  $x$  and  $z$  depend on the location of the origin. Hence, for any values of  $x$  and  $z$  the scalar product  $\mathbf{h}\mathbf{w}$  is  $k/2$  and the necessary condition for a nonzero value of a  $0k0$  reflection is

<sup>4</sup> The reflection condition in the fourth line of Table 1.6.3.2 is a consequence of the fact that a *d* glide appears only with Bravais lattices of types *I* and *F*.

1.6. METHODS OF SPACE-GROUP DETERMINATION

**Table 1.6.3.1**

Effect of lattice type on conditions for possible reflections

Lattice type	$\mathbf{w}_L^T$	$h\mathbf{w}_L$	Conditions for possible reflections
<i>P</i>	(0, 0, 0)	Integer	None
<i>A</i>	(0, $\frac{1}{2}$ , $\frac{1}{2}$ )	( <i>k</i> + <i>l</i> )/2	<i>hkl</i> : <i>k</i> + <i>l</i> = 2 <i>n</i>
<i>B</i>	( $\frac{1}{2}$ , 0, $\frac{1}{2}$ )	( <i>h</i> + <i>l</i> )/2	<i>hkl</i> : <i>h</i> + <i>l</i> = 2 <i>n</i>
<i>C</i>	( $\frac{1}{2}$ , $\frac{1}{2}$ , 0)	( <i>h</i> + <i>k</i> )/2	<i>hkl</i> : <i>h</i> + <i>k</i> = 2 <i>n</i>
<i>I</i>	( $\frac{1}{2}$ , $\frac{1}{2}$ , $\frac{1}{2}$ )	( <i>h</i> + <i>k</i> + <i>l</i> )/2	<i>hkl</i> : <i>h</i> + <i>k</i> + <i>l</i> = 2 <i>n</i>
<i>F</i>	(0, $\frac{1}{2}$ , $\frac{1}{2}$ )	( <i>k</i> + <i>l</i> )/2	<i>h</i> , <i>k</i> and <i>l</i> are all even or all odd (simultaneous fulfillment of the conditions for types <i>A</i> , <i>B</i> and <i>C</i> ).
	( $\frac{1}{2}$ , 0, $\frac{1}{2}$ )	( <i>h</i> + <i>l</i> )/2	
	( $\frac{1}{2}$ , $\frac{1}{2}$ , 0)	( <i>h</i> + <i>k</i> )/2	
<i>R<sub>obv</sub></i>	( $\frac{2}{3}$ , $\frac{1}{3}$ , $\frac{1}{3}$ )	(2 <i>h</i> + <i>k</i> + <i>l</i> )/3	<i>hkl</i> : - <i>h</i> + <i>k</i> + <i>l</i> = 3 <i>n</i>
	( $\frac{1}{3}$ , $\frac{2}{3}$ , $\frac{2}{3}$ )	( <i>h</i> + 2 <i>k</i> + 2 <i>l</i> )/3	(triple hexagonal cell in obverse orientation)
<i>R<sub>rev</sub></i>	( $\frac{1}{3}$ , $\frac{2}{3}$ , $\frac{1}{3}$ )	( <i>h</i> + 2 <i>k</i> + <i>l</i> )/3	<i>hkl</i> : <i>h</i> - <i>k</i> + <i>l</i> = 3 <i>n</i>
	( $\frac{2}{3}$ , $\frac{1}{3}$ , $\frac{2}{3}$ )	(2 <i>h</i> + <i>k</i> + 2 <i>l</i> )/3	(triple hexagonal cell in reverse orientation)

**Table 1.6.3.2**

Effect of some glide reflections on conditions for possible reflections

Glide reflection	$\mathbf{w}^T$	$\mathbf{h}$	Conditions for possible reflections
<i>a</i> ⊥ [001]	(1/2, 0, <i>z</i> )	( <i>hk</i> 0)	<i>hk</i> 0: <i>h</i> = 2 <i>n</i>
<i>b</i> ⊥ [001]	(0, 1/2, <i>z</i> )	( <i>hk</i> 0)	<i>hk</i> 0: <i>k</i> = 2 <i>n</i>
<i>n</i> ⊥ [001]	(1/2, 1/2, <i>z</i> )	( <i>hk</i> 0)	<i>hk</i> 0: <i>h</i> + <i>k</i> = 2 <i>n</i>
<i>d</i> ⊥ [001]	(1/4, ±1/4, <i>z</i> )	( <i>hk</i> 0)	<i>hk</i> 0: <i>h</i> + <i>k</i> = 4 <i>n</i> ( <i>h</i> , <i>k</i> = 2 <i>n</i> )

