

## 2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

ED patterns. The ellipses ( $hk = \text{constant}$ ) and layer lines ( $l = \text{constant}$ ) for orthogonal lattices are the main characteristic lines of ED patterns along which the reflections are arranged. The shortcoming of oblique-texture ED patterns is the absence of reflections lying inside the cone formed by rotation of the straight line coming from the point 000 at an angle  $(90^\circ - \varphi)$  around the axis  $c^*$  and, in particular, of reflections 00 $l$ . However, at  $\varphi \lesssim 60\text{--}70^\circ$  the set of reflections is usually sufficient for structural determination.

For unit-cell determination and reflection indexing the values  $d$  (i.e.  $|\mathbf{h}|$ ) are used, and the reflection positions defined by the ellipses  $hk$  to which they belong and the values  $\eta$  are considered. The periods  $a^*, b^*$  are obtained directly from  $h_{100}$  and  $h_{010}$  values. The period  $c^*$ , if it is normal to the plane  $a^*b^*$  ( $\gamma^*$  being arbitrary), is calculated as

$$c^* = \eta/l = (h_{hkl}^2 - h_{hk0}^2)^{1/2}/l. \quad (2.5.4.5a)$$

For oblique-angled lattices

$$c^* = [(h_{l+l}^2 + h_{l-l}^2 - 2h_l^2)/2]^{1/2}/l. \quad (2.5.4.5b)$$

In the general case of oblique-angled lattices the coaxial cylinders  $hk$  have radii

$$b_{hk} = (1/\sin \gamma)[(h^2/a^2) + (k^2/b^2) - (2hk \cos \gamma/ab)]^{1/2} \quad (2.5.4.6)$$

and it is always possible to use the measured or calculated values  $b_{hk}$  in (2.5.4.5a) instead of  $h_{hk0}$ , since

$$\eta = (h_{hkl}^2 - b_{hk}^2)^{1/2}. \quad (2.5.4.7)$$

In OT patterns the  $b_{hk}$  and  $\eta$  values are represented by the lengths of the small axes of the ellipses  $B_{hk} = L\lambda b_{hk}$  and the distances of the reflections  $hkl$  from the line of small axes (equatorial line of the pattern)

$$D_{hkl} = L\lambda\eta/\sin \varphi = hp + ks + lq. \quad (2.5.4.8)$$

Analysis of the  $B_{hk}$  values gives  $a, b, \gamma$ , while  $p, s$  and  $q$  are calculated from the  $D_{hkl}$  values. It is essential that the components of the normal projections  $c_n$  of the axis  $c$  on the plane  $ab$  measured in the units of  $a$  and  $b$  are

$$\begin{aligned} x_n &= (c/a)(\cos \beta - \cos \alpha \cos \gamma)/\sin^2 \gamma \\ &= -p/q, \\ y_n &= (c/b)(\cos \alpha - \cos \beta \cos \gamma)/\sin^2 \gamma \\ &= -s/q. \end{aligned} \quad (2.5.4.9)$$

Obtaining  $x_n, y_n$  one can calculate

$$c_n = [(x_n a)^2 + (y_n b)^2 + 2x_n y_n ab \cos \gamma]^{1/2}.$$

Since

$$\begin{aligned} d_{001} &= L\lambda/q \sin \varphi, \\ c &= (c_n^2 + d_{001}^2)^{1/2}. \end{aligned} \quad (2.5.4.10)$$

The  $\alpha, \beta$  values are then defined by the relations

$$\begin{aligned} \cos \alpha &= (x_n a \cos \gamma + y_n b)/c, \\ \cos \beta &= (x_n a + y_n b \cos \gamma)/c. \end{aligned} \quad (2.5.4.11)$$

Because of the small particle dimensions in textured specimens, the kinematic approximation is more reliable for OT patterns, enabling a more precise calculation of the structure amplitudes from the intensities of reflections.

