

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Wilson (1949, especially Section 2.1.1) suggested that the regions of averaging should be chosen so that at least one index of every reflection is ≥ 2 if $\langle I \rangle$ is to be identified with Σ , and this has proven to be a useful rule-of-thumb.

The third process of averaging replaces the sum over integral values of the indices by an integration over continuous values, the appropriate values of the limits in this example being $-(H + 1/2)$ to $+(H + 1/2)$. The effect is to replace the sines in the denominators, but not in the numerators, of equation (2.1.2.6) by their arguments, and this is equivalent to the approximation $\sin x \approx x$ in the denominators only. This is a good approximation for atoms close together in the structure and thus giving the largest terms in the sums in equation (2.1.2.6), and gives the correct sign and order of magnitude even for x having its maximum value of $\pi/2$.

2.1.2.2. Physical background

The preceding section has used mathematical arguments. From a physical point of view, the radiation diffracted by atoms that are resolved will interfere destructively, so that the resulting intensity will be the sum of the intensities diffracted by individual atoms, whereas that from completely unresolved atoms will interfere constructively, so that *amplitudes* rather than intensities add. In intermediate cases there will be partial constructive interference. Resolution in accordance with the Rayleigh (1879) criterion requires that $s = (2 \sin \theta) / \lambda$ should be greater than half the reciprocal of the minimum interatomic distance in the crystal (Wilson, 1979); full resolution requires a substantial multiple of this. This criterion is essentially equivalent to that proposed from the study of a special case of the second process in the preceding section.

2.1.2.3. An approximation for organic compounds

In organic compounds there are very many interatomic distances of about 1.5 or 1.4 Å. Adoption of the preceding criterion would mean that the inner portion of the region of reciprocal space accessible by the use of copper $K\alpha$ radiation is not within the sphere of intensity statistics based on fixed-index (first process) averaging. No substantial results are available for fixed-parameter (second process) averaging, and very few from the approximation to it (third process).

To the extent to which the third process is acceptable, an approximation to the variation of $\langle I \rangle$ with $\sin \theta$ is obtainable. The exponent in equation (2.1.2.2) can be written as

$$2\pi i s r_{jk} \cos \psi, \quad (2.1.2.9)$$

where s is the radial distance in reciprocal space, r_{jk} is the distance from the j th to the k th atom and ψ is the angle between the vectors \mathbf{s} and \mathbf{r} . Averaging over a sphere of radius s , with ψ treated as the colatitude, gives

$$\langle I \rangle = \sum_j \sum_k f_j f_k \frac{\sin 2\pi s r_{jk}}{2\pi s r_{jk}}. \quad (2.1.2.10)$$

This is the familiar Debye expression. It has the correct limits for s zero and s large, and is in accord with the argument from resolution.

2.1.2.4. Effect of centring

In the preceding discussion there has been a tacit assumption that the lattice is primitive. A centred crystal can always be referred to a primitive lattice and if this is done no change is required. If the centred lattice is retained, many reflections are identically zero and the intensity of the nonzero reflections is enhanced by a factor of two (I and C lattices) or four (F lattice), so that the average intensity of all the reflections, zero and nonzero taken together, is unchanged.

Table 2.1.3.1. Intensity-distribution effects of symmetry elements and centred lattices causing systematic absences

Abbreviations and orientation of axes: A = acentric distribution, C = centric distribution, Z = systematically zero, S = distribution parameter, $\langle I \rangle$ = average intensity. Axes are parallel to \mathbf{c} , planes are perpendicular to \mathbf{c} .

