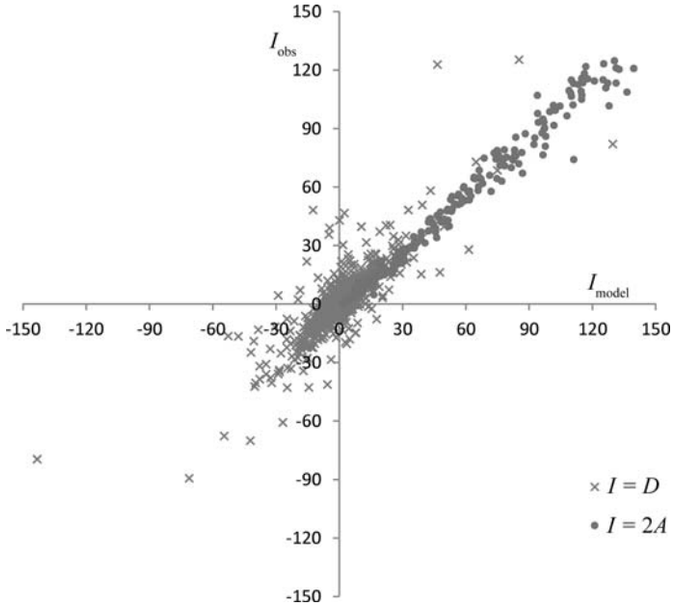

Figure 1.6.5.1
Data-evaluation plot for crystal Ex2. The plot shows a scattergram of all (D_{obs}, D_{model}) pairs and those ($2A_{obs}$, $2A_{model}$) pairs in the same intensity range as the D values.

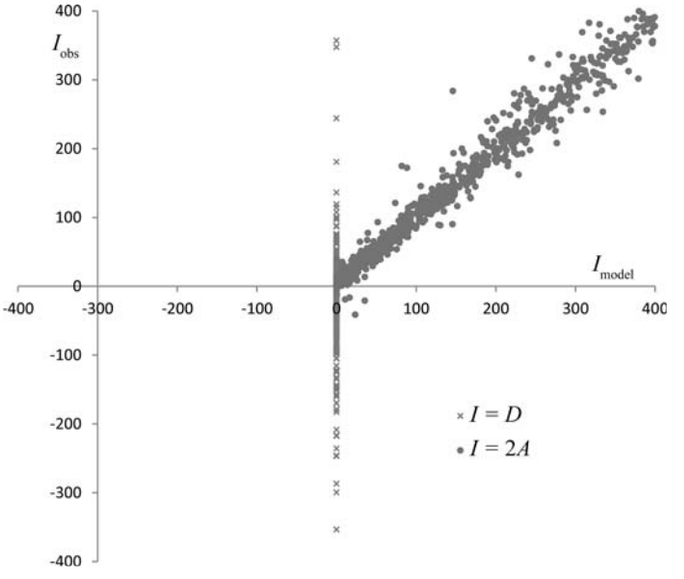

Figure 1.6.5.2
Data-evaluation plot for crystal Ex1. The plot shows a scattergram of all (D_{obs}, D_{model}) and some ($2A_{obs}$, $2A_{model}$) data points.

as 25% must be permitted in order to assemble an optimal set of operations to describe the diffraction symmetry. Another interesting procedure, accompanied by experimental proof, has been devised by Sauter *et al.* (2006). They show that it is clearer to calculate R_{merge} values individually for each potential symmetry operation of a target point group rather than comparing R_{merge} values for target point groups globally. According to Sauter *et al.* (2006) the reason for this improvement lies in the lack of intensity data relating some target symmetry operations.

The second characteristic of macromolecular crystals is that the compound is known, or presumed, to be chiral and enantiomerically pure, so that the crystal structure is chiral. This limits the choice of space group to the 65 Sohncke space groups containing only translations, pure rotations or screw rotations. For ease of use, these have been typeset in bold in Tables 1.6.4.2–1.6.4.30.

For the evaluation of protein structures, Poon *et al.* (2010) apply similar techniques to those described in Section 1.6.2.3. The major tactical objective is to identify pairs of α-helices that have been declared to be symmetry-independent in the structure solution but which may well be related by a rotational symmetry of the crystal structure. Poon *et al.* (2010) have been careful to test their methodology against generated structural data before proceeding to tests on real data. Their results indicate that some 2% of X-ray structures in the Protein Data Bank potentially fit in a higher-symmetry space group. Zwart *et al.* (2008) have studied the problems of under-assigned translational symmetry operations, suspected incorrect symmetry and twinned data with ambiguous space-group choices, and give illustrations of the uses of group–subgroup relations.

1.6.5.3. Space-group determination from powder diffraction

In powder diffraction, the reciprocal lattice is projected onto a single dimension. This projection gives rise to the major difficulty in interpreting powder-diffraction patterns. Reflections overlap each other either exactly, owing to the symmetry of the lattice metric, or approximately. This makes the extraction of the integrated intensities of individual Bragg reflections liable to error. Experimentally, the use of synchrotron radiation with its exceedingly fine and highly monochromatic beam has enabled considerable progress to be made over recent years. Other obstacles to the interpretation of powder-diffraction patterns, which occur at all stages of the analysis, are background interpretation, preferred orientation, pseudo-translational symmetry and impurity phases. These are general powder-diffraction problems and will not be treated at all in the current chapter. The reader should consult David *et al.* (2002) and David & Shankland (2008) or the forthcoming new volume of *International Tables for Crystallography* (Volume H, *Powder Diffraction*) for further information.

It goes without saying that the main use of the powder method is in structural studies of compounds for which single crystals cannot be grown.

Let us start by running through the three stages of extraction of symmetry information from the diffraction pattern described in Section 1.6.2.1 to see how they apply to powder diffraction.

(1) Stage 1 concerns the determination of the Bravais lattice from the experimentally determined cell dimensions. As such, this process is identical to that described in Section 1.6.2.1. The obstacle, arising from peak overlap, is the initial indexing of the powder pattern and the determination of a unit cell, see David *et al.* (2002) and David & Shankland (2008).

(2) Stage 2 concerns the determination of the point-group symmetry of the intensities of the Bragg reflections. As a preparation to stages 2 and 3, the integrated Bragg intensities have to be extracted from the powder-diffraction pattern by one of the commonly used profile analysis techniques [see David *et al.* (2002) and David & Shankland (2008)]. The intensities of severely overlapped reflections are subject to error. Moreover, the exact overlap of reflections owing to the symmetry of the lattice metric makes it impossible to distinguish between high- and low-symmetry Laue groups in the same family *e.g.* between 4/*m* and 4/*mmm* in the tetragonal family and $m\bar{3}$ and $m\bar{3}m$ in the cubic family. Likewise,