

tive phase shifts in the scattered wave. This contrasts with the first Born approximation and the usual formulation of small-angle scattering, which require the scattered field to be small. Furthermore, the first Born approximation breaks down if the scattering is weak but extends over a region that is large compared with the incident wavelength (Gottfried, 1966). In this case, (25) is not valid.

The fact that refraction phenomena and scattering are intimately related is not new. Ewald and Oseen (Born & Wolf, 1964) have provided rigorous derivations of the laws of refraction and reflection of light from considerations of scattering of electromagnetic radiation from electric dipoles in optical media (the Ewald–Oseen extinction theorem). Here, a unified treatment of small-angle scattering and refraction of X-rays has been obtained using the Rytov approximation for the X-ray phase.

References

AZÁROFF, L. V., KAPLOW, R., KATO, N., WEISS, R. J., WILSON, A. J. C. & YOUNG, R. A. (1974). *X-ray Diffraction*, pp. 180–183. Sydney: McGraw-Hill.

BERK, N. F. & HARDMAN-RHYNE, K. A. (1986). *Physica (Utrecht)*, **136B&C**, 218–222.

BORN, M. & WOLF, E. (1964). *Principles of Optics*, 2nd. ed. New York: Pergamon.

CHERNOV, L. A. (1960). *Wave Propagation in a Random Medium*. New York: McGraw-Hill.

DEANS, S. R. (1983). *The Radon Transform and some of its Applications*. New York: Wiley.

DEVANEY, A. J. (1981). *Opt. Lett.* **6**, 374–376.

DEVANEY, A. J. (1986). *Inverse Probl.* **2**, 161–183.

GANS, R. (1925). *Ann. Phys.* **76**, 29–38.

GOTTFRIED, K. (1966). *Quantum Mechanics*. Vol. I. *Fundamentals*. Sydney: Benjamin.

GUINIER, A. & FOURNET, G. (1955). *Small-Angle Scattering of X-rays*. New York: Wiley.

KELLER, J. B. (1969). *J. Opt. Soc. Am.* **59**, 1003–1004.

MORSE, P. M. & FESHBACH, H. (1953). *Methods of Theoretical Physics*, Part I, Section 7.2, pp. 803–834. New York: McGraw-Hill.

NARDROFF, R. VON (1926). *Phys. Rev.* **28**, 240–246.

ORISTAGLIO, M. L. (1985). *J. Opt. Soc. Am.* **2**, 1987–1993.

POROD, G. (1982). *Small Angle X-ray Scattering*, edited by O. GLATTER & O. KRATKY, ch. 2. New York: Academic Press.

RAYLEIGH, LORD (1911). *Proc. R. Soc. (London)*. *Ser. A*, **84**, 25–46.

RYTOV, S. M. (1937). *Izv. Akad. Nauk SSSR Ser. Fiz.* No. 2, p. 223.

TAKAGI, S. (1969). *J. Phys. Soc. Jpn*, **26**, 1239–1253.

VAN DE HULST, H. C. (1957). *Light Scattering by Small Particles*. New York: Wiley.

VAN KAMPEN, N. G. (1949). *Physica (Utrecht)*, **14**, 575–589.

WEISS, R. J. (1951). *Phys. Rev.* **83**, 379–389.

Acta Cryst. (1994). **A50**, 690–703

A More General Expression for the Average X-ray Diffraction Intensity of Crystals with an Incommensurate One-Dimensional Modulation

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(Received 1 February 1994; accepted 5 April 1994)

Abstract

Statistical methods are used to derive an expression for the average X-ray diffraction intensity, as a function of $(\sin\theta)/\lambda$, of crystals with an incommensurate one-dimensional modulation. Displacive and density modulations are considered, as well as a combination of these two. The atomic modulation functions are given by truncated Fourier series that may contain higher-order harmonics. The resulting expression for the average X-ray diffraction intensity

is valid for main reflections and low-order satellite reflections. The modulation of individual atoms is taken into account by the introduction of overall modulation amplitudes. The accuracy of this expression for the average X-ray diffraction intensity is illustrated by comparison with model structures. A definition is presented for normalized structure factors of crystals with an incommensurate one-dimensional modulation that can be used in direct-methods procedures for solving the phase problem in X-ray crystallography. A numerical fitting procedure

is described that can extract a scale factor, an overall temperature parameter and overall modulation amplitudes from experimental reflection intensities.

