

## 8.8. Accurate structure-factor determination with electron diffraction

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Several techniques have been developed for accurate determination of structure factors with electrons, mostly based on convergent-beam electron diffraction (CBED) and interpreted by dynamical scattering theory. Intensities are measured as one- or two-dimensional rocking curves, or as special intensity features in the CBED patterns, *e.g.* critical voltages. The main application of these methods so far has been to strong inner reflections from simple structures in relation to bonding effects, occupation numbers or ordering. Low-order reflections in electron diffraction are particularly sensitive to details in the distribution of valence electrons, through the difference  $Z - f^X$  in the expression for the atomic scattering amplitude

$$f^{\text{el}}(2\theta) = \frac{2}{a_H} \frac{Z - f^X}{(2\pi q)^2}, \quad (8.8.1)$$

where  $a_H = \hbar^2/m_0e^2$  is the first Bohr radius; the diffraction variable  $q = 2 \sin \theta/\lambda$ , and  $f^X$  is the X-ray scattering factor for atomic number  $Z$ . A further advantage is that these methods can provide absolute measurement of structure factors, *i.e.* without a scaling procedure. The limitation to inner reflections may be overcome by measurement of intensities integrated across Kossel-line features in CBED patterns (Vincent, Bird & Steeds, 1984; Gjønnnes & Bøe, 1994; Tsuda & Tanaka, 1995; Tomokiyo & Kuroiwa, 1990).

As distinct from the X-ray case where scattering from one electron is a convenient unit, commonly agreed upon for the atomic scattering factor as well as for the amplitude of the structure factor, there are several units and definitions possible in electron diffraction; see Cowley (1992), Spence & Zuo (1992). The *scattering amplitude* associated with the unit cell may have the same unit as the atomic scattering factor, *i.e.* length. The *structure factor* (or *Fourier potential*) is usually defined as the Fourier component,  $U_g$ , of the scattering potential that appears in the wave equation, and is expressed either in volts, as an SI unit, or in reciprocal-length squared. The latter unit follows from the common way of writing the Schrödinger equation in scattering theory, *viz*

$$\{\nabla_r^2 + 4\pi^2 k^2 + 4\pi^2 U(r)\}\psi(r) = 0, \quad (8.8.2)$$

with the factor  $4\pi^2$  introduced in order to conform with crystallographic conventions for reciprocal vectors and wave vectors. In this notation, the structure factor or Fourier potential may appear in units of (length) $^{-2}$ :

$$U_g = \frac{m}{m_0} \frac{1}{\Omega} \sum_j f^{\text{el}}(2\theta) \exp[-M_g^j] \exp[2\pi i \mathbf{g} \cdot \mathbf{r}_j], \quad (8.8.3)$$

where  $\Omega$  is the volume of the unit cell,  $m$  is the relativistic electron mass corresponding to the accelerating voltage and  $\exp[-M]$  the Debye–Waller factor. The translation to volts is given by  $U_g(\text{volts}) = 0.00665 U_g(\text{\AA}^{-2})$ . Results are usually quoted for the rest mass  $m_0$ , but in scattering calculations the factor  $m/m_0$  must be included. For comparison with theoretical calculations of charge distributions, the electron results are usually transformed to X-ray scattering factors. The structure factor associated with forward scattering has a special meaning, quite different from the X-ray case where  $F_0^X$  is a measure of the number of electrons. In electron diffraction,  $U_0$  is the mean inner potential – a measure of the average screening of the nuclear

charges, or the average extent of the electron clouds. For spherical neutral atoms, we obtain from (1) in the limit  $q \rightarrow 0$

$$f^{\text{el}}(0) = \frac{2}{3a_H} \sum \langle r_j^2 \rangle, \quad (8.8.4)$$

where the sum is over atomic electrons. For ions, this will diverge, but a limit can still be found by adding contributions from positive and negative ions, in which case the measured inner potential will depend upon the direction of the incident beam.  $U_0$  can be measured by interference experiments, *e.g.* by a biprism. For a review of experiments, see Spence (1993) and Saldin & Spence (1994).