Element	Reflections	Distribution	S/Σ	$\langle I \rangle / \Sigma$
2_1	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(Z + A)/2$	1	2
$3_1, 3_2$	hkl	A	1	1
	$hk0$	A	1	1
	$00l$	$(2Z + A)/3$	1	3
$4_1, 4_3$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(3Z + A)/4$	1	4
4_2	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(Z + A)/2$	2	4
$6_1, 6_5$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(5Z + A)/6$	1	6
$6_2, 6_4$	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(2Z + A)/3$	2	6
6_3	hkl	A	1	1
	$hk0$	C	1	1
	$00l$	$(Z + A)/2$	3	6
a	hkl	A	1	1
	$hk0$	$(Z + A)/2$	1	2
	$00l$	C	1	1
	$0k0$	A	2	2
C, I	All	$(Z + A)/2$	1	2
F	All	$(3Z + A)/2$	1	4

Other symmetry elements affect only zones and rows of reflections, and so do not affect the general average when the total number of reflections is large. Their effect on zones and rows is discussed in Section 2.1.3.

2.1.3. The average intensity of zones and rows

2.1.3.1. Symmetry elements producing systematic absences

Symmetry elements can be divided into two types: those that cause systematic absences and those that do not. Those producing systematic absences (glide planes and screw axes) produce at the same time groups of reflections (confined to zones and rows in reciprocal space, respectively) with an average intensity an integral¹ multiple of the general average. The effects for single symmetry elements of this type are given in Table 2.1.3.1 for the general reflections hkl and separately for any zones and rows that are affected. The 'average multipliers' are given in the column headed $\langle I \rangle / \Sigma$; 'distribution' and 'distribution parameters' are treated in Section 2.1.5. As for the centring, the fraction of reflections missing and the integer multiplying the average are related in such a way that the overall intensity is unchanged. The mechanism for compensation for the reflections with enhanced intensity is obvious.

2.1.3.2. Symmetry elements not producing systematic absences

Certain symmetry elements not producing absences (mirror planes and rotation axes) cause equivalent atoms to coincide in a

¹The multiple is given as an exact integer for fixed-index averaging, an approximate integer for fixed-parameter averaging. Statements should be understood to refer to fixed-index averaging unless the contrary is explicitly stated.

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Table 2.1.3.2. Intensity-distribution effects of symmetry elements not causing systematic absences

Abbreviations and orientation of axes: *A* = acentric distribution, *C* = centric distribution, *S* = distribution parameter, *I* = average intensity. Axes are parallel to **c**, planes are perpendicular to **c**.

Element	Reflections	Distribution	$S/\Sigma = \langle I \rangle / \Sigma$
1	All	<i>A</i>	1
$\bar{1}$	All	<i>C</i>	1
2	<i>hkl</i> <i>hk0</i> <i>00l</i>	<i>A</i> <i>C</i> <i>A</i>	1 1 2
$\bar{2} = m$	<i>hkl</i> <i>hk0</i> <i>00l</i>	<i>A</i> <i>A</i> <i>C</i>	1 2 1
3	<i>hkl</i> <i>hk0</i> <i>00l</i>	<i>A</i> <i>A</i> <i>A</i>	1 1 3
$\bar{3}$	<i>hkl</i> <i>hk0</i> <i>00l</i>	<i>C</i> <i>C</i> <i>C</i>	1 1 3
4	<i>hkl</i> <i>hk0</i> <i>00l</i>	<i>A</i> <i>C</i> <i>A</i>	1 1 4
$\bar{4}$	<i>hkl</i> <i>hk0</i> <i>00l</i>	<i>A</i> <i>C</i> <i>C</i>	1 1 2
6	<i>hkl</i> <i>hk0</i> <i>00l</i>	<i>A</i> <i>C</i> <i>A</i>	1 1 6
$\bar{6} = 3/m$	<i>hkl</i> <i>hk0</i> <i>00l</i>	<i>A</i> <i>A</i> <i>C</i>	1 2 3