*Polycrystal ED patterns.* In this case, the RL is a set of concentric spheres with radii  $h_{hkl}$ . The ED pattern, like an X-ray powder pattern, is a set of rings with radii

$$r_{hkl} = h_{hkl}L\lambda. \quad (2.5.4.12)$$

## 2.5.4.3. Intensities of diffraction beams

The intensities of scattering by a crystal are determined by the scattering amplitudes of atoms in the crystal, given by (see also Section 5.2.1)

$$\begin{aligned} f_e^{\text{abs}}(s) &= 4\pi K \int \varphi(r)r^2 \frac{\sin sr}{sr} dr, \\ K &= \frac{2\pi me}{h^2}; f_e = K^{-1}f_e^{\text{abs}}, \end{aligned} \quad (2.5.4.13)$$

where  $\varphi(r)$  is the potential of an atom and  $s = 4\pi(\sin \theta)/\lambda$ . The absolute values of  $f_e^{\text{abs}}$  have the dimensionality of length  $L$ . In EDSA it is convenient to use  $f_e$  without  $K$ . The dimensionality of  $f_e$  is [potential  $L^3$ ]. With the expression of  $f_e$  in  $\text{V \AA}^3$  the value  $K^{-1}$  in (2.5.4.13) is  $47.87 \text{ V \AA}^2$ .

The scattering atomic amplitudes  $f_e(s)$  differ from the respective  $f_x(s)$  X-ray values in the following: while  $f_x(0) = Z$  (electron shell charge), the atomic amplitude at  $s = 0$

$$f_e(0) = 4\pi \int \varphi(r)r^2 dr \quad (2.5.4.14)$$

is the ‘full potential’ of the atom. On average,  $f_e(0) \simeq Z^{1/3}$ , but for small atomic numbers  $Z$ , owing to the peculiarities in the filling of the electron shells,  $f_e(0)$  exhibits within periods of the periodic table of elements ‘reverse motion’, i.e. they decrease with  $Z$  increasing (Vainshtein, 1952, 1964). At large  $(\sin \theta)/\lambda$ ,  $f_e \simeq Z$ . The atomic amplitudes and, consequently, the reflection intensities, are recorded, in practice, up to values of  $(\sin \theta)/\lambda \simeq 0.8\text{--}1.2 \text{ \AA}^{-1}$ , i.e. up to  $d_{\text{min}} \simeq 0.4\text{--}0.6 \text{ \AA}$ .

The structure amplitude  $\Phi_{hkl}$  of a crystal is determined by the Fourier integral of the unit-cell potential (see Chapter 1.2),

$$\Phi_{hkl} = \int_{\Omega} \varphi(\mathbf{r}) \exp\{2\pi i(\mathbf{r} \cdot \mathbf{h})\} dv_r, \quad (2.5.4.15)$$

where  $\Omega$  is the unit-cell volume. The potential of the unit cell can be expressed by the potentials of the atoms of which it is composed:

$$\varphi(\mathbf{r}) = \sum_{\text{cell}, i} \varphi_{\text{at } i}(\mathbf{r} - \mathbf{r}_i). \quad (2.5.4.16)$$

The thermal motion of atoms in a crystal is taken into account by the convolution of the potential of an atom at rest with the probability function  $w(\mathbf{r})$  describing the thermal motion:

$$\varphi_{\text{at}} = \varphi_{\text{at}}(\mathbf{r}) * w(\mathbf{r}). \quad (2.5.4.17)$$

Accordingly, the atomic temperature factor of the atom in a crystal is

$$f_{eT}[(\sin \theta)/\lambda] = f_e f_T = f_e [(\sin \theta)/\lambda] \exp\{-B[(\sin \theta)/\lambda]^2\}, \quad (2.5.4.18)$$

where the Debye temperature factor is written for the case of isotropic thermal vibrations. Consequently, the structure amplitude is

$$\Phi_{hkl} = \sum_{\text{cell}, i} f_{eT,i} \exp\{2\pi i(hx_i + ky_i + lz_i)\}. \quad (2.5.4.19)$$

This general expression is transformed (see IT I, 1952) according to the space group of a given crystal.