**Table 1.6.3.3**

Effect of some screw rotations on conditions for possible reflections

Screw rotation	$\mathbf{w}^T$	$\mathbf{h}$	Conditions for possible reflections
2 <sub>1</sub>    [100]	(1/2, <i>y</i> , <i>z</i> )	( <i>h</i> 00)	<i>h</i> 00: <i>h</i> = 2 <i>n</i>
2 <sub>1</sub>    [010]	( <i>x</i> , 1/2, <i>z</i> )	(0 <i>k</i> 0)	0 <i>k</i> 0: <i>k</i> = 2 <i>n</i>
2 <sub>1</sub>    [001]	( <i>x</i> , <i>y</i> , 1/2)	(00 <i>l</i> )	00 <i>l</i> : <i>l</i> = 2 <i>n</i>
2 <sub>1</sub>    [110]	(1/2, 1/2, <i>z</i> )	( <i>h</i> <i>h</i> 0)	None
3 <sub>1</sub>    [001]	( <i>x</i> , <i>y</i> , 1/3)	(00 <i>l</i> )	00 <i>l</i> : <i>l</i> = 3 <i>n</i>
3 <sub>1</sub>    [111]	(1/3, 1/3, 1/3)	( <i>h</i> <i>h</i> <i>h</i> )	None
4 <sub>1</sub>    [001]	( <i>x</i> , <i>y</i> , 1/4)	(00 <i>l</i> )	00 <i>l</i> : <i>l</i> = 4 <i>n</i>
6 <sub>1</sub>    [001]	( <i>x</i> , <i>y</i> , 1/6)	(00 <i>l</i> )	00 <i>l</i> : <i>l</i> = 6 <i>n</i>

*k* = 2*n*. 0*k*0 reflections with odd *k* will be systematically absent. A brief summary of the effects of various screw rotations on the conditions for possible reflections from the corresponding special subsets of *hkl* is given in Table 1.6.3.3. Note, however, that while the presence of a twofold screw axis parallel to **h** ensures the condition 0*k*0: *k* = 2*n*, the actual observation of such a condition can be taken as an indication but not as absolute proof of the presence of a screw axis in the crystal.

It is interesting to note that some diagonal screw axes do not give rise to conditions for possible reflections. For example, let **W** be the matrix of a threefold rotation operation parallel to [111] and  $\mathbf{w}^T$  be given by (1/3, 1/3, 1/3). It is easy to show that the diffraction vector that remains unchanged when postmultiplied by **W** has the form **h** = (*h**h**h*) and, obviously, for such **h** and **w**, **hw** = *h*. Since this scalar product is an integer there are, according to equation (1.6.3.7), no values of the index *h* for which the structure factor *F*(*h**h**h*) must be absent.

*A short discussion of special reflection conditions*

The conditions for possible reflections arising from lattice types, glide reflections and screw rotations are related to general equivalent positions and are known as *general reflection conditions*. There are also *special* or ‘*extra*’ reflection conditions that arise from the presence of atoms in special positions. These conditions are observable if the atoms located in special positions

are much heavier than the rest. The minimal special conditions are listed in the space-group tables in Chapter 2.3. They can sometimes be understood if the geometry of a given specific site is examined. For example, Wyckoff position 4*i* in space group *P*4<sub>2</sub>22 (93) can host four atoms, at coordinates

$$4i: 0, \frac{1}{2}, z; \frac{1}{2}, 0, z + \frac{1}{2}; 0, \frac{1}{2}, \bar{z}; \frac{1}{2}, 0, \bar{z} + \frac{1}{2}.$$

It is seen that the second and fourth coordinates are obtained from the first and third coordinates, respectively, upon the addition of the vector  $t(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ . An additional *I*-centring is therefore present in this set of special positions. Hence, the special reflection condition for this set is *hkl*: *h* + *k* + *l* = 2*n*.

It should be pointed out, however, that only the general reflection conditions are used for a complete or partial determination of the space group and that the special reflection conditions only apply to spherical atoms. By the latter assumption we understand not only the assumption of spherical distribution of the atomic electron density but also isotropic displacement parameters of the equivalent atoms that belong to the set of corresponding special positions.