1. Introduction

For nonmodulated crystals, a statistical method exists that allows for the determination of a scale factor and an overall isotropic temperature parameter from X-ray diffraction data (Wilson, 1942). The results are then used to bring the intensities from a relative to an absolute scale and to calculate normalized structure-factor amplitudes. This method cannot be applied to X-ray diffraction data of incommensurately modulated crystals, because of the different behavior of the intensities of main and satellite reflections.

Recently, an expression has been derived for the average X-ray diffraction intensity, as a function of $(\sin\theta)/\lambda$, of crystals with an incommensurate one-dimensional displacive modulation (Lam, Beurskens & van Smaalen, 1992a). Averages for main reflections and averages for first-order satellites were used together in a fitting procedure similar to that of Wilson (1942). In this way, a scale factor, an overall isotropic temperature factor and an overall modulation amplitude could be determined directly from the measured intensities. The overall modulation amplitude was interpreted as a weighted average of the individual modulation amplitudes. The results were used to calculate normalized structure-factor amplitudes (Lam, Beurskens & van Smaalen, 1993). However, because the Fourier series for the displacive modulation were truncated at the first-order harmonic, this expression for the average X-ray diffraction intensity is only valid for main reflections and first-order satellites.

In the present paper, a more general expression is derived for the average X-ray diffraction intensity of incommensurate one-dimensionally modulated crystals. This expression incorporates displacive and density (occupational) modulations and it allows higher-order harmonics in the Fourier series of the modulation functions. The average intensities of satellites of any order can thus be described. The modulation is taken into account by the introduction of one overall modulation amplitude for each harmonic of the displacive modulation and for each harmonic of the density modulation. In addition, the expression for the average X-ray diffraction intensity is used to define normalized structure factors for crystals with an incommensurate one-dimensional modulation.

2. Structure-factor formalism

An incommensurately modulated crystal can be considered as a three-dimensional translationally sym-

metric crystal (the basic structure), upon which a periodic deviation (the modulation) is superimposed. The wavelength of the modulation is incommensurate with respect to the lattice of the basic structure. Therefore, an incommensurately modulated crystal does not have three-dimensional translational symmetry. However, long-range order does exist. The unit cell of the basic structure is spanned by the vectors \mathbf{a}_i ($i = 1, 2, 3$). The reciprocal basic vectors \mathbf{a}_i^* are defined by $\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij}$. The periodicity of the incommensurate one-dimensional modulation is given by the wave vector $\mathbf{q} = \sum_{i=1}^3 q_i \mathbf{a}_i^*$, where at least one of the q_i is an irrational number.

Two types of modulations are generally distinguished: displacive modulation and density modulation. If displacive modulation occurs, the positions of the atoms are subject to periodic variations. Let the position of an atom μ in the basic structure be given by $\mathbf{r}_{0,L}^\mu = \mathbf{r}_0^\mu + \mathbf{L}$, where \mathbf{r}_0^μ is the position of the atom in the basic-structure unit cell and \mathbf{L} is a basic-structure lattice vector. The position of the same atom in the modulated crystal is then given by $\mathbf{r}_L^\mu = \mathbf{r}_{0,L}^\mu + \mathbf{u}^\mu(\mathbf{q} \cdot \mathbf{r}_{0,L}^\mu)$, where \mathbf{u}^μ describes the atomic displacement. The function \mathbf{u}^μ is periodic and can be written as a truncated Fourier series,