Experimental determinations of structure factors  $U_g$  have been based on various techniques: thickness fringes in bright-field or dark-field electron micrographs, Kikuchi patterns, and, in recent years, especially by convergent-beam diffraction. The intensity distribution within the CBED discs can be recorded photographically, with image plates, or by a CCD camera connected to a YAG screen in the microscope – preferably with an energy filter, which will improve the signal-to-noise ratio and facilitate background subtraction (Burgess, Preston, Bolton, Zaluzec & Humphreys, 1994). Alternatives to the parallel recording in CBED may be to scan the pattern over the slit in an EELS system – or in a modified PEELS as described by Holmestad, Krivanek, Høier, Marthinsen & Spence (1993).

Because of dynamical interactions between beams, the scattered intensity will depend upon several structure factors. Refinement of structure factors must therefore be based on extensive calculations. These are usually performed in the Bloch-wave representation, which is the most convenient theoretical basis (in contrast to higher-resolution imaging, where multislice dynamical calculations are commonly used). The diffracted intensity as a function of the thickness  $t$  and the diffraction condition, defined by the components  $k_x, k_y$  of the incident wave vector, can be expressed as

$$\begin{aligned} I_g(t, k_x, k_y) = & \sum_i |C_0^i C_g^i|^2 \exp[-2\pi\mu^i t] \\ & + \sum_{i \neq j} C_0^{i*} C_g^i C_0^j C_g^{j*} \exp[2\pi i(\gamma^j - \gamma^i)t] \\ & \times \exp[-\pi(\mu^i + \mu^j)t], \end{aligned} \quad (8.8.5)$$

where the Bloch-wave coefficients  $C_h^j$  are eigenvectors, and the *Anpassungen*  $\gamma^j$  are eigenvalues obtained by the diagonalization. The absorption coefficients  $\mu^j$  for the Bloch waves  $j$  can be calculated from the imaginary potential  $U'(r)$  by a perturbation procedure or by non-Hermitian diagonalization (Bird, 1990).  $U'(r)$  describes the spatial variation within the unit cell of the diffuse scattering power, derived mainly from thermal scattering (Yoshioka & Kainuma, 1962). Calculations are usually based on an Einstein model (Radi, 1970; Bird & King, 1990).

The CBED patterns are used in measurement strategies based on different beam configurations, Fig. 8.8.1, *viz* (a) two-beam-like intensity profiles in systematic rows; (b) three- or four-beam cases in non-systematic configurations; (c) patterns in dense zones with strong many-beam dynamical interactions. The one- or two-dimensional intensity distributions are fitted to theoretical calculations by a least-squares procedure with low-order structure factors and certain experimental parameters as free variables.

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*Systematic row.* Measurement of *s*-fringe profiles in CBED discs from strong inner reflections in systematic rows was tried by MacGillavry (1940) and developed into a method for structure-factor determination by Goodman & Lehmpfuhl (1967) and later authors. At present, this may be the commonest method for refinement of low-order structure factors from CBED. A detailed account is given in the book by Spence & Zuo (1992) and in Spence (1993). Strong non-systematic interactions should be avoided. The intensity profiles can often be approximated by the two-beam expression

$$I_g(s_g) = \frac{(U_g/k)^2}{s^2 + (U_g/k)^2} \sin^2 \left[ \pi t \sqrt{s_g^2 + (U_g/k)^2} \right], \quad (8.8.6)$$

especially when  $U_g$  is substituted by an 'effective potential' which may be defined by the corresponding gap at the dispersion surface, viz.  $U_g^{\text{eff}} = k(\gamma^i - \gamma^j)_{\text{min}} = k/\xi^{ij}$ , where  $\xi^{ij}$  is an extinction distance. The outer part of the profile (large  $s_g$ ) depends mainly on the thickness, whereas the inner part is sensitive to the product  $tU_g$ . Different perturbation expressions have been proposed for the effective potential. The Bethe potential

$$U_g^{\text{eff}} = U_g - \sum_h \frac{U_h U_{g-h}}{2ks_h} \quad (8.8.7)$$

is often used, *e.g.* in the early steps of the refinement procedure (Gjønnnes, Gjønnnes, Zuo & Spence, 1988), and especially in order to treat weak beams beyond the typically 60–80 beams included in the Bloch-wave diagonalization (Zuo, 1993). Procedures and computer programs adapted to least-squares

