

4. PRODUCTION AND PROPERTIES OF RADIATIONS

$$V_i(s) = f_i^B(s)/K, \quad (4.3.1.12)$$

where $s = 4\pi\lambda^{-1} \sin \theta = |\mathbf{k} - \mathbf{k}_0|$ and the f^B are the Born electron scattering amplitudes, as conventionally defined, in units of Å. Here θ is half the scattering angle and, again, $K = \sigma/\lambda$. Some values of $f^B(s)$ listed in the accompanying Tables 4.3.1.1 and 4.3.1.2 are obtained from the atomic potentials $\varphi_0(\mathbf{r})$ for isolated, spherically symmetrical atoms or ions by the relation

$$f^B(s) = 4\pi K \int_0^\infty r^2 \varphi(r) \frac{\sin sr}{sr} dr. \quad (4.3.1.13)$$

By the use of Poisson's equation relating the potential and charge-density distributions, it is possible to derive the Mott-Bethe formula for $f^B(s)$ in terms of the atomic scattering factors for X-rays, $f_x(s)$:

$$f^B(s) = 2\pi \frac{me^2}{h^2 \varepsilon_0} \{Z - f_x(s)\}/s^2, \quad (4.3.1.14)$$

where ε_0 is the permittivity of vacuum, or

$$f^B(s) = 0.023934 \lambda^2 \{Z - f_x(s)\}/\sin^2 \theta \quad (4.3.1.15)$$

[for λ in Å, $f^B(s)$ in Å, and $f_x(s)$ in electron units]. This was used for the other listed $f^B(s)$ values.

4.3.1.3. Approximations of restricted validity

(a) *Kinematical approximation.* In the limiting case of a vanishingly weak interaction of the incident electrons with the scattering potential of the crystal, the Born series (4.3.1.5) may be terminated at the term ψ_1 , corresponding to single scattering. Then the diffracted wave is given for a potential $\varphi(r)$ as $\psi(\mathbf{s})(\exp -ikR)/R$, with

$$\psi(\mathbf{s}) = K \int \varphi(\mathbf{r}) \exp\{i[\mathbf{r} \cdot \mathbf{s}]\} d\tau_r, \quad (4.3.1.16)$$

where R is the distance to the point of observation. For a periodic potential, $\varphi(\mathbf{r})$, the scattering amplitude for the \mathbf{h} beam is

$$\psi(\mathbf{h}) = NK \int \varphi(\mathbf{r}) \exp\{2\pi i \mathbf{h} \cdot \mathbf{r}\} d\tau_r, \quad (4.3.1.17)$$

where the integral is taken over one unit cell and N is the number of unit cells. From (4.3.1.16), it then follows that the scattering amplitude $\psi(\mathbf{h})$ is proportional to the structure amplitude, $V(\mathbf{h})$;

$$\psi(\mathbf{h}) = NKV(\mathbf{h}) \quad (4.3.1.18)$$

$$= NK \sum_i f_{\text{el},i}(\mathbf{h}) \exp\{2\pi i \mathbf{h} \cdot \mathbf{r}_i\}. \quad (4.3.1.19)$$

The intensity of the \mathbf{h} diffracted beam is then proportional to $\psi(\mathbf{h})\psi^*(\mathbf{h})$, and so to $|V(\mathbf{h})|^2$.

Similarly, we may write the differential scattering cross section for the scattering from a single isolated atom as

$$|f^B(s)|^2 = K^2 |V_i(s)|^2. \quad (4.3.1.20)$$

(b) *Two-beam approximation.* For some specific orientations of a crystal of relatively simple structure, the incident beam may be close to the Bragg angle for a strong, inner reflection but not for any other reflection. Then the approximation may be made that only those beams with indices $\mathbf{0}$ and \mathbf{h} have appreciable intensity. The intensities of these beams for a parallel-sided, plate-shaped, centrosymmetric crystal are given in MacGillary's (1940) development of the theory of Bethe (1928) as

$$I(\mathbf{h}) = I_0 \{\sigma V(\mathbf{h})\}^2 \frac{\sin^2 \{\pi t (\zeta_{\mathbf{h}}^2 + \xi_{\mathbf{h}}^{-2})^{1/2}\}}{\pi^2 (\zeta_{\mathbf{h}}^2 + \xi_{\mathbf{h}}^{-2})} \quad (4.3.1.21)$$

and $I(\mathbf{0}) = I_0 - I(\mathbf{h})$, where I_0 is the incident-beam intensity, t is the crystal thickness, $\xi_{\mathbf{h}}$ is the extinction distance given by $\xi_{\mathbf{h}} = \pi/\sigma V(\mathbf{h})$, and $\zeta_{\mathbf{h}}$ is the excitation error which measures the distance of the reciprocal-lattice point \mathbf{h} from the Ewald sphere.

A formula due to Blackman (1939), obtained by integrating (4.3.1.21) over $\xi_{\mathbf{h}}$, provides a useful first approximation for the intensities of ring or arc patterns given by polycrystalline material (see Section 2.5.2).