$$\mathbf{u}^\mu(\mathbf{q} \cdot \mathbf{r}_{0,L}^\mu) = \sum_{k_u=1}^{K_u} \left[\sum_{i=1}^3 U_{k_u,i}^\mu \sin(2\pi k_u \mathbf{q} \cdot \mathbf{r}_{0,L}^\mu - \alpha_{k_u,i}^\mu) \mathbf{a}_i \right], \quad (1)$$

where $U_{k_u,i}^\mu$ and $\alpha_{k_u,i}^\mu$ are the three amplitudes and three phases, respectively, of the k_u th harmonic and K_u is the maximum number of harmonics contributing to this series. Equation (1) can also be written as

$$\mathbf{u}^\mu(\mathbf{q} \cdot \mathbf{r}_{0,L}^\mu) = \sum_{k_u=1}^{K_u} [\mathbf{U}_{k_u}^{\mu,c} \sin(2\pi k_u \mathbf{q} \cdot \mathbf{r}_{0,L}^\mu) - \mathbf{U}_{k_u}^{\mu,s} \cos(2\pi k_u \mathbf{q} \cdot \mathbf{r}_{0,L}^\mu)], \quad (2)$$

with the vectors $\mathbf{U}_{k_u}^{\mu,c}$ and $\mathbf{U}_{k_u}^{\mu,s}$ given by

$$\mathbf{U}_{k_u}^{\mu,c} = \sum_{i=1}^3 U_{k_u,i}^\mu \cos(\alpha_{k_u,i}^\mu) \mathbf{a}_i \quad (3)$$

and

$$\mathbf{U}_{k_u}^{\mu,s} = \sum_{i=1}^3 U_{k_u,i}^\mu \sin(\alpha_{k_u,i}^\mu) \mathbf{a}_i, \quad (4)$$

respectively.

In the case of a density modulation, it is the occupancy factor that shows a periodic variation. For an atom at basic-structure position $\mathbf{r}_{0,L}^\mu$, the occupancy factor, $p_L^\mu = p^\mu(\mathbf{q} \cdot \mathbf{r}_{0,L}^\mu)$, can be written as the truncated Fourier series

$$p^\mu(\mathbf{q} \cdot \mathbf{r}_{0,L}^\mu) = P_0^\mu + \sum_{k_p=1}^{K_p} P_{k_p}^\mu \sin(2\pi k_p \mathbf{q} \cdot \mathbf{r}_{0,L}^\mu - \beta_{k_p}^\mu), \quad (5)$$

where $P_{k_p}^\mu$ and $\beta_{k_p}^\mu$ are the amplitude and phase, respectively, of the k_p th harmonic and P_0^μ is the average occupancy factor of atom μ . The maximum number of harmonics contributing to this series is denoted K_p . Equation (5) can be rewritten as

$$p^\mu(\mathbf{q} \cdot \mathbf{r}_{0,L}^\mu) = \sum_{k_p = -K_p}^{K_p} p_{k_p}^\mu \exp(2\pi i k_p \mathbf{q} \cdot \mathbf{r}_{0,L}^\mu), \quad (6)$$

with the complex amplitudes $p_{k_p}^\mu$ given by

$$p_{k_p}^\mu = \begin{cases} -(iP_{k_p}^\mu/2) \exp(-i\beta_{k_p}^\mu) & k_p > 0 \\ P_0^\mu & k_p = 0 \\ (iP_{-k_p}^\mu/2) \exp(i\beta_{-k_p}^\mu) & k_p < 0. \end{cases} \quad (7)$$

The diffraction pattern of an incommensurate one-dimensionally modulated crystal consists of main reflections at the nodes of the reciprocal lattice of the basic structure, accompanied by satellite reflections that are usually weaker. Diffraction vectors $\mathbf{S} = \sum_{i=1}^3 S_i \mathbf{a}_i^*$ are defined as $\mathbf{S} = \mathbf{H} + m\mathbf{q}$, where $\mathbf{H} = \sum_{i=1}^3 H_i \mathbf{a}_i^*$ is a diffraction vector of the basic structure and m is the satellite index. This means that, for a given modulation wave vector \mathbf{q} , each diffraction vector \mathbf{S} is uniquely characterized by a set of four integers (H_1, H_2, H_3, m).[†] There are two kinds of reflections: main reflections ($m = 0$) and satellite reflections ($m \neq 0$). The order of a reflection is denoted $|m|$.