To determine the structure amplitudes in EDSA experimentally, one has to use specimens satisfying the kinematic scattering condition, i.e. those consisting of extremely thin crystallites. The

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limit of the applicability of the kinematic approximation (Blackman, 1939; Vainshtein, 1964) can be estimated from the formula

$$A = \lambda \left| \frac{\langle \Phi_{\mathbf{h}} \rangle}{\Omega} \right| t \lesssim 1, \quad (2.5.4.20)$$

where  $\langle \Phi_{\mathbf{h}} \rangle$  is the averaged absolute value of  $\Phi_{\mathbf{h}}$  (see also Section 5.2.1). Since  $\langle \Phi_{\mathbf{h}} \rangle$  are proportional to  $Z^{0.8}$ , condition (2.5.4.20) is better fulfilled for crystals with light and medium atoms. Condition (2.5.4.20) is usually satisfied for textured and polycrystalline specimens. But for mosaic single crystals as well, the kinematic approximation limit is, in view of their real structure, substantially wider than estimated by (2.5.4.20) for ideal crystals. The fulfillment of the kinematic law for scattering can be, to a greater or lesser extent, estimated by comparing the decrease of experimental intensity  $I_{\mathbf{h}}[(\sin \theta)/\lambda]$  averaged over definite angular intervals, and sums  $\sum f_{\text{obs}}^2[(\sin \theta)/\lambda]$  calculated for the same angular intervals.

For mosaic single-crystal films the integral intensity of reflection is

$$I_{\mathbf{h}} = j_0 S \lambda^2 \left| \frac{\Phi_{\mathbf{h}}}{\Omega} \right|^2 \frac{t d_{\mathbf{h}}}{\alpha} \simeq \Phi_{\mathbf{h}}^2 d_{\mathbf{h}}; \quad (2.5.4.21)$$

for textures

$$I_{\mathbf{h}} = j_0 S \lambda^2 \left| \frac{\Phi_{\mathbf{h}}}{\Omega} \right|^2 \frac{t L p}{2 \pi R' \sin \varphi} \simeq \Phi_{\mathbf{h}}^2 p / R'. \quad (2.5.4.22)$$

Here  $j_0$  is the incident electron-beam density,  $S$  is the irradiated specimen area,  $t$  is the thickness of the specimen,  $\alpha$  is the average angular spread of mosaic blocks,  $R'$  is the horizontal coordinate of the reflection in the diffraction pattern and  $p$  is the multiplicity factor. In the case of polycrystalline specimens the local intensity in the maximum of the ring reflection

$$I_{\mathbf{h}} = j_0 S \lambda^2 \left| \frac{\Phi_{\mathbf{h}}}{\Omega} \right|^2 \frac{t d_{\mathbf{h}}^2 p \Delta S}{4 \pi L \lambda} \simeq \Phi_{\mathbf{h}}^2 d_{\mathbf{h}}^2 p \quad (2.5.4.23)$$

is measured, where  $\Delta S$  is the measured area of the ring.

The transition from kinematic to dynamic scattering occurs at critical thicknesses of crystals when  $A \geq 1$  (2.5.4.20). Mosaic or polycrystalline specimens then result in an uneven contribution of various crystallites to the intensity of the reflections. It is possible to introduce corrections to the experimental structure amplitudes of the first strong reflections most influenced by dynamic scattering by applying in simple cases the two-wave approximation (Blackman, 1939) or by taking into account multibeam theories (Fujimoto, 1959; Cowley, 1981; Avilov *et al.* 1984; see also Chapter 5.2).

The application of kinematic scattering formulae to specimens of thin crystals (5–20 nm) or dynamic corrections to thicker specimens (20–50 nm) permits one to obtain reliability factors between the calculated  $\Phi^{\text{calc}}$  and observed  $\Phi^{\text{obs}}$  structure amplitudes of  $R = 5$ –15%, which is sufficient for structural determinations.

With the use of electron diffractometry techniques, reliability factors as small as  $R = 2$ –3% have been reached and more detailed data on the distribution of the inner-crystalline potential field have been obtained, characterizing the state and bonds of atoms, including hydrogen (Zhukhlistov *et al.*, 1997, 1998; Avilov *et al.*, 1999).

The applicability of kinematics formulae becomes poorer in the case of structures with many heavy atoms for which the atomic amplitudes also contain an imaginary component (Shoemaker & Glauber, 1952). The experimental intensity measurement is made by a photo method or by direct recording (Avilov, 1979). In some cases the amplitudes  $\Phi_{hkl}$  can be determined from dynamic

scattering patterns – the bands of equal thickness from a wedge-shaped crystal (Cowley, 1981), or from rocking curves.