refinement of structure factors from energy-filtered line profiles are described by Spence (1993), Zuo (1993) and Deininger, Necker & Mayer (1994). The refinement will usually include experimental parameters (thickness, beam orientations) as well as elastic and absorptive parts of a few low-order structure factors for each profile – but not high-order structure factors and thermal parameters, which are assumed. Low-order structure factors for a number of simple substances have been determined. Errors in the best results, referred to as X-ray structure amplitudes, are of the order of 0.1% – which may be a tenth of the bonding effect in covalent compounds. See, for example, the recent study of the intermetallic compound TiAl and a variant doped with 5% Mn (Holmestad, Weickenmeier, Zuo, Spence & Horita, 1993), where the charge-density deformation distribution

$$\Delta\rho(\mathbf{r}) = \frac{1}{\Omega} \sum_g [F_g^X(\text{crystal}) - F_g^X(\text{free atom})] \exp[2\pi i \mathbf{g} \cdot \mathbf{r}] \quad (8.8.8)$$

was constructed from nine-low-order structure factors.

*Three- and four-beam, non-systematic cases.* Several magnitudes can be extracted from Kikuchi or CBED patterns in such configurations, see *e.g.* Gjønnnes & Høier (1971). In the non-systematic critical-voltage method, the condition for extinction of line contrast is measured; in the IKL (intersecting Kikuchi line) method, one measures the separation between line segments of the split line appearing at the intersection with a strong Kikuchi band. The precision of these methods, originally developed for Kikuchi patterns, was increased considerably when CBED was used instead (Matsuhata, Tomokiyo, Watanabe & Eguchi, 1982; Taftø & Gjønnnes, 1985).

A further improvement is expected when the intensity distribution over the whole CBED discs is recorded and fitted to dynamical calculations. This has been explored recently by Høier, Bakken, Marthinsen & Holmestad (1993); the addition of non-systematic reflections in a parallel row can be seen as an extension of the systematic row configuration above. The experience so far is that the three- and four-beam configurations are very sensitive to structure-factor phases, but may not yield as accurate values for structure amplitudes as those obtained from the line profiles in the systematic row.

*Zone axis CBED.* Convergent-beam patterns around the axis of a dense zone contain extensive multiple-beam dynamical interaction. Bird & Saunders (1992) claim that this leads to high sensitivity as well as a high number of structure factors that can be determined from one CBED pattern. Their results from refinement of structure amplitudes in f.c.c., diamond and sphalerite structures may confirm this. From filtered intensities measured with a CCD camera, Saunders, Bird, Midgley & Vincent (1994) determined structure factors for silicon up to 331 from one pattern in the [110] zone. The point-spread function for the detector was deconvoluted from the raw data. Thickness, background level and a scaling factor were included in the refinement from a grid of  $21 \times 21$  intensities in each disc. Starting values were neutral atom scattering factors, absorptive scattering amplitude calculated from TDS and a preliminary thickness determination. 121 beams were included in the diagonalization, a further 270 beams by perturbation.

*Critical voltage and intersecting-Kikuchi-line (IKL) method.* The above methods, based on line scans or two-dimensional intensity distributions in CBED discs, rely on extensive