The structure factor for X-ray scattering from a crystal with an incommensurate one-dimensional modulation is written as (de Wolff, 1974; Yamamoto, 1982)

$$F(\mathbf{S}, m) = \sum_{\mu=1}^N g^\mu(\mathbf{S}, m) f^\mu(\mathbf{S}) \exp[2\pi i(\mathbf{S} - m\mathbf{q}) \cdot \mathbf{r}_0^\mu], \quad (8)$$

where the summation extends over all atoms (N) in the basic-structure unit cell. The effect of the modulation on the X-ray diffraction intensity is given by the atomic modulation factor

$$g^\mu(\mathbf{S}, m) = \int_0^1 p^\mu(\tau) \exp\{2\pi i[\mathbf{S} \cdot \mathbf{u}^\mu(\tau) + m\tau]\} d\tau, \quad (9)$$

where p^μ and \mathbf{u}^μ are the atomic modulation functions for the density modulation and the displacive modulation, respectively. The atomic scattering factor f^μ may be approximated by

$$f^\mu(\mathbf{S}) = f_0^\mu(s) \exp(-Bs^2), \quad (10)$$

where f_0^μ is the form factor for atoms at rest, B is an overall isotropic temperature parameter and $s = (\sin\theta)/\lambda = S/2$, with S being the length of the diffraction vector \mathbf{S} . For the theoretical evaluations, f_0^μ may

[†] (H_1, H_2, H_3) are usually denoted (h, k, l).

be approximated by

$$f_0^\mu(s) = Z_\mu \left\{ (1/\sigma) \sum_{\nu=1}^N [f_0^\nu(s)]^2 \right\}^{1/2}, \quad (11)$$

where Z_μ is the atomic number and $\sigma = \sum_{\mu=1}^N Z_\mu^2$. Note that, with the assumption of no anomalous scattering, the atomic form factor is a real function. From this and from the fact that $g^\mu(\mathbf{S}, m) = [g^\mu(-\mathbf{S}, -m)]^*$, where $*$ denotes the complex conjugate, it follows that Friedel's law applies to the structure factor.

Note that, for crystals with density modulation, the atomic form factor f_0^μ may actually represent the scattering factor of an averaged atom. However, this requires proper adjustment of the values of the amplitudes $P_{k_p}^\mu$.

3. An expression for the average intensity

To derive the expression for the average X-ray diffraction intensity, the atomic modulation factor g^μ is evaluated first. From expression (2) for the atomic displacement \mathbf{u}^μ , a straightforward calculation leads to

$$\mathbf{S} \cdot \mathbf{u}^\mu(\mathbf{q} \cdot \mathbf{r}_{0,L}^\mu) = \sum_{k_u=1}^{K_u} C_{k_u}^\mu(\mathbf{S}) \sin[2\pi k_u \mathbf{q} \cdot \mathbf{r}_{0,L}^\mu - \eta_{k_u}^\mu(\mathbf{S})], \quad (12)$$

with the amplitude $C_{k_u}^\mu$ and phase $\eta_{k_u}^\mu$ defined by the transformation (Petříček, Coppens & Becker, 1985; Petříček & Coppens, 1988)

$$\begin{cases} \mathbf{S} \cdot \mathbf{U}_{k_u}^{\mu,c} = C_{k_u}^\mu(\mathbf{S}) \cos[\eta_{k_u}^\mu(\mathbf{S})] \\ \mathbf{S} \cdot \mathbf{U}_{k_u}^{\mu,s} = C_{k_u}^\mu(\mathbf{S}) \sin[\eta_{k_u}^\mu(\mathbf{S})] \end{cases} \quad (13)$$

