$$\varphi_{\rm at}(r) = \frac{1}{2\pi^2}\int f_{eT}(s)\frac{\sin sr}{sr}s^2\ {\rm d}s \qquad (2.5.4.31)$$

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

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

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 Å 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

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

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

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

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

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

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 $\varphi'(\mathbf{x}) * A(\mathbf{x})$ 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 reconstruction* (B. K. VAINSHTEIN)

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:

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

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

$$\psi_I = \mathscr{F}^{-1}T\mathscr{F}q\psi_0. \qquad (2.5.5.2)$$

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

* Questions related to this section may be addressed to Dr D. L. Dorset (see list of contributing authors). Dr Dorset kindly checked the proofs of this section.

described by the two-dimensional Fourier operator:

$$\mathscr{F}q = Q(\mathbf{u}) = \int q(\mathbf{x}) \exp[2\pi i(\mathbf{xu})]\ \mathrm{d}\mathbf{x}. \qquad (2.5.5.3)$$

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 $\mathscr{F}^{-1}TQ$.

The process of the diffraction $\mathscr{F}q\psi_0 = Q$, as seen from (2.5.5.1), is the same in both TEM and EDSA. Thus, in TEM under the lens actions $\mathscr{F}^{-1}TQ$ 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 $\mathscr{F}^{-1}Q$.

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 $I(xy) \sim |\psi_I|^2$ 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 $\varphi(\mathbf{x})$,

$$\varphi(\mathbf{x}) = \int_0^b \varphi(\mathbf{r})\ \mathrm{d}z, \qquad (2.5.5.4)$$

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 $q(\mathbf{x}) = \exp[-i\sigma\varphi(\mathbf{x})]$ (2.5.2.42), and for weak phase objects the approximation $[\sigma\varphi \ll 1]$

$$q(\mathbf{x}) = 1 - i\sigma\varphi(\mathbf{x}) \qquad (2.5.5.5)$$

is valid.

In the back focal plane of the objective lens the wave has the form

$$Q(uv) \cdot T(U) \qquad (2.5.5.6)$$

$$T = A(U) \exp(i\chi U) \qquad (2.5.5.7a)$$

$$\chi(U) = \pi\Delta f \lambda U^2 + \frac{\pi}{2} C_s \lambda^3 U^4, \qquad (2.5.5.7b)$$

where $U = (u^2 + v^2)^{1/2}$; $\exp[i\chi(U)]$ is the Scherzer phase function (Scherzer, 1949) of an objective lens (Fig. 2.5.5.1), $A(U)$ is the aperture function, C_s the spherical aberration coefficient, and Δf the defocus value [(2.5.2.32)–(2.5.2.35)].

The bright-field image intensity (in object coordinates) is

$$I(xy) = |\psi_I(xy) * t(xy)|^2, \qquad (2.5.5.8)$$

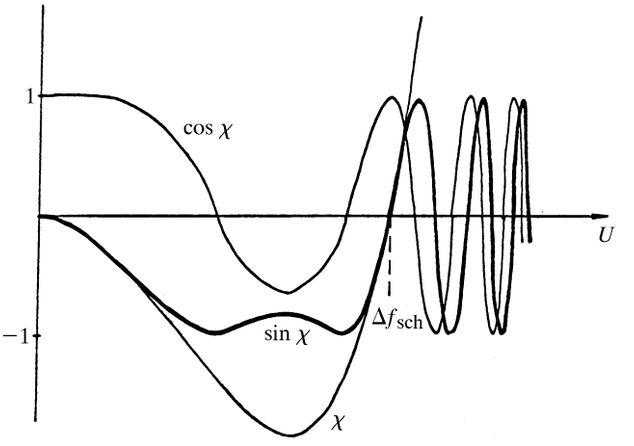

Fig. 2.5.5.1. The χ function and two components of the Scherzer phase function $\sin\chi(U)$ and $\cos\chi(U)$.

where $t = \mathscr{F}^{-1}[T]$. The phase function (2.5.5.7) depends on defocus, and for a weak phase object (Cowley, 1981)

$$I(xy) = 1 + 2\sigma\varphi(xy) * s(xy), \qquad (2.5.5.9)$$

where $s = \mathscr{F}^{-1}[A(U)\sin\chi]$, which includes only an imaginary part of function (2.5.5.6). While selecting defocus in such a way that under the Scherzer defocus conditions [(2.5.2.44), (2.5.2.45)] $|\sin\chi| \simeq 1$, one could obtain

$$I(xy) = 1 + 2\sigma\varphi(xy) * a(xy). \qquad (2.5.5.10)$$

In this very simple case the image reflects directly the structure of the object – the two-dimensional distribution of the projection of the potential convoluted with the spread function $a = \mathscr{F}^{-1}A$. In this case, no image restoration is necessary. Contrast reversal may be achieved by a change of defocus.

At high resolution, this method enables one to obtain an image of projections of the atomic structure of crystals and defects in the atomic arrangement – vacancies, replacements by foreign atoms, amorphous structures and so on; at resolution worse than atomic one obtains images of dislocations as continuous lines, inserted phases, inclusions *etc.* (Cowley, 1981). It is also possible to obtain images of thin biological crystals, individual molecules, biological macromolecules and their associations.

Image restoration. In the case just considered (2.5.5.10), the projection of potential $\varphi(xy)$, convoluted with the spread function, can be directly observed. In the general case (2.5.5.9), when the aperture becomes larger, the contribution to image formation is made by large values of spatial frequencies U, in which the function $\sin\chi$ oscillates, changing its sign. Naturally, this distorts the image just in the region of appropriate high resolution. However, if one knows the form of the function $\sin\chi$ (2.5.5.7), the true function $\varphi(xy)$ can be restored.

This could be carried out experimentally if one were to place in the back focal plane of an objective lens a zone plate transmitting only one-sign regions of $\sin\chi$ (Hoppe, 1971). In this case, the information on $\varphi(xy)$ is partly lost, but not distorted. To perform such a filtration in an electron microscope is a rather complicated task.

Another method is used (Erickson & Klug, 1971). It consists of a Fourier transformation $\mathscr{F}^{-1}$ of the measured intensity distribution TQ (2.5.5.6) and division of this transform, according to (2.5.5.7*a*,*b*), by the phase function $\sin\chi$. This gives

references