

2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

f_e is [potential L^3]. With the expression of f_e in V \AA^3 the value K^{-1} in (2.5.4.13) is 47.87 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 $d_{\min} \simeq 0.4\text{--}0.6 \text{ \AA}$.

The structure amplitude Φ_{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 Ω 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 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 2.5.2). 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. Condi-

tion (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, α 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 ΔS 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 Φ^{calc} and observed Φ^{obs} structure amplitudes of $R = 5\text{--}15\%$, which is sufficient for structural determinations.

With the use of electron-diffractometry techniques, reliability factors as small as $R = 2\text{--}3\%$ 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 Φ_{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 extinc-

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tions. It is also possible to use the method of converging beams (Section 2.5.3). 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

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

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 Φ_{hkl} are expressed in $\text{V}\text{\AA}^3$ and the volume Ω or the cell area S in \AA^3 and \AA^2 , respectively, then the potential φ is obtained directly in volts, while the projection of the potential φ' is in $\text{V}\text{\AA}$. 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 Φ_{000} defines the mean inner potential of a crystal, and is calculated from $f_c(0)$ [(2.5.4.13), (2.5.4.19)]

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

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

$$\varphi_{\text{at}}(r) = \frac{1}{2\pi^2} \int f_{eT}(s) \frac{\sin sr}{sr} s^2 ds \quad (2.5.4.31)$$

are more 'blurred' and exhibit a larger half-width than the electron-density peaks $\rho_{\text{at}}(r)$. On average, this half-width corresponds to the 'resolution' of an electron-diffraction pattern – about 0.5 \AA or better. The potential in the maximum ('peak height') does not depend as strongly on the atomic number as in X-ray analysis:

$$\varphi(0) = \frac{1}{2\pi^2} \int f_{eT}(s) s^2 ds \sim Z^{0.75}, \quad (2.5.4.32)$$

while in X-ray diffraction $\rho(0) \sim Z^{1.2}$. In such a way, in EDSA the light atoms are more easily revealed in the presence of heavy atoms than in X-ray diffraction, permitting, in particular, hydrogen atoms to be revealed directly without resorting to difference syntheses as in X-ray diffraction. Typical values of the atomic potential $\varphi(0)$ (which depend on thermal motion) in organic crystals are: H ~ 35 , C ~ 165 , O 215 V; in Al crystals 330 V, in Cu crystals 750 V.

The EDSA method may be used for crystal structure determination, depending on the types of electron-diffraction patterns, for crystals containing up to several tens of atoms in the unit cell. The accuracy in determination of atomic coordinates in EDSA is about 0.01–0.005 \AA on average. The precision of EDSA makes it possible to determine accurately the potential distribution, to investigate atomic ionization, to obtain values for the potential between the atoms and, thereby, to obtain data on the nature of the chemical bond.

If the positions in the cell are occupied only partly, then the measurement of $\varphi_i(0)$ gives information on population percentage.

There is a relationship between the nuclear distribution, electron density and the potential as given by the Poisson equation

$$\nabla^2 \varphi(\mathbf{r}) = -4\pi e[\rho_+(\mathbf{r}) - \rho_-(\mathbf{r})]. \quad (2.5.4.33)$$

This makes it possible to interrelate X-ray diffraction, EDSA and neutron-diffraction data. Thus for the atomic amplitudes

$$f_e(s) = 4\pi K e [Z - f_x(s)] s^{-2}, \quad (2.5.4.34)$$

where Z is the nuclear charge and f_x the X-ray atomic scattering amplitude, and for structure amplitudes

$$\Phi_{hkl} = \pi K e [Z_{hkl} - F_{hkl}] |\mathbf{h}|^{-2}, \quad (2.5.4.35)$$

where F_{hkl} is the X-ray structure amplitude of the electron density of a crystal and Z_{hkl} is the amplitude of scattering from charges of nuclei in the cell taking into account their thermal motion. The values Z_{hkl} can be calculated easily from neutron-diffraction data, since the charges of the nuclei are known and the experiment gives the parameters of their thermal motion.

In connection with the development of high-resolution electron-microscopy methods (HREM) it has been found possible to combine the data from direct observations with EDSA methods. However, EDSA permits one to determine the

atomic positions to a greater accuracy, since practically the whole of reciprocal space with 1.0–0.4 Å resolution is used and the three-dimensional arrangement of atoms is calculated. At the same time, in electron microscopy, owing to the peculiarities of electron optics and the necessity for an objective aperture, the image of the atoms in a crystal $\psi'(\mathbf{x}) * A(\mathbf{x})$ is a convolution, with the aperture function blurring the image up to 1.5–2 Å resolution. In practice, in TEM one obtains only the images of the heaviest atoms of an object. However, the possibility of obtaining a direct image of a structure with all the defects in the atomic arrangement is the undoubted merit of TEM.

2.5.5. Image reconstruction³

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2.5.5.1. Introduction

In many fields of physical measurements, instrumental and informative techniques, including electron microscopy and computational or analogue methods for processing and transforming signals from objects investigated, find a wide application in obtaining the most accurate structural data. The signal may be radiation from an object, or radiation transmitted through the object, or reflected by it, which is transformed and recorded by a detector.