and with $C_{k_u}^\mu(\mathbf{S}) \geq 0$. Note that, from (13), it follows that $\tan[\eta_{k_u}^\mu(\mathbf{S})]$, and therefore $\eta_{k_u}^\mu(\mathbf{S})$ itself, depends only on the orientation of \mathbf{S} and not on its length. From (13), by substitution of (3) and (4), the amplitude $C_{k_u}^\mu$ can be derived as (Lam, Beurskens & van Smaalen, 1992a)

$$C_{k_u}^\mu(\mathbf{S}) = \left[\sum_{i,j=1}^3 S_i (\mathbf{U}_{k_u}^{\mu})_{ij} S_j \right]^{1/2}, \quad (14)$$

where $\mathbf{U}_{k_u}^\mu$ is a symmetric tensor that depends on the amplitudes and phases of the k_u th harmonic of the atomic displacement, through the definition of its components

$$(\mathbf{U}_{k_u}^\mu)_{ij} = U_{k_u,i}^\mu U_{k_u,j}^\mu \cos(\alpha_{k_u,i}^\mu - \alpha_{k_u,j}^\mu). \quad (15)$$

Equation (14) clearly illustrates the anisotropic behavior of the displacive modulation. It can be shown that the displacive modulation simulates an anisotropic temperature effect (see Appendix A). For the benefit of this paper, however, an isotropic approach to the displacive modulation is needed.

From (13), the amplitude $C_{k_u}^\mu$ can also be written as

$$C_{k_u}^\mu(\mathbf{S}) = 2s \{ (U_{k_u}^{\mu,c})^2 \cos^2 [\delta_{k_u}^{\mu,c}(\mathbf{S})] + (U_{k_u}^{\mu,s})^2 \cos^2 [\delta_{k_u}^{\mu,s}(\mathbf{S})] \}^{1/2}. \quad (16)$$

Here, $U_{k_u}^{\mu,c}$ and $U_{k_u}^{\mu,s}$ are the lengths of the vectors $\mathbf{U}_{k_u}^{\mu,c}$ and $\mathbf{U}_{k_u}^{\mu,s}$, respectively. The angles between the vectors \mathbf{S} and $\mathbf{U}_{k_u}^{\mu,c}$ and between the vectors \mathbf{S} and $\mathbf{U}_{k_u}^{\mu,s}$ are denoted $\delta_{k_u}^{\mu,c}$ and $\delta_{k_u}^{\mu,s}$, respectively. Note that both angles depend only on the orientation of \mathbf{S} and not on its length.

By substitution of (6) and (12) and by use of a relation between exponential functions and Bessel functions [equation (8.511-4) of Gradshteyn & Ryzik (1980)], the integrand of (9) becomes

$$\sum_{k_p=-K_p}^{K_p} p_{k_p}^\mu \exp[2\pi i(k_p + m)\tau] \times \prod_{k_u=1}^{K_u} \left(\sum_{m_{k_u}^\mu=-\infty}^{\infty} J_{m_{k_u}^\mu} [2\pi C_{k_u}^\mu(\mathbf{S})] \times \exp \{ i m_{k_u}^\mu [\eta_{k_u}^\mu(\mathbf{S}) + \pi - 2\pi k_u \tau] \} \right), \quad (17)$$

where J_n is the n th-order Bessel function of the first kind. The multiple product with respect to k_u and the summation with respect to $m_{k_u}^\mu$ can be interchanged, which causes (17) to become

$$\sum_{k_p=-K_p}^{K_p} \sum_{m_1^\mu=-\infty}^{\infty} \cdots \sum_{m_{K_u}^\mu=-\infty}^{\infty} p_{k_p}^\mu \left\{ \prod_{k_u=1}^{K_u} J_{m_{k_u}^\mu} [2\pi C_{k_u}^\mu(\mathbf{S})] \right\} \times \exp \left\{ i \sum_{k_u=1}^{K_u} m_{k_u}^\mu [\eta_{k_u}^\mu(\mathbf{S}) + \pi] \right\} \times \exp \left[2\pi i \left(k_p + m - \sum_{k_u=1}^{K_u} m_{k_u}^\mu k_u \right) \tau \right]. \quad (18)$$

