

1. INTRODUCTION TO SPACE-GROUP SYMMETRY

Table 1.6.5.1

R_{merge} values for Ex2 for the 589 sets of general reflections of mmm which have all eight measurements in the set

| R_{merge} (%) | mmm | $2mm$ | $m2m$ | $mm2$ | 222 |
|------------------------|-------|-------|-------|-------|------|
| R_A | 1.30 | 1.30 | 1.30 | 1.30 | 1.30 |
| R_D | 100.0 | 254.4 | 235.7 | 258.1 | 82.9 |

data set is unsatisfactorily dominated by random uncertainty and systematic error.

Example 3

The crystals of compound Ex3 (Zhu & Jiang, 2007) occur in Laue group $\bar{1}$. One finds $\text{Friedif}_{\text{stat}} = 70$ and $\text{Friedif}_{\text{obs}} = 499$. The huge discrepancy between the two shows that the observed values of D are dominated by random uncertainty and systematic error.

1.6.5.1.3. Resolution of noncentrosymmetric ambiguities

It was shown in Section 1.6.5.1.2 that under certain circumstances it is possible to determine whether or not the space group of the crystal investigated is centrosymmetric. Suppose that the space group was found to be noncentrosymmetric. In each Laue class, there is one centrosymmetric point group and one or more noncentrosymmetric point groups. For example, in the Laue class mmm we need to distinguish between the point groups 222, $2mm$, $m2m$ and $mm2$, and of course between the space groups based on them. We shall show that it is possible in practice to distinguish between these noncentrosymmetric point groups using intensity differences between Friedel opposites caused by resonant scattering.

An excellent intensity data set from a crystal (Ex2 above) of potassium hydrogen (2R, 3R) tartrate, measured with a wavelength of 0.7469 Å at 100 K, was used. The Laue group was assumed to be mmm . The raw data set was initially merged and averaged in point group 1 and all special reflections of the Laue group mmm (i.e. $0kl$, $h0l$, $hk0$, $h00$, $0k0$, $00l$) were set aside. The remaining data were organized into sets of reflections symmetry-equivalent under the Laue group mmm , and only those sets (589 in all) containing all 8 of the mmm -symmetry-equivalent reflections were retained. Each of these sets provides 4 A_{obs} and 4 D_{obs} values which can be used to calculate R_{merge} values appropriate to the five point groups in the Laue class mmm . The results are given in Table 1.6.5.1. The value of 100% for R_{merge} in a centrosymmetric point group, such as mmm or $2/m$, arises by definition and not by coincidence. The R_D of the true point group has the lowest value, which is noticeably different from the other choices of point group.

The crystal of Ex1 above (space group $P2_1/c$) was treated in a similar manner. Table 1.6.5.2 shows that R_D values display no preference between the three point groups in Laue class $2/m$.

Intensity measurements comprising a full sphere of reflections are essential to the success of the R_{merge} tests described in this section.

1.6.5.1.4. Data evaluation after structure refinement

There is an excellent way in which to evaluate both data measurement and treatment procedures, and the fit of the model to the data, including the space-group assignment, at the completion of structure refinement. This technique is applicable both to noncentrosymmetric and to centrosymmetric crystals. A scattergram of D_{obs} against D_{model} , and $2A_{\text{obs}}$ against $2A_{\text{model}}$

Table 1.6.5.2

R_{merge} values for Ex1 for the 724 sets of general reflections of $2/m$ which have all four measurements in the set

| R_{merge} (%) | $2/m$ | m | 2 |
|------------------------|-------|------|-------|
| R_A | 1.29 | 1.29 | 1.29 |
| R_D | 100.0 | 98.3 | 101.7 |

pairs are plotted on the same graph. All (D_{obs} , D_{model}) pairs are plotted together with those ($2A_{\text{obs}}$, $2A_{\text{model}}$) pairs which have $2A_{\text{obs}} < |D_{\text{obs}}|_{\text{max}}$. The range of values on the axes of the model and of the observed values should be identical. For acentric reflections, for both A and D , a good fit of the observed to the model quantities shows itself as a straight line of slope 1 passing through the origin, with some scatter about this ideal straight line. For an individual reflection, $2A$ and D are, respectively, the sum and the difference of the same quantities and they have identical standard uncertainties. It is thus natural to select $2A$ and D to plot on the same graph. In practice one sees that the spread of the $2A$ plot increases with increasing value of $2A$. Fig. 1.6.5.1 shows the $2AD$ plot for Ex2 of Example 2 in Section 1.6.5.1.2, which is most satisfactory and confirms the choice of point group from the use of R_{merge} . The conventional R value for all reflections is 3.1% and for those shown in Fig. 1.6.5.1 it is 10.4%. The R value for all D values is good at 51.1%. Fig. 1.6.5.2 shows the $2AD$ plot for Ex1 of Example 1 in Section 1.6.5.1.2. The structure model is centrosymmetric so all D_{model} values are zero. The conventional R value on A for all reflections is 4.3% and for those shown in Fig. 1.6.5.2 it is 9.1%. The R value on all the D values is 100%.

1.6.5.2. Space-group determination in macromolecular crystallography

For macromolecular crystallography, succinct descriptions of space-group determination have been given by Kabsch (2010*a,b*, 2012) and Evans (2006, 2011). Two characteristics of macromolecular crystals give rise to variations on the small-molecule procedures described above.

The first characteristic is the large size of the unit cell of macromolecular crystals and the variation of the cell dimensions from one crystal to another. This makes the determination of the Bravais lattice by cell reduction problematic, as small changes of cell dimensions give rise to differences in the assignment. Kabsch (2010*a,b*, 2012) uses a 'quality index' from each of Niggli's 44 lattice characters to come to a best choice. Grosse-Kunstleve *et al.* (2004) and Sauter *et al.* (2004) have found that some commonly used methods to determine the Bravais lattice are susceptible to numerical instability, making it possible for high-symmetry Bravais lattice types to be improperly identified. Sauter *et al.* (2004, 2006) find from practical experience that a deviation δ as high as 1.4° from perfect alignment of direct and reciprocal lattice rows must be allowed to construct the highest-symmetry Bravais type consistent with the data. Evans (2006) uses a value of 3.0° . The large unit-cell size also gives rise to a large number of reflections in the asymmetric region of reciprocal space, and taken with the tendency of macromolecular crystals to decompose in the X-ray beam, full-sphere data sets are uncommon. This means that confirmation of the Laue class by means of values of R_{int} (R_{merge}) are rarer than with small-molecule crystallography, although Kabsch (2010*b*) does use a 'redundancy-independent R factor'. Evans (2006, 2011) describes methods very similar to those given as the second stage in Section 1.6.2.1. The conclusion of Sauter *et al.* (2006) and Evans (2006) is that R_{int} values as high