(c) *Phase-grating approximations.* For extremely thin crystals, the scattering can be approximated by that of a two-dimensional potential distribution given by projection of the three-dimensional distribution in the beam direction. Then, by analogy with (4.3.1.6), the emerging wave is

$$\psi(xy) = \exp\{-i\sigma\varphi(xy)\} \quad (4.3.1.22)$$

when

$$\varphi(xy) = \int_0^H \varphi(xyz) dz \quad (4.3.1.23)$$

and the diffraction amplitudes are given by the Fourier transform of this expression.

For thicker crystals, this approximation applies in the limit of very high electron-accelerating voltage, with the value of σ appropriate for the Compton wavelength, $\lambda = 0.024262$ Å, viz $\sigma = 0.0005068$.

It may be noted that for the special case of a single layer of atoms the solution of the wave equations (4.3.1.2) or (4.3.1.4), with the real potential (4.3.1.1) inserted, leads to a form equivalent to the Moliere high-energy approximation for the scattering by single atoms, namely

$$KV(s) = -\frac{i}{\lambda} \int_{-\infty}^{\infty} \{\exp[-i\sigma\varphi(\boldsymbol{\rho})] - 1\} \exp\{i\boldsymbol{\rho} \cdot \mathbf{s}\} d^2\boldsymbol{\rho}, \quad (4.3.1.24)$$

where $\boldsymbol{\rho}$ is a two-dimensional vector with components x, y , and

$$\varphi(\boldsymbol{\rho}) = \int_{-\infty}^{\infty} \varphi(\boldsymbol{\rho}, z) dz, \quad (4.3.1.25)$$

and this, in the low-angle approximation, is the same as (4.3.1.23). Then the scattered amplitude can be considered as made up from contributions from individual atoms that are equal (apart from bonding effects) to the complex atomic scattering amplitudes tabulated in connection with the diffraction of electrons by gases.

4.3.1.4. Relativistic effects

It has been shown by Fujiwara (1961) that, at least for electron energies up to 1 MeV or so, the relativistic effects on diffraction amplitudes and geometry are adequately described by the use of relativistically corrected values for the mass and wavelength of the electrons;

$$m = m_0(1 - \beta^2)^{-1/2} \quad (4.3.1.26)$$

$$\lambda = h \left/ \left[2em_0E \left(1 + \frac{eE}{2m_0c^2} \right) \right]^{1/2} = \lambda_c \frac{(1 - \beta^2)^{1/2}}{\beta} \right. \\ \left. = 12.2639/(E + 0.97845 \times 10^{-6} E^2)^{1/2}, \quad (4.3.1.27)$$

where m_0 is the rest mass, λ_c is the Compton wavelength $\beta = v/c$, and λ is given in Å if E is in volts. Consequently, σ varies with the incident electron energy as $[1 + h^2/m_0^2 c^2 \lambda^2]^{1/2}$, or

$$\sigma = 2\pi/\{\lambda E[1 + (1 - \beta^2)^{1/2}]\}.$$

4.3. ELECTRON DIFFRACTION

Values of λ , λ^{-1} , m/m_0 , $\beta = v/c$, and σ are listed for various values of the accelerating voltage, E , in Table 4.3.2.1 with λ in Å and E in volts.

4.3.1.5. Absorption effects

Any scattering process, whether elastic or inelastic, which removes energy from the set of diffracted beams being considered, may be said to constitute an absorption process. For example, for a measurement of the intensities of the elastically scattered, sharp Bragg reflections from a crystal, any process which gives diffuse background scattering or results in a detectable loss of energy gives rise to absorption.

The diffracted amplitudes in such cases may be calculated, at least as a first approximation, in terms of a complex potential, $\varphi_c(\mathbf{r})$, containing an imaginary part $\varphi_i(r)$ due to an 'absorption function' and a small added real part $\Delta\varphi(r)$. Then under the crystallographic sign convention, $\varphi_c(r) = \varphi(r) - i\varphi_i(r) + \Delta\varphi(r)$. Correspondingly, for a centrosymmetric crystal, the structure amplitude becomes complex and may be written

$$V(\mathbf{h}) = V_0(\mathbf{h}) - iV'(\mathbf{h}) + V''(\mathbf{h}). \quad (4.3.1.28)$$

Under the appropriate conditions of observation, important contributions to the imaginary and real additions to the structure amplitudes may be given by the excitation of phonons, plasmons, or electron transitions, or by diffuse scattering due to crystal defects or disorder.

The additional terms $iV'(\mathbf{h})$ and $V''(\mathbf{h})$, however, are not invariant properties of the crystal structure but depend on the conditions of the diffraction experiment, such as the accelerating voltage and orientation of the incident beam, the aperture or resolution of the recording system, and the use of energy filtering or discrimination. In spite of this, it may often be convenient to treat them as being produced by phenomenological complex potentials, defined for a limited range of experimental conditions.