With (18) for the integrand of (9), the integral with respect to τ can be evaluated. It follows that a term in the multiple summation of (18) only contributes to the integral if the condition

$$\sum_{k_u=1}^{K_u} m_{k_u}^\mu k_u = k_p + m \quad (19)$$

is fulfilled. This leads to the following expression for the atomic modulation factor:

$$g^\mu(\mathbf{S}, m) = \sum_{k_p=-K_p}^{K_p} \sum_{m_1^\mu=-\infty}^{\infty} \cdots \sum_{m_{K_u}^\mu=-\infty}^{\infty} p_{k_p}^\mu \left\{ \prod_{k_u=1}^{K_u} J_{m_{k_u}^\mu} [2\pi C_{k_u}^\mu(\mathbf{S})] \right\} \times \exp \left\{ i \sum_{k_u=1}^{K_u} m_{k_u}^\mu [\eta_{k_u}^\mu(\mathbf{S}) + \pi] \right\}. \quad (20)$$

Note that (19) and (20) resemble similar expressions implicitly given by (7) of Petříček & Coppens (1988), where a more general case of displacive modulation

is considered but where the effect of density modulation is not taken into account.

An expression for the intensity $|F|^2$ can be derived from (8), by substitution of (20) for the atomic modulation factor. Amongst other things, this expression depends on the average positions \mathbf{r}_0^μ and on the modulation parameters of the individual atoms. As for nonmodulated crystals (Wilson, 1942), the average of $|F|^2$ is calculated over a sufficiently large set of reflections in a narrow s interval. This set contains all diffraction vectors that have approximately the same length S and therefore have their end points within a thin shell of radius $S = 2s$ in reciprocal space. For a modulated crystal, the behavior of the intensity of main reflections is quite different from that of satellite reflections. Therefore, for reflection order $|m|$, the average is calculated separately.* The average of $|F|^2$ over such a set of reflections is denoted $\langle |F|^2 \rangle_{s,|m|}$. Note that the expression for $|F|^2$ contains a number of terms that will cancel when $\langle |F|^2 \rangle_{s,|m|}$ is evaluated. Which terms these are and the conditions under which they cancel are briefly described below.

To evaluate the expression for $|F|^2$, the structure factor [(8)] is first multiplied by its complex conjugate. Some of the terms in the resulting multiple summation depend on a nonzero interatomic distance vector $\mathbf{r}_0^\mu - \mathbf{r}_0^\nu$, where μ and ν denote different atoms in the basic-structure unit cell. From the same assumptions as used by Wilson (1942), it can be shown that these terms will cancel when $\langle |F|^2 \rangle_{s,|m|}$ is evaluated. Thus, in the expression for $|F|^2$ at hand, only the term $\sum_{\mu=1}^N |g^\mu f^\mu|^2$ has to be considered.

The next step involves the evaluation of $|g^\mu f^\mu|^2$ by substitution of (20) for the atomic modulation factor. In the resulting multiple summation, terms occur that contain a factor $\exp [i \sum_{k_u=1}^{K_u} (m_{k_u}^\mu - m_{k_u}^{\nu\mu}) \eta_{k_u}^\mu(\mathbf{S})]$, with not all integer differences $m_{k_u}^\mu - m_{k_u}^{\nu\mu}$ equal to zero. From (13), with the vectors $\mathbf{U}_{k_u}^{\mu,c}$ and $\mathbf{U}_{k_u}^{\mu,s}$ being nonzero and not parallel to one another for each pair (μ, k_u) , it follows that, with the previously specified set of reflections, the numerical values of $\eta_{k_u}^\mu(\mathbf{S})$ (modulo 2π) are uniformly distributed throughout the interval $[0, 2\pi]$.† Consequently,

* Let there be a large set of satellite reflections, with all satellites having their end points in a thin shell of radius S in reciprocal space and with the same reflection order $|m|$. This set can be divided into two other sets: one containing the $m < 0$ satellites and the other containing the $m > 0$ satellites. Because Friedel's law applies, a reflection in one of these two sets will always have a Friedel-related reflection, having the same structure-factor amplitude, in the other set. This means that the average intensity is the same for both sets of reflections. Consequently, the average intensity is independent of the sign of the satellite index m .