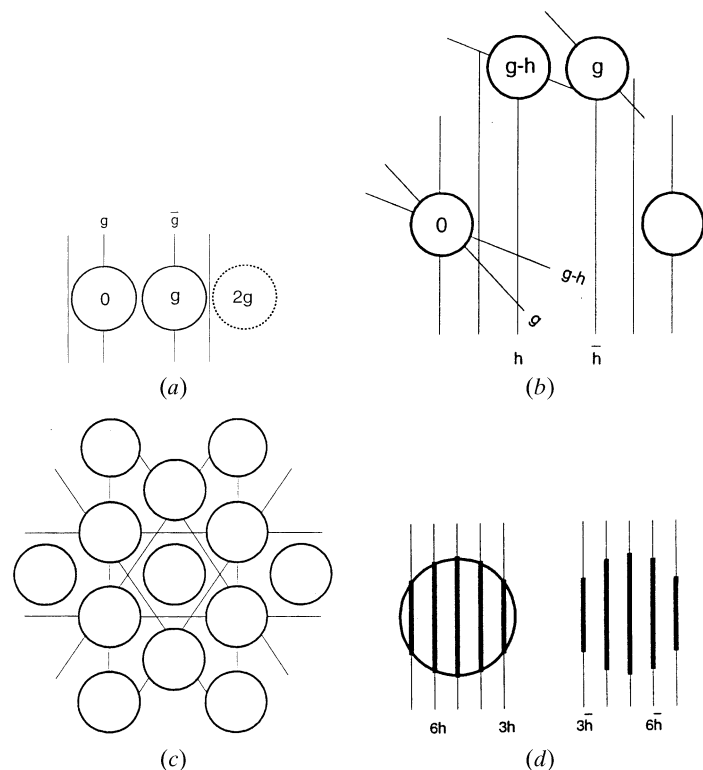


Fig. 8.8.1. Schematic representations of four convergent-beam configurations used for structure-factor determination: (a) intensity profile of a low-order reflection,  $g$ ; (b) non-systematic three- or four-beam configuration with a strong coupling reflection,  $h$ ; (c) symmetric many-beam configuration in a dense zone; (d) integrated intensity measurement of high-order reflections using a wide aperture (Taftø & Metzger, 1985).

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calculations of dynamical scattering at a number of incident-beam directions. In calculations of the critical-voltage effect (Watanabe, Uyeda & Fukuhara, 1969; Gjønnnes & Høier, 1971; Matsuhata & Steeds, 1987; Matsuhata & Gjønnnes, 1994), which corresponds to an accidental degeneracy of Bloch waves, only one beam direction is considered. The condition for the associated vanishing contrast (or contrast reversal) of a Kikuchi or Kossel line is determined from CBED patterns taken at a series of voltages and compared with the Bloch-wave calculations for the particular direction. This is a very sensitive method – with the disadvantage that only a relation between structure factors is obtained. In the original experiment by Watanabe, Uyeda & Fukuhara (1969), the relation between the structure factors for a strong first-order reflection and its second order was determined from measurement of the disappearance voltage for the second-order line, *cf.* formula (4.3.7.8). This second-order critical voltage depends on high-voltage microscopy – and a strong first-order reflection. A number of metals and simple alloy phases have been studied with this method in recent years by Fox and co-workers, see the review by Fox & Fisher (1988) and Fox & Tabbernor (1991). The extension to non-systematic cases in the normal accelerating-voltage range was first shown by Gjønnnes & Høier (1971). In principle, the Bloch-wave degeneracy will appear at a certain combination of excitation errors for any non-systematic three-beam configuration in centrosymmetric crystals. The difficulty is to find conditions that can be measured with sufficient precision. Matsuhata & Gjønnnes (1994) analysed a number of non-systematic critical voltages in symmetrical configurations and showed how they can be measured in the range below 2–300 kV for simple structures. From rutile-type SnO<sub>2</sub>, Matsuhata, Gjønnnes & Taftø (1994) measured four critical voltages, which were analysed in terms of ionicity; structure factors were determined for two low-order reflections. The calculations are simpler and less time consuming than for the intensity profiles, but also more dependent on known high-order structure factors and temperature factors. An alternative to the measurement of a critical voltage is to measure the position in the pattern where the degeneracy occurs – as in the IKL method (Gjønnnes & Høier, 1971; Taftø & Gjønnnes, 1985; Matsumura, Tomokiyo & Oki, 1989; Wang & Peng, 1994).

*Phases and absorption in multiple-beam cases.* Centrosymmetry was assumed in the original derivations of the accidental Bloch-wave degeneracy leading to the critical-voltage effect. In non-centrosymmetrical crystals, we can find degeneracies related to other symmetry elements, *i.e.* mirror planes or rotation axes or ‘pseudocritical voltages’ when the deviation from centrosymmetry is small (Matsuhata & Gjønnnes, 1994). For larger deviations, the position of minimum contrast can be used to determine structure-factor phase invariants, based again on the Bethe approximation. Høier & Marthinsen (1983) give the expression

$$|U_g^{\text{eff}}| = |U_g| \sqrt{\left\{ 1 - \left| \frac{U_h U_{g-h}}{U_h} \right| \frac{\cos \varphi}{2ks_g} \right\}^2 + \left| \frac{U_h U_{g-h}}{U_g 2ks_h} \right|^2 \sin^2 \varphi}, \quad (8.8.9)$$

