Table 1.6.4.30
Reflection conditions and possible space groups with Bravais lattice *cF* and Laue class $m\bar{3}m$; *hkl* are permutable; Patterson symmetry $Fm\bar{3}m$

Reflection conditions				Space group	No.	Space group	No.	Space group	No.
hkl	0*kl*	$h \pm hl$	*h*00						
$h+k, h+l, k+l$	k, l	$h+l$	h	***F*432**	209	$F\bar{4}3m$	216	$Fm\bar{3}m$	225
$h+k, h+l, k+l$	k, l	$h+l$	$h=4n$	***F*4$_1$32**	210				
$h+k, h+l, k+l$	k, l	h, l	h	$F\bar{4}3c$	219	$Fm\bar{3}c$	226		
$h+k, h+l, k+l$	$k+l=4n; k, l$	$h+l$	$h=4n$	$Fd\bar{3}m$	227				
$h+k, h+l, k+l$	$k+l=4n; k, l$	h, l	$h=4n$	$Fd\bar{3}c$	228				

and have not yet enjoyed widespread distribution, use and acceptance by the community. Flack *et al.* (2011) and Parsons *et al.* (2012) give detailed information on these calculations.

1.6.5.1.2. Status of centrosymmetry and resonant scattering

The basic starting point in this analysis is the following linear transformation of $|F(hkl)|^2$ and $|F(\overline{hkl})|^2$, applicable to both observed and model values, to give the average (A) and difference (D) intensities:

$$A(hkl) = \tfrac{1}{2}[|F(hkl)|^2 + |F(\overline{hkl})|^2],$$
$$D(hkl) = |F(hkl)|^2 - |F(\overline{hkl})|^2.$$

In equation (1.6.2.1), $A(hkl)$ was denoted by $|F_{\rm av}(hkl)|^2$. The expression for $D(hkl)$ corresponding to that for $A(hkl)$ given in equation (1.6.2.1) and using the same nomenclature is

$$D(\mathbf{h}) = \sum_{i,j}[(f_i + f_i')f_j'' - (f_j + f_j')f_i'']\sin[2\pi\mathbf{h}(\boldsymbol{r}_i - \boldsymbol{r}_j)].$$

In general $|D(hkl)|$ is small compared to $A(hkl)$. A compound with an appreciable resonant-scattering contribution has $|D(hkl)| \approx 0.01A(hkl)$, whereas a compound with a small resonant-scattering contribution has $|D(hkl)| \approx 0.0001A(hkl)$. For centric reflections, $D_{\rm model} = 0$, and so the values of $D_{\rm obs}(hkl)$ of these are entirely due to random uncertainties and systematic errors in the intensity measurements. $D_{\rm obs}(hkl)$ of acentric reflections contains contributions both from the random uncertainties and the systematic errors of the data measurements, and from the differences between $|F(hkl)|^2$ and $|F(\overline{hkl})|^2$ which arise through the effect of resonant scattering. A slight experimental limitation is that a data set of intensities needs to contain both reflections *hkl* and $\overline{hkl}$ in order to obtain $A_{\rm obs}(hkl)$ and $D_{\rm obs}(hkl)$.

The Bijvoet ratio, defined by

$$\chi = \frac{\langle D^2\rangle^{1/2}}{\langle A\rangle},$$

is the ratio of the root-mean-square value of D to the mean value of A. In a structure analysis, two independent estimates of the Bijvoet ratio are available and their comparison leads to useful information as to whether the crystal structure is centrosymmetric or not.

The first estimate arises from considerations of intensity statistics leading to the definition of the Bijvoet ratio as a value called Friedif$_{\rm stat}$, whose functional form was derived by Flack & Shmueli (2007) and Shmueli & Flack (2009). One needs only to know the chemical composition of the compound and the wavelength of the X-radiation to calculate Friedif$_{\rm stat}$ using various available software.

The second estimate of the Bijvoet ratio, Friedif$_{\rm obs}$, is obtained from the observed diffraction intensities. One problematic point in the evaluation of Friedif$_{\rm obs}$ arises because A and D do not have the same dependence on $\sin\theta/\lambda$ and it is necessary to eliminate this difference as far as possible. A second problematic point in the calculation is to make sure that only acentric reflections of any of the noncentrosymmetric point groups in the chosen Laue class are selected for the calculation of Friedif$_{\rm obs}$. In this way one is sure that if the point group of the crystal is centrosymmetric, all of the chosen reflections are centric, and if the point group of the crystal is noncentrosymmetric, all of the chosen reflections are acentric. The necessary selection is achieved by taking only those reflections that are general in the Laue group. To date (2015), the calculation of Friedif$_{\rm obs}$ is not available in distributed software. On comparison of Friedif$_{\rm stat}$ with Friedif$_{\rm obs}$, one is able to state with some confidence that:

(1) if Friedif$_{\rm obs}$ is much lower than Friedif$_{\rm stat}$, then the crystal structure is either centrosymmetric, and random uncertainties and systematic errors in the data set are minor, or noncentrosymmetric with the crystal twinned by inversion in a proportion close to 50:50;
(2) if Friedif$_{\rm obs}$ is close in value to Friedif$_{\rm stat}$, then the crystal is probably noncentrosymmetric and random uncertainties and systematic errors in the data set are minor. However, data from a centrosymmetric crystal with large random uncertainties and systematic errors may also produce this result; and
(3) if Friedif$_{\rm obs}$ is much larger than Friedif$_{\rm stat}$ then either the data set is dominated by random uncertainties and systematic errors or the chemical formula is erroneous.

Example 1

The crystal of compound Ex1 (Udupa & Krebs, 1979) is known to be centrosymmetric (space group $P2_1/c$) and has a significant resonant-scattering contribution, Friedif$_{\rm stat}$ = 498 and Friedif$_{\rm obs}$ = 164. The comparison of Friedif$_{\rm stat}$ and Friedif$_{\rm obs}$ indicates that the crystal structure is centrosymmetric.

Example 2

The crystal of compound Ex2, potassium hydrogen (2*R*,3*R*) tartrate, is known to be enantiomerically pure and appears in space group $P2_12_12_1$. The value of Friedif$_{\rm obs}$ is 217 compared to a Friedif$_{\rm stat}$ value of 174. The agreement is good and allows the deduction that the crystal is neither centrosymmetric, nor twinned by inversion in a proportion near to 50:50, nor that the