† It is realized that this is not true for special cases of the vectors $\mathbf{U}_{k_u}^{\mu,c}$ and $\mathbf{U}_{k_u}^{\mu,s}$, but such cases are not considered here. Also note that, as in the conventional Wilson plot, atoms are supposed not to be on special positions.

these terms will also cancel when $\langle |F|^2 \rangle_{s,|m|}$ is evaluated.

Herewith, the average intensity $\langle |F|^2 \rangle_{s,|m|}$ can be written as

$$\langle |F|^2 \rangle_{s,|m|} = \exp(-2Bs^2) \left\{ \sum_{\mu=1}^N [f_0^\mu(s)]^2 \right\} \Gamma(s; |m|). \quad (21)$$

The function Γ is written as a multiple summation of discrete averages,

$$\Gamma(s; |m|) = \sum_{\mu=1}^N \sum_{k_p=-K_p}^{K_p} \sum_{m_i^{\mu}=-\infty}^{\infty} \cdots \sum_{m_{k_u}^{\mu}=-\infty}^{\infty} (Z_{\mu}^2 |p_{k_p}^{\mu}|^2 / \sigma) \times \left\langle \prod_{k_u=1}^{K_u} J_{m_{k_u}^{\mu}}^2 [2\pi C_{k_u}^{\mu}(S)] \right\rangle_{s,|m|}, \quad (22)$$

where (10) and (11) have been used. The first two factors in (21) make up the average intensity for nonmodulated crystals (Wilson, 1942) while the last factor (Γ) is the modification that describes the deviation from this average intensity caused by the displacive modulation and/or the density modulation. Note that the contribution of the displacive modulation to the average intensity is not only weighted by Z_{μ}^2 but, when density modulation occurs, also by a factor $|p_{k_p}^{\mu}|^2$. Thus, in the general case of displacive modulation and density modulation, mixing of different harmonics occurs in each term of (22).

In the limit of diminishing modulation (for all atoms μ ; $U_{k_u, i}^{\mu} \rightarrow 0$ for all k_u and i , $P_0^{\mu} \rightarrow 1$ and $P_{k_p}^{\mu} \rightarrow 0$ for $k_p \neq 0$), (21) reduces to the average intensity for nonmodulated crystals. For main reflections ($m=0$), $\Gamma \rightarrow 1$ and (21) becomes identical to the average intensity for nonmodulated crystals. For satellite reflections ($m \neq 0$), $\Gamma \rightarrow 0$ and thus $\langle |F|^2 \rangle_{s,|m|} \rightarrow 0$, *i.e.* the satellite reflections disappear.

4. Normalization of structure factors

For a proper evaluation of the average X-ray diffraction intensities, the symmetry of the crystal must be taken into account. It can be shown that its main effect is to enlarge the intensities of particular groups of reflections by a factor ϵ , the symmetry-enhancement factor, which can be defined as for nonmodulated crystals (Wilson, 1950; Giacobozzo, 1980; Lam, Beurskens & van Smaalen, 1993). One can then define the partially normalized structure factor E_a by

$$E_a(\mathbf{S}) = F(\mathbf{S}) \left\{ \epsilon(\mathbf{S}) \sum_{\mu=1}^N [f_0^\mu(s)]^2 \right\}^{-1/2} \quad (23)$$

and, by use of (21), write its mean square as

$$\langle |E_a|^2 \rangle_{s,|m|} = \exp(-2Bs^2) \Gamma(s; |m|). \quad (24)$$

As the experimental intensities I are on a relative scale, a scale factor K is introduced and defined by