plane or a line projection and hence produce a zone or row in reciprocal space for which the average intensity is an integral multiple of the general average (Wilson, 1950); the effects of single such symmetry elements are given in Table 2.1.3.2. There is, however, no obvious mechanism for compensation for this enhancement. When reflections are few this may be an important matter in assigning an approximate absolute scale by comparing observed and calculated intensities. Wilson (1964), Nigam (1972) and Nigam & Wilson (1980), noting that in such cases the finite size of atoms results in forbidden ranges of positional parameters, have shown that there is a diminution of the intensity of layers (rows) in the immediate neighbourhood of the enhanced zones (rows), just sufficient to compensate for the enhancement. In forming general averages, therefore, reflections from enhanced zones or rows should be included at their full intensity, not divided by the multiplier; the matter is discussed in more detail by Wilson (1987*a*). It should be noted, however, that organic structures containing molecules related by rotation axes are rare, and such structures related by mirror planes are even rarer (Wilson, 1993).

2.1.3.3. More than one symmetry element

Further alterations of the intensities occur if two or more such symmetry elements are present in the space group. The effects were treated in detail by Rogers (1950), who used them to construct a table for the determination of space groups by supplementing the usual knowledge of Laue group with statistical information. Only two pairs of space groups, the orthorhombic *I*222 and *I*2₁2₁2₁, and their cubic supergroups *I*23 and *I*2₁3₁, remained unresolved. Examination of this table shows that what statistical information does is to resolve the Laue group into point groups; the further resolution into space groups is equivalent to the use of Table 3.1.4.1 in *IT A* (2005). The

Table 2.1.3.3. Average multiples for the 32 point groups (modified from Rogers, 1950)

The multiple gives S/Σ for the row and zone corresponding to the principal axis of the point-group symbol; those for the secondary and tertiary axes are given when the symbol contains such axes.

Point group	Principal		Secondary		Tertiary	
	Row	Zone	Row	Zone	Row	Zone
1	1	1				
$\bar{1}$	1	1				
2	2	1				
<i>m</i>	1	2				
<i>2/m</i>	2	2				
222	2	1	2	1	2	1
<i>mm2</i>	2	2	2	2	4	1
<i>mmm</i>	4	2	4	2	4	2
4	4	1				
$\bar{4}$	2	1				
<i>4/m</i>	4	2				
422	4	1†	2	1	2	1
<i>4mm</i>	8	1	2	2	2	2
$\bar{4}2m$	4	1	2	1	2	2
<i>4/mmm</i>	8	2	4	2	4	2
3	3	1				
$\bar{3}$	3	1				
321	3	1	2	1	1	1
<i>3m1</i>	6	1	1	2	2	
<i>31m</i>	6	1	2	2	2	1
6	6	1				
$\bar{6}$	3	2				
<i>6/m</i>	6	2				
622	6	1	2	1	2	1
<i>6mm</i>	12	1	2	2	2	2
$\bar{6}m2$	6	2	2	2	4	1
<i>6/mmm</i>	12	2	4	2	4	2
231	2	1	3	1	1	1
$m\bar{3}1$	4	2	3	1	1	1
432	4	1	3	1	2	1
$\bar{4}3m$	4	1	6	1	2	2
<i>m\bar{3}m</i>	8	2	6	2	4	2

Note. The pairs of point groups, 1 and $\bar{1}$ and 3 and $\bar{3}$, not distinguished by average multiples, may be distinguished by their centric and acentric probability density functions. † The entry for the principal zone for the point group 422 was given incorrectly as 2 in the first edition of this volume.

statistical consequences of each point group, as given by Rogers, are reproduced in Table 2.1.3.3.

2.1.4. Probability density distributions – mathematical preliminaries

For the purpose of this chapter, ‘ideal’ probability distributions or probability density functions are the asymptotic forms obtained by the use of the central-limit theorem when the number of atoms in the unit cell, *N*, is sufficiently large. In order to derive them it is necessary to outline the properties of characteristic functions and to state alternative conditions for the validity of the central-limit theorem; the distributions themselves are derived in Section 2.1.5.

2.1.4.1. Characteristic functions

The average value of $\exp(itx)$ is very important in probability theory; it is called the characteristic function of the distribution $f(x)$ and is denoted by $C_x(t)$ or, when no confusion can arise, by