where the phase invariant  $\varphi = \varphi_h + \varphi_{g-h} + \varphi_{-g}$ . Subsequent studies, *e.g.* Zuo, Høier & Spence (1989), showed this three-beam effect to be very sensitive to the phase invariant. From CBED profile measurements, Zuo, Spence, Downs & Mayer (1993) determined the structure-factor phase of the 00.2

reflection in Be with the remarkable precision of 0.1°. Bird (1990) pointed out that the treatment of the absorptive part needs special attention in non-centrosymmetrical crystals.

*Thickness fringes.* Thickness fringes were used for structure-factor determination at an early stage, *e.g.* Ando, Ichimiya & Uyeda (1974). The analogous effect in the diffraction pattern is the measurement of a split reflection from a wedge, which is an interesting visualization of Bloch waves; see Lehmpfuhl (1974). Today these techniques may appear to have mainly historical interest, although thickness fringes can be an alternative for determination of Bloch-wave absorption parameters  $\mu^j$  and thereby the imaginary Fourier potentials.

*Comparison, evaluation and extension to integrated intensities.* The convergent-beam electron-diffraction methods for determination of structure factors from small unit cells have been developed to high precision during the last 5–10 years. Least-squares fit of one- and two-dimensional intensity distributions within CBED discs appears today as the most sensitive method for determination of the lowest-order components of the charge distribution in organic structures with small unit cells. The accuracy may be as good as or better than the best X-ray methods – with the important provision that other structure parameters, high-order structure factors and Debye–Waller factors, are known to sufficient accuracy. Measurements of special features, *e.g.* critical voltages, offer an important supplement with less extensive computation efforts. Applications have been mainly to simple structures with atoms in special positions and refinement of low-order structure factors only. It should be noted that the deformation density  $\Delta\rho$  may have significant components beyond the low-order structure factors that are usually determined by CBED methods – and in a range where  $f^X < Z/2$  and X-rays thus inherently more sensitive to charge redistribution.

The extension of precise measurements to more reflections and to larger unit cells with position parameters is thus seen as a main challenge – which may be attacked along different avenues. Higher-order reflection profiles are narrower, less dynamic in character and not so suitable for the profile fitting described above. An alternative is to measure integrated intensities across Kossel-line segments, as has been done in several beam configurations. Vincent *et al.* (1984) measured integrated intensities of HOLZ-line segments, *i.e.* with the central CBED disc around the zone axis. Holmestad, Weickenmeier, Zuo, Spence & Horita (1993) measured selected HOLZ reflections in less-dense zones for determination of Debye–Waller factors. Taftø & Metzger (1985) showed the sensitivity of high-order lines in a dense systematic row to atomic coordinates. This wide-angle CBED technique has been applied to coordinate refinement in intermetallic compounds (Ma, Rømming, Lebeck, Gjønnnes & Taftø, 1992). Gjønnnes & Bøe (1994) measured intensities of a range of reflections in the 00 $l$  row from the superconductors YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> and a Co-substituted variant. Since the high-order lines are narrow, it is possible to measure relative intensities from a number of reflections in one exposure. Assuming a two-beam-like shape, the integral may be related to the gap at the dispersion surface, according to the Blackman formula (Blackman, 1939)

$$\int I_g^{\text{two beam}}(s_g, t) ds_g = (A_g/t) \int_0^{A_g} J_0(x) dx, \quad (8.8.10)$$

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where  $A_g = U_g^{\text{eff}} t$ , and  $J_0$  is the Bessel function of zero order. For a small gap, the intensity is proportional to  $|U^{\text{eff}}|^2$ . By many-beam calculations, Gjønnes & Bøe (1994) showed the integrated intensities to be less sensitive to dynamical interactions along the row than that indicated from the Bethe potentials, and that relative intensities are fairly independent of thickness. Coordinate refinement based on intensities from

a few high-order Kossel-line segments appear to produce accuracies roughly one order of magnitude poorer than good single-crystal X-ray determination. This may suggest that if some form of three-dimensional intensity data could be collected in electron diffraction the same level of accuracies as with X-rays may be attainable – which, however, remains to be seen.

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