### 2.5.4.4. Structure analysis

The unit cell is defined on the basis of the geometric theory of electron-diffraction patterns, and the space group from extinctions. It is also possible to use the method of converging beams (Section 5.2.2). The structural determination is based on experimental sets of values  $|\Phi_{hkl}|^2$  or  $|\Phi_{hkl}|$  (Vainshtein, 1964).

The trial-and-error method may be used for the simplest structures. The main method of determination is the construction of the Patterson functions

$$P(xyz) = \frac{1}{\Omega} \left[ \Phi_{000}^2 + 2 \sum_{hkl=-\infty}^{hkl=+\infty} |\Phi_{hkl}|^2 \cos 2\pi(hx + ky + lz) \right] \quad (2.5.4.24)$$

and their analysis on the basis of heavy-atom methods, superposition methods and so on (see Chapter 2.3). Direct methods are also used (Dorset *et al.*, 1979). Thus the phases of structure factors are calculated and assigned to the observed moduli

$$\Phi_{\mathbf{h}} = |\Phi_{\mathbf{h}, \text{obs}}| \exp\{i\alpha_{\text{calc}}\}. \quad (2.5.4.25)$$

The distribution of the potential in the unit cell, and, thereby, the arrangement in it of atoms (peaks of the potential) are revealed by the construction of three-dimensional Fourier series of the potential (see also Chapter 1.3)

$$\varphi(xyz) = \frac{1}{\Omega} \sum_{\mathbf{h}} \Phi_{hkl} \exp\{-2\pi i(hx + ky + lz)\} \quad (2.5.4.26a)$$

or projections

$$\varphi'(xy) = \frac{1}{S} \sum_{\mathbf{h}} \Phi_{hk0} \exp\{-2\pi i(hx + ky)\}. \quad (2.5.4.26b)$$

The general formulae (2.5.4.26a) and (2.5.4.26b) transform, according to known rules, to the expressions for each space group (see IT I, 1952). If  $\Phi_{hkl}$  are expressed in  $\text{V \AA}^3$  and the volume  $\Omega$  or the cell area  $S$  in  $\text{\AA}^3$  and  $\text{\AA}^2$ , respectively, then the potential  $\varphi$  is obtained directly in volts, while the projection of the potential  $\varphi'$  is in  $\text{V \AA}$ . The amplitudes  $|\Phi_{hkl}|$  are reduced to an absolute scale either according to a group of strong reflections

$$\sum |\Phi_{\mathbf{h}}|^{\text{calc}} = \sum |\Phi_{\mathbf{h}}|^{\text{obs}} \quad (2.5.4.27)$$

or using the Parseval equality

$$\sum_{\mathbf{h}=-\infty}^{+\infty} |\Phi_{\mathbf{h}}|^2 = \Omega^2 \langle \varphi^2 \rangle = \Omega \sum_{i(\text{cell})} \frac{1}{2\pi^2} \int_0^{\infty} f_{eT_i}^2(s) s^2 ds \quad (2.5.4.28)$$

or Wilson's statistical method

$$\langle \Phi^2[(\sin \theta)/\lambda] \rangle = \sum_i f_{eT_i}^2[(\sin \theta)/\lambda]. \quad (2.5.4.29)$$

The term  $\Phi_{000}$  defines the mean inner potential of a crystal, and is calculated from  $f_e(0)$  [(2.5.4.13), (2.5.4.19)]

$$\langle \varphi_{\text{cr}} \rangle = \Phi_{000}/\Omega = \frac{1}{\Omega} \sum f_e(0). \quad (2.5.4.30)$$

The Fourier series of the potential in EDSA possess some peculiarities (Vainshtein, 1954, 1964) which make them different from the electron-density Fourier series in X-ray analysis. Owing to the peculiarities in the behaviour of the atomic amplitudes (2.5.4.13), which decrease more rapidly with increasing  $(\sin \theta)/\lambda$  compared with  $f_x$ , the peaks of the atomic potential