One method of finding the minimal special reflection conditions for a given set of special positions is the evaluation of the trigonometric structure factor for the set in question. For example, consider the Wyckoff position 4*c* of the space group *Pbcm* (57). The coordinates of the special equivalent positions are

$$4c: x, \frac{1}{4}, 0; \bar{x}, \frac{3}{4}, \frac{1}{2}; \bar{x}, \frac{3}{4}, 0; x, \frac{1}{4}, \frac{1}{2}$$

and the corresponding trigonometric structure factor is

$$S(\mathbf{h}) = \exp\left[2\pi i\left(hx + \frac{k}{4}\right)\right] + \exp\left[2\pi i\left(-hx + \frac{3k}{4} + \frac{l}{2}\right)\right] + \exp\left[2\pi i\left(-hx + \frac{3k}{4}\right)\right] + \exp\left[2\pi i\left(hx + \frac{k}{4} + \frac{l}{2}\right)\right].$$

It can be easily shown that

$$S(\mathbf{h}) = 2 \cos\left[2\pi\left(hx + \frac{k}{4}\right)\right][1 + \exp(\pi il)]$$

and the last factor equals 2 for *l* even and equals zero for *l* odd. The special reflection condition is therefore: *hkl*: *l* = 2*n*.

Another approach is provided by considerations of the eigensymmetry group and the extraordinary orbits of the space group (see Section 1.4.4.4). We recall that the eigensymmetry group is a group of all the operations that leave the orbit of a point under the space group considered invariant, and the extraordinary orbit is associated with the eigensymmetry group that contains translations not present in the space group (see Chapter 1.4). In the above example the orbit is extraordinary, since its eigensymmetry group contains a translation corresponding to  $\frac{1}{2}\mathbf{c}$ . If this is taken as a basis vector, we have the Laue equation  $\frac{1}{2}\mathbf{c} \cdot \mathbf{h} = l$ , where **h** is represented as a reciprocal-lattice vector and *l* is an integer which also equals *l*/2. But for *l*/2 to be an integer we must have even *l*. We again obtain the condition *hkl*: *l* = 2*n*.

## 1. INTRODUCTION TO SPACE-GROUP SYMMETRY

These reflection conditions that are not related to space-group operations are given in Chapter 2.3 only for special positions. They may arise, however, also for different reasons. For example, a heavy atom at the origin of the space group  $P2_12_12_1$  would generate  $F$ -centring with corresponding apparent absences (cf. the special position  $4a$  of the space group  $Pbca$  and the absences it generates).

We wish to point out that the most common ‘special-position absence’ in molecular structures is due to a heavy atom at the origin of the space group  $P2_1/c$ .

### 1.6.4. Tables of reflection conditions and possible space groups

BY H. D. FLACK AND U. SHMUELI

#### 1.6.4.1. Introduction

The primary order of presentation of these tables of reflection conditions of space groups is the Bravais lattice. This order has been chosen because cell reduction on unit-cell dimensions leads to the Bravais lattice as described as stage 1 in Section 1.6.2.1. Within the space groups of a given Bravais lattice, the entries are arranged by Laue class, which may be obtained as described as stage 2 in Section 1.6.2.1. As a consequence of these decisions about the way the tables are structured, in the hexagonal family one finds for the Bravais lattice  $hP$  that the Laue classes  $\bar{3}$ ,  $\bar{3}m1$ ,  $\bar{3}1m$ ,  $6/m$  and  $6/mmm$  are grouped together.

As an aid in the study of naturally occurring macromolecules and compounds made by enantioselective synthesis, the space groups of enantiomerically pure compounds (Sohncke space groups) are typeset in bold.

The tables show, on the left, sets of reflection conditions and, on the right, those space groups that are compatible with the given set of reflection conditions. The reflection conditions, e.g.  $h$  or  $k + l$ , are to be understood as  $h = 2n$  or  $k + l = 2n$ , respectively. All of the space groups in each table correspond to the same Patterson symmetry, which is indicated in the table header. This makes for easy comparison with the entries for the individual space groups in Chapter 2.3 of this volume, in which the Patterson symmetry is also very clearly shown. All space groups with a conventional choice of unit cell are included in Tables 1.6.4.2–1.6.4.30. All alternative settings displayed in Chapter 2.3 are thus included. The following further alternative settings, not displayed in Chapter 2.3, are also included: space group  $Pb\bar{3}$  (205) and all the space groups with an  $hR$  Bravais lattice in the reverse setting with hexagonal axes.