The image is the two-dimensional signal $I(xy)$ on the observation plane recorded from the whole three-dimensional volume of the object, or from its surface, which provides information on its structure. In an object this information may change owing to transformation of the scattered wave inside an instrument. The real image $J(xy)$ is composed of $I(xy)$ and noise $N(xy)$ from signal disturbances:

$$J(xy) = I(xy) + N(xy). \quad (2.5.5.1)$$

Image-reconstruction methods are aimed at obtaining the most accurate information on the structure of the object; they are subdivided into two types (*Picture Processing and Digital Filtering*, 1975; Rozenfeld, 1969):

(a) Image restoration – separation of $I(xy)$ from the image by means of compensation of distortions introduced in it by an image-forming system as well as by an account of the available quantitative data reflecting its structure.

(b) Image enhancement – maximum exclusion from the observed image $J(xy)$ (2.5.5.1) of all its imperfections $N(xy)$ from both accidental distortions in objects and various ‘noise’ in signals and detector, and obtaining $I(xy)$ as the result.

These two methods may be used separately or in combination.

The image should be represented in the form convenient for perception and analysis, e.g. in digital form, in lines of equal density, in points of different density, in half-tones or colour form and using, if necessary, a change or reversal of contrast.

Reconstructed images may be used for the three-dimensional reconstruction of the spatial structure of an object, e.g. of the density distribution in it (see Section 2.5.6).

This section is connected with an application of the methods of image processing in transmission electron microscopy (TEM). In TEM (see Section 2.5.2), the source-emitted electrons are transmitted through an object and, with the aid of a system of lenses, form a two-dimensional image subject to processing.

Another possibility for obtaining information on the structure of an object is structural analysis with the aid of electron

diffraction – EDSA. This method makes use of information in reciprocal space – observation and measurement of electron-diffraction patterns and calculation from them of a two-dimensional projection or three-dimensional structure of an object using the Fourier synthesis. To do this, one has to find the relative phases of the scattered beams.

The wavefunction of an electron-microscopic image is written as

$$\psi_1 = \mathcal{F}^{-1} T \mathcal{F} q \psi_0. \quad (2.5.5.2)$$

Here ψ_0 is the incident plane wave. When the wave is transmitted through an object, it interacts with the electrostatic potential $\varphi(\mathbf{r})$ [$\mathbf{r}(xyz)$ is the three-dimensional vector in the space of the object]; this process is described by the Schrödinger equation (Section 2.5.2.1). As a result, on the exit surface of an object the wave takes the form $q\psi_0(\mathbf{x})$ where q is the transmission function and \mathbf{x} is the two-dimensional vector $\mathbf{x}(xy)$. The diffraction of the wave $q\psi_0$ is described by the two-dimensional Fourier operator:

$$\mathcal{F} q = Q(\mathbf{u}) = \int q(\mathbf{x}) \exp[2\pi i(\mathbf{x}\mathbf{u})] d\mathbf{x}. \quad (2.5.5.3)$$

Here, we assume the initial wave amplitude to be equal to unity and the initial phase to be zero, so that $q\psi_0 = q$, which defines, in this case, the wavefunction in the back focal plane of an objective lens with the reciprocal-space coordinates $\mathbf{u}(u, v)$. The function Q is modified in reciprocal space by the lens transfer function $T(\mathbf{u})$. The scattered wave transformation into an image is described by the inverse Fourier operator $\mathcal{F}^{-1} T Q$.

The process of the diffraction $\mathcal{F} q \psi_0 = Q$, as seen from (2.5.5.1), is the same in both TEM and EDSA. Thus, in TEM under the lens actions $\mathcal{F}^{-1} T Q$ the image formation from a diffraction pattern takes place with an account of the phases, but these phases are modified by the objective-lens transfer function. In EDSA, on the other hand, there is no distorting action of the transfer function and the ‘image’ is obtained by computing the operation $\mathcal{F}^{-1} Q$.

The computation of projections, images and Fourier transformation is made by discretization of two-dimensional functions on a two-dimensional network of points – pixels in real space $\mathbf{x}(x_j, y_k)$ and in reciprocal space $\mathbf{u}(u_m, v_n)$.

2.5.5.2. Thin weak phase objects at optimal defocus

The intensity distribution $I(xy) \sim |\psi_1|^2$ of an electron wave in the image plane depends not only on the coherent and inelastic scattering, but also on the instrumental functions. The electron wave transmitted through an object interacts with the electrostatic potential $\varphi(\mathbf{r})$ which is produced by the nuclei charges and the electronic shells of the atoms. The scattering and absorption of electrons depend on the structure and thickness of a specimen, and the atomic numbers of the atoms of which it is composed. If an object with the three-dimensional distribution of potential $\varphi(\mathbf{r})$ is sufficiently thin, then the interaction of a plane electron wave ψ_0 with it can be described as the interaction with a two-dimensional distribution of potential projection $\varphi(\mathbf{x})$,

$$\varphi(\mathbf{x}) = \int_0^b \varphi(\mathbf{r}) dz, \quad (2.5.5.4)$$

where b is the specimen thickness. It should be noted that, unlike the three-dimensional function of potential $\varphi(\mathbf{r})$ with dimension $[M^{1/2} L^{3/2} T^{-1}]$, the two-dimensional function of potential projection $\varphi(\mathbf{x})$ has the potential-length dimension $[M^{1/2} L^{1/2} T^{-1}]$ which, formally, coincides with the charge dimension. The transmission function, in the general case, has the form

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