4.3.1.6. Tables of atomic scattering amplitudes for electrons

Tables 4.3.1.1 and 4.3.1.2 list values of $f^B(s)$ in Å for all neutral atoms and most chemically significant ions, respectively. The values have been given by Doyle & Turner (1968) for several cases, denoted by RHF using the relativistic Hartree-Fock atomic potentials of Coulthard (1967). For all other atoms and ions, $f^B(s)$ has been found using the Mott-Bethe formula [equation (4.3.1.15)] for $s \neq 0$, and the X-ray scattering factors of Table 2.2A of *IT IV* (1974). Thus all other neutral atoms except hydrogen are based on the relativistic Hartree-Fock wavefunctions of Mann (1968). These are designated by *RHF. For H and for ions below Rb, denoted by HF, $f^B(s)$ is ultimately based on the nonrelativistic Hartree-Fock wavefunctions of Mann (1968). For ions above Rb, denoted by *DS, modified relativistic Dirac-Slater wavefunctions calculated by Cromer & Waber (1974) are used.

For low values of s , the Mott formula becomes less accurate, since $[Z - f_x(s)]$ tends to zero with s for neutral atoms. Except for the RHF atoms, $f^B(s)$ for s from 0.01 to 0.03 are omitted in Table 4.3.1.1 and for s from 0.04 to 0.11, only two decimal places are given. $f^B(s)$ is then accurate to the figure quoted. For these atoms, $f^B(0)$ was found using the formula given by Ibers (1958):

$$f^B(0) = \frac{4\pi m e^2}{3h^2} Z \langle r^2 \rangle, \quad (4.3.1.29)$$

where $\langle r^2 \rangle$ is the mean-square atomic radius.

For ionized atoms, $f_{el}(0) = \pm\infty$. The values listed at $s = 0$ in Table 4.3.1.2 for RHF atoms were calculated by Doyle & Turner (1968) with $\varphi(r)$ in equation (4.3.1.13) replaced by $\varphi'(\mathbf{r})$, where

$$\varphi'(\mathbf{r}) = \varphi(\mathbf{r}) - e\Delta Z/r. \quad (4.3.1.30)$$

Here, ΔZ is the ionic charge. This approach omits the Coulomb field due to the excess or deficiency of charge on the nucleus. With the use of these values, the structure factor for forward scattering by a neutral unit cell containing ions may be found in the conventional way. Similar values are not available for other ions because the atomic potential data are lacking.

For computer applications, numerical approximations to the $f(s)$ of these tables have been given by Doyle & Turner (1968) as sums of Gaussians for the range $s = 0$ to 2 \AA^{-1} . An alternative is to make Gaussian fits to X-ray scattering factors, then use the Mott formula to derive electron scattering factors. As discussed by Peng & Cowley (1988), this practice may lead to problems for small values of s . An additional problem occurs in high-resolution electron-microscopy (HREM) image-simulation programs, where it is usually necessary to have electron scattering factors for the range 0 to 6 \AA^{-1} . Fox, O'Keefe & Taberner (1989) point out that extrapolation of the Gaussian fits of Doyle & Turner (1968) to values past 2 \AA^{-1} can be highly inaccurate. For the range of s from 2 to 6 \AA^{-1} , Fox *et al.* have used sums of polynomials to make accurate fits to the X-ray scattering factors of Doyle & Turner (1968) for many elements (Section 6.1.1), and electron scattering factors can be generated from these data by use of the Mott formula.

Recently, Rez, Rez & Grant (1994) have published new tables of X-ray scattering factors obtained using a multiconfiguration Dirac-Fock code and two parameterizations in terms of four Gaussians, one of higher accuracy over the range of about 2 \AA^{-1} and the other of lower accuracy over the extended range of about 6 \AA^{-1} . These authors suggest that electron scattering factors may best be obtained from these X-ray scattering factors by using the Mott formula. They provide a table of values for the electron scattering factor values for zero scattering angle, $f_{el}(0)$, for many elements and ions, which may be of value for the calculation of mean inner potentials.

4.3.1.7. Use of Tables 4.3.1.1 and 4.3.1.2

In order to calculate the Fourier coefficients $V(\mathbf{h})$ of the potential distribution $\varphi(\mathbf{r})$, for insertion in the formulae used to calculate intensities [such as (4.3.1.6), (4.3.1.20), (4.3.1.21)], or in the numerical methods for dynamical diffraction calculations, use

$$V(\mathbf{h}) \text{ (in volts)} = 47.87801 \Phi(\mathbf{h}) / \Omega, \quad (4.3.1.31)$$

where

$$\Phi(\mathbf{h}) = \sum_i f_i \exp\{2\pi i \mathbf{h} \cdot \mathbf{r}_i\}. \quad (4.3.1.32)$$

The f_i values are obtained from Tables 4.3.1.1 and 4.3.1.2, and Ω is the unit-cell volume in \AA^3 . The $V(\mathbf{h})$ and the f_i tabulated are properties of the crystal structure and the isolated atoms, respectively, and are independent of the particular scattering theory assumed.

Expressions for the calculation of intensities in the kinematical approximation are given for powder patterns and oblique texture patterns in Section 2.5.3, and for thin crystal plates in Section 2.5.1 of Volume B (*IT B*, 1992). Since the formulas for kinematical scattering, such as (4.3.1.19) and (4.3.1.20), include the parameter $K = \sigma/\lambda$, which varies with the energy of the electron beam through relativistic effects, it may be considered