Table 1.6.2.1 gives some relevant statistics drawn from Tables 1.6.4.2–1.6.4.30. The total number of space-group settings mentioned in these tables is 416. This number is considerably larger than the 230 space-group types described in Part 2 of this volume. The following example shows why the tables include data for several descriptions of the space-group types. At the stage of space-group determination for a crystal in the crystal class  $mm2$ , it is not yet known whether the twofold rotation axis lies along **a**, **b** or **c**. Consequently, space groups based on the three point groups  $2mm$ ,  $m2m$  and  $mm2$  need to be considered.

In some texts dealing with space-group determination, a ‘diffraction symbol’ (sometimes also called an ‘extinction symbol’) in the form of a Hermann–Mauguin space-group symbol is used as a shorthand code for the reflection conditions and Laue class. These symbols were introduced by Buerger (1935, 1942,

1969) and a concise description is to be found in Looijenga-Vos & Buerger (2002). Nespolo *et al.* (2014) use them.

#### 1.6.4.2. Examples of the use of the tables

- (1) If the Bravais lattice is  $oI$  and the Laue class is  $mmm$ , Table 1.6.4.1 directs us to Table 1.6.4.11. Given the observed reflection conditions

$$hkl: h + k + l = 2n, \quad 0kl: k = 2n, l = 2n, \quad h0l: h + l = 2n, \\ hk0: h + k = 2n, \quad h00: h = 2n, \quad 0k0: k = 2n, \quad 00l: l = 2n,$$

it is seen from Table 1.6.4.11 that the possible settings of the space groups are:  $Ibm2$  (46),  $Ic2m$  (46),  $Ibmm$  (74) and  $Icmm$  (74).

- (2) If the Bravais lattice is  $oP$  and the Laue class is  $mmm$ , Table 1.6.4.1 directs us to Table 1.6.4.7. If there are no conditions on  $0kl$ , the space groups  $P222$  to  $Pmnn$  should be searched. If the condition is  $0kl: k = 2n$  or  $l = 2n$ , the space groups  $Pbm2$  to  $Pcnn$  should be searched. If the condition is  $0kl: k + l = 2n$ , the space groups  $Pnm2_1$  to  $Pnnn$  should be searched.
- (3) If the Bravais lattice is  $cP$  and the Laue class is  $m\bar{3}$ , Table 1.6.4.1 directs us to Table 1.6.4.25. If the conditions are  $0kl: k = 2n$  and  $h00: h = 2n$ , it is readily seen that the space group is  $Pa\bar{3}$ .
- (4) If only the Bravais lattice is known or assumed, which is the case in powder-diffraction work (see Section 1.6.5.3), all tables of this section corresponding to this Bravais lattice need to be consulted. For example, if it is known that the Bravais lattice is of type  $cP$ , Table 1.6.4.1 tells us that the possible Laue classes are  $m\bar{3}$  and  $m\bar{3}m$ , and the possible space groups can be found in Tables 1.6.4.25 and 1.6.4.26, respectively. The appropriate reflection conditions are of course given in these tables. All relevant tables can thus be located with the aid of Table 1.6.4.1 if the Bravais lattice is known.

### 1.6.5. Specialized methods of space-group determination

BY H. D. FLACK

#### 1.6.5.1. Applications of resonant scattering to symmetry determination

##### 1.6.5.1.1. Introduction

In small-molecule crystallography, it has been customary in crystal-structure analysis to make no use of the contribution of resonant scattering (otherwise called anomalous scattering and in older literature anomalous dispersion) other than in the specific area of absolute-structure and absolute-configuration determination. One may trace the causes of this situation to the weakness of the resonant-scattering contribution, to the high cost in time and labour of collecting intensity data sets containing measurements of all Friedel opposites and for a lack of any perceived or real need for the additional information that might be obtained from the effects of resonant scattering.

On the experimental side, the turning point came with the widespread distribution of area detectors for small-molecule crystallography, giving the potential to measure, at no extra cost, full-sphere data sets leading to the intensity differences between Friedel opposites  $hkl$  and  $\bar{h}\bar{k}\bar{l}$ . In 2015, the new methods of data analysis briefly presented here are in the stage of development

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