9.2.1.7.2. *Determination of the lattice type*

When the structure has a hexagonal lattice, the positions of spots are symmetrical about the zero layer line on the *c*-axis oscillation photograph. However, the intensities of the reflections on the two sides of the zero layer line are the same only if the structure possesses a 6_3 axis, and not for the trigonal system. An apparent mirror symmetry perpendicular to the *c* axis results from the combination of the 6_3 axis with the centre of symmetry introduced by X-ray diffraction. For a structure with a rhombohedral lattice, the positions of X-ray diffraction spots are not symmetrical about the zero layer line because the hexagonal unit cell is non-primitive causing the reflections *hkl* to be absent when $-h + k + l \neq 3n$ ($\pm n = 0, 1, 2, \ldots$). For the 10.*l* row, this means that the permitted reflections will have $l = 3n + 1$, which implies above the zero layer line $10.\bar{1}$, $10.\bar{4}$, $10.\bar{7}$, *etc*. reflections and below the zero layer line $10.\bar{2}$, $10.\bar{5}$, $10.\bar{8}$, *etc*. The zero layer line will therefore divide the distance between the nearest spots on either side (namely 10.1 and $10.\bar{2}$) approximately in the ratio 1:2. This enables a quick identification of a rhombohedral lattice. It is also possible to identify rhombohedral lattices by the appearance of an apparent 'doubling' of spots along the Bernal row lines on a rotation photograph. This is because of the threefold symmetry which makes reciprocal-lattice rows such as 10.*l*, $\bar{1}1.l$, and $01.\bar{l}$ identical with each other but different from the other identical set, 01.*l*, $\bar{1}0.l$, and $1\bar{1}.l$. The extinction condition for the second set requires $l = 3n - 1$, *i.e.* $l = 2, 5, 8$, and $\bar{1}, \bar{4}, \bar{7}$, *etc.*, which is different from that for the first set. Consequently, on the rotation photograph, reciprocal-lattice rows with $\xi = |\mathbf{a}^*|$ will have spots for $l = 3n \pm 1$ causing the apparent 'doubling'.

In crystals of layer structures, such as CdI_2, where *a*-axis oscillation photographs are normally taken, the identification of the rhombohedral lattice is performed by checking for the non-coincidence of the diffraction spots with those for the 2*H* or 4*H* structures. In an alternative method, one compares the positions of spots in two rows of the type 10.*l* and 20.*l*. This can conveniently be done by taking a Weissenberg photograph (Chadha, 1977).

9.2.1.7.3. *Determination of the identity period*

The number of layers, *n*, in the hexagonal unit cell can be found by determining the *c* parameter from the *c*-axis rotation or oscillation photographs and dividing this by the layer spacing *h* for that compound which can be found from reflections with $h - k = 0 \bmod 3$. The density of reciprocal-lattice points along rows parallel to $\mathbf{c}^*$ depends on the periodicity along the *c* axis. The larger the identity period along $\mathbf{c}$, the more closely spaced are the diffraction spots along $\mathbf{c}^*$. In situations where there are not many structural extinctions, *n* can be determined by counting the number of spacings after which the sequence of relative intensities begins to repeat along the 10.*l* row of spots on an oscillation or Weissenberg photograph (Krishna & Verma, 1963). If the structure contains a random stacking disorder of close-packed layers (stacking faults), this will effectively make the $\mathbf{c}$ parameter infinite ($\mathbf{c}^* \rightarrow 0$) and lead to the production of characteristic continuous diffuse streaks along reciprocal-lattice rows parallel to $\mathbf{c}^*$ for reflections with $h - k \neq 0 \bmod 3$ (Wilson, 1942). It is therefore difficult to distinguish by X-ray diffraction between structures of very large unresolvable periodicities and those with random stacking faults. Lattice resolution in the electron microscope has been used in recent years to identify such structures (Dubey, Singh & Van Tendeloo, 1977). A better resolution of diffraction spots along the 10.*l* reciprocal-lattice row can be obtained by using the Laue method. Standard charts for rapid identification of SiC polytypes from Laue films are available in the literature (Mitchell, 1953). Identity periods as large as 594 layers have been resolved by this method (Honjo, Miyake & Tomita, 1950). Synchrotron radiation has been used for taking Laue photographs of ZnS polytypes (Steinberger, Bordas & Kalman, 1977).

9.2.1.7.4. *Determination of the stacking sequence of layers*

For an *nH* or 3*nR* polytype, the *n* close-packed layers in the unit cell can be stacked in 2^{n-1} possible ways, all of which cannot be considered for ultimate intensity calculations. A variety of considerations has therefore been used for restricting the number of trial structures. To begin with, symmetry and space-group considerations discussed in Subsection 9.2.1.4 and 9.2.1.5 can considerably reduce the number of trial structures.

When the short-period structures act as 'basic structures' for the generation of long-period polytypes, the number of trial structures is considerably reduced since the crystallographic unit cells of the latter will contain several units of the small-period structures with faults between or at the end of such units. The basic structure of an unknown polytype can be guessed by noting the intensities of 10.*l* reflections that are maximum near the positions corresponding to the basic structure. If the unknown polytype belongs to a well known structure series, such as $(33)_n32$ and $(33)_n34$ based on SiC-6*H*, empirical rules framed by Mitchell (1953) and Krishna & Verma (1962) can allow the direct identification of the layer-stacking sequence without elaborate intensity calculations.

It is possible to restrict the number of probable structures for an unknown polytype on the basis of the faulted matrix model of polytypism for the origin of polytype structures (for details see Pandey & Krishna, 1983). The most probable series of structures as predicted on the basis of this model for SiC contains the numbers 2, 3, 4, 5 and 6 in their Zhdanov sequence (Pandey & Krishna, 1975, 1976*a*). For CdI_2 and PbI_2 polytypes, the possible Zhdanov numbers are 1, 2 and 3 (Pandey & Krishna, 1983; Pandey, 1985). On the basis of the faulted matrix model, it is not only possible to restrict the numbers occurring in the Zhdanov sequence but also to restrict drastically the number of trial structures for a new polytype.

Structure determination of ZnS polytypes is more difficult since they are not based on any simple polytype and any number can appear in the Zhadanov sequence. It has been observed that the birefringence of polytype structures in ZnS varies linearly with the percentage hexagonality (Brafman & Steinberger, 1966), which in turn is related to the number of reversals in the stacking sequence, *i.e.* the number of numbers in the Zhdanov sequence. This drastically reduces the number of trial structures for ZnS (Brafman, Alexander & Steinberger, 1967).

Singh and his co-workers have successfully used lattice imaging in conjunction with X-ray diffraction for determining the structures of long-period polytypes of SiC that are not based on a simple basic structure. After recording X-ray diffraction patterns, single crystals of these polytypes were crushed to yield electron-beam-transparent flakes. The one- and two-dimensional lattice images were used to propose the possible structures for the polytypes. Usually this approach leads to a very few possibilities and the correct structure is easily determined by comparing the observed and calculated X-ray intensities for the proposed structures (Dubey & Singh, 1978; Rai, Singh, Dubey & Singh, 1986).

Direct methods for the structure determination of polytypes from X-ray data have also been suggested by several workers (Tokonami & Hosoya, 1965; Dornberger-Schiff & Farkas-

references