Table 3.4.2
Examples of lattices leading to geometrical ambiguities

$\boldsymbol{P} = \{P_{ij}\}$ is the transformation matrix from lattice I to lattice II, described by the vectors $\{\mathbf{a}_i\}$ and $\{\mathbf{b}_i\}$, respectively, with $\mathbf{b}_i = \sum_j P_{ij}\mathbf{a}_j$.

Lattice I	Lattice II	$\boldsymbol{P}$
Cubic *P*	Tetragonal *P*	$\begin{pmatrix} 0 & -1/2 & 1/2 \\ 0 & 1/2 & 1/2 \\ -1 & 0 & 0 \end{pmatrix}$
Cubic *I*	Tetragonal *P*	$\begin{pmatrix} 0 & -1/2 & 1/2 \\ 0 & -1/2 & -1/2 \\ 1/2 & 0 & 0 \end{pmatrix}$
	Orthorhombic *F*	$\begin{pmatrix} -1/3 & -1/3 & 0 \\ 0 & 0 & -1 \\ 1 & -1 & 0 \end{pmatrix}$
	Orthorhombic *P*	$\begin{pmatrix} 1/4 & -1/4 & 0 \\ 0 & 0 & 1/2 \\ -1/2 & -1/2 & 0 \end{pmatrix}$
Cubic *F*	Orthorhombic *C*	$\begin{pmatrix} -1/2 & 0 & 1/2 \\ 0 & 1 & 0 \\ -1/4 & 0 & -1/4 \end{pmatrix}$
	Orthorhombic *I*	$\begin{pmatrix} -1/6 & 0 & -1/6 \\ 1/2 & 0 & -1/2 \\ 0 & -1 & 0 \end{pmatrix}$
Hexagonal	Orthorhombic *P*	$\begin{pmatrix} 1/2 & 1/2 & 0 \\ 1/2 & -1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
Rhombohedral	Monoclinic *P*	$\begin{pmatrix} -1/2 & 0 & -1/2 \\ 1/2 & 0 & -1/2 \\ 0 & -1 & 0 \end{pmatrix}$

3.4.3. Indexing methods

Indexing methods aim to reconstruct the three-dimensional direct lattice from the one-dimensional distribution of d_{hkl} values. Systematic or accidental peak overlap, inaccuracy of peak positions, zero shift in the $2\theta_{hkl}$ Bragg angles and/or the presence of impurity peaks make the reconstruction difficult. Data accuracy is fundamental for increasing the probability of success; as emphasized by de Wolff: '*The 'indexing problem' is essentially a puzzle: it cannot be stated in rigorous terms (...). It would be quite an easy puzzle if errors of measurements did not exist*' (de Wolff, 1957).

Different approaches have been proposed for solving the indexing puzzle since the pioneering work of Runge (1917). As suggested by Shirley (2003), indexing procedures work in parameter space, or in index space, or in both spaces. As a general consideration, the parameter space allows the inclusion of the cell information and constraints, while the index space is more suitable in cases where there are accidental or systematic absences (Shirley, 1980). In this section an outline of the strategies and search methods adopted by the main traditional and non-traditional indexing approaches is given. For more details see the papers by Shirley (2003) and Bergmann *et al.* (2004).

Among the main indexing procedures, zone indexing (Section 3.4.3.1.1), SIW heuristic (Section 3.4.3.1.2), successive dichotomy (Section 3.4.3.1.5), the topographs method (Section 3.4.3.2.1) and global-optimization methods (Section 3.4.3.2.2) operate in the parameter space; index heuristics (Section 3.4.3.1.3) and index permutation (Section 3.4.3.1.4) work in the index space; and scan/covariance (Bergmann, 2007) operates both in index and parameter space. Each method can be classified as exhaustive or not. An exhaustive method systematically and rigorously searches in the solution space; a non-exhaustive method exploits coincidences and relations between the observed lines with the aim of finding the solution quickly. The classification is not rigorous: approaches that try to combine rigour and speed can be defined as semi-exhaustive (Table 3.4.3).

Indexing procedures can also be classified as traditional and non-traditional. Each indexing method generates a list of possible cells. Their reliability is assessed by FOMs with the aim of selecting the correct one (see Section 3.4.2.1).

3.4.3.1. *Traditional indexing methods*

The traditional indexing approaches adopted over the last century are based on the following strategies and search methods: (1) zone indexing, (2) SIW heuristic, (3) index heuristics, (4) index permutation and (5) successive dichotomy. All of them exploit information about a limited number of observed peak positions.

3.4.3.1.1. *Zone-indexing strategy*

The zone-indexing strategy was originally developed by Runge (1917), successively proposed by Ito (1949, 1950), generalized by de Wolff (1957, 1958) and enhanced by Visser (1969). This approach is based on the search for zones, *i.e.*, crystallographic planes, in the reciprocal lattice, defined by the origin O and two lattice points. If $\mathbf{r}^*_{hkl}$ and $\mathbf{r}^*_{h'k'l'}$ are two vectors in reciprocal space, *i.e.* the positional vectors of the lattice points A and A′, they describe a zone containing any lattice point B whose positional vector is of type $m\mathbf{r}^*_{hkl} \pm n\mathbf{r}^*_{h'k'l'}$, where m and n are positive integers. If ω is the angle between $\mathbf{r}^*_{hkl}$ and $\mathbf{r}^*_{h'k'l'}$, the squared distance of B from O (*i.e.*, $Q_{m,n}$) can be expressed by (de Wolff, 1958; Visser, 1969)

$$Q_{m,n} = m^2 Q_{\rm A} + n^2 Q_{\rm A'} \pm mnR, \qquad (3.4.6)$$

where $Q_{\rm A} = Q(hkl)$ and $Q_{\rm A'} = Q(h'k'l')$ are the squared distances of A and A′ from O, respectively, and $R = 2(Q_{\rm A}Q_{\rm A'})^{1/2}\cos\omega$. R can be derived as

$$R = |Q_{m,n} - m^2 Q_{\rm A} - n^2 Q_{\rm A'}|/mn. \qquad (3.4.7)$$

The method is applied as follows: $Q_{\rm A}$ and $Q_{\rm A'}$ are chosen among the first experimental Q_i values; the $\{Q_i\}$, up to a reasonable resolution, are introduced in (3.4.7) in place of $Q_{m,n}$; and a few positive integer values are assigned to m and n. Equation (3.4.7) provides a large number of R values; equal R values (within error limits) define a zone, for which the ω angle can easily be calculated. The search for zones is performed using different $(Q_{\rm A}, Q_{\rm A'})$ pairs. The R values that are obtained many times identify the most important crystallographic zones. The zones are sorted according to a quality figure, enabling selection of the best ones. In order to find the lattice, all possible combinations of the best zones are tried. For every pair of zones the intersection line is found, then the angle between them is determined and the lattice is obtained.