$$|F(\mathbf{S})|^2 = K^2 I(\mathbf{S}). \quad (25)$$

From (23), (24) and (25), the observed average of $|E_a|^2$ on a relative scale, denoted $G_o(s; |m|)$, can then be written as

$$G_o(s; |m|) = \left\langle I(\mathbf{S}) \left\{ \epsilon \sum_{\mu=1}^N [f_0^\mu(s)]^2 \right\}^{-1} \right\rangle_{s,|m|}, \quad (26)$$

while the theoretical expectation value, denoted $G_c(s; |m|)$, is equal to

$$G_c(s; |m|) = K^{-2} \exp(-2Bs^2) \Gamma(s; |m|). \quad (27)$$

After reflections have been sorted, for each reflection order $|m|$, into suitable intervals of s , expressions (26) and (27) can be employed by a fitting procedure to estimate overall structural parameters (*e.g.* K , B and possibly modulation parameters) from average intensities.

Unfortunately, expression (22) for Γ is not very suitable for use with a fitting procedure. For nonmodulated crystals, the average X-ray diffraction intensity can be estimated without any prior knowledge of the crystal structure, except for the contents of the unit cell (Wilson, 1942). Expression (22) not only depends on the contents of the basic-structure unit cell but also on the modulation parameters of individual atoms. Consequently, evaluation of the average intensity of an incommensurately modulated crystal also requires knowledge of the complete atomic modulation functions (p^{μ} and u^{μ}). Therefore, to obtain an expression for the average intensity that is suitable for use with a fitting procedure and that does not depend on modulation parameters of individual atoms, further approximation of Γ [(22)] and introduction of overall modulation amplitudes is necessary. When this has been done (see §§ 5 and 6), normalized structure factors can be defined by [(23), (24)]

$$E(\mathbf{S}) = F(\mathbf{S}) \exp(Bs^2) \left\{ \epsilon(\mathbf{S}) \Gamma(s; |m|) \sum_{\mu=1}^N [f_0^\mu(s)]^2 \right\}^{-1/2}. \quad (28)$$

5. A low-order approximation to Γ

As a first approximation to Γ , the discrete average is replaced by a continuous average, *i.e.* the last factor on the right-hand side of (22) is replaced by

$$(1/4\pi) \iint_{\Omega} \left\{ \prod_{k_u=1}^{K_u} J_{m_{k_u}^{\mu}}^2 [2\pi C_{k_u}^{\mu}(\mathbf{S})] \right\} d\Omega, \quad (29)$$

where the twofold integral with respect to Ω extends over all orientations of the diffraction vector, while s and $|m|$ do not change.

Furthermore, as in Lam, Beurskens & van Smaalen (1992a), it is assumed that the modulation amplitudes of the individual atoms are small. For this reason, all contributions to Γ as a result of integrals (29) will be neglected if the integrands are of order higher than 2 in the modulation amplitudes. Consequently, for all atoms μ , the multiple summation with respect to the integers $m_{k_u}^\mu$ in (22) can be restricted to terms of the following types:

type 1,

$$m_{k_u}^\mu = 0 \quad \text{for all } k_u; \quad (30)$$

type 2(a),

$$m_k^\mu = 1 \quad \text{and} \quad m_{k_u}^\mu = 0 \quad \text{for } k_u \neq k; \quad (31)$$

type 2(b),

$$m_k^\mu = -1 \quad \text{and} \quad m_{k_u}^\mu = 0 \quad \text{for } k_u \neq k. \quad (32)$$

Of course, each of the conditions (30), (31) and (32) restricts the summation with respect to k_p as well. For each of these terms, the contribution to Γ is evaluated as follows.

For terms of type 1, combination of conditions (19) and (30) results in the extra condition $k_p = -m$, *i.e.* the summation with respect to k_p in (22) no longer exists for this case. As a result, a nonzero contribution to Γ for terms of type 1 is only possible if the condition $-K_p \leq m \leq K_p$ is fulfilled. As is discussed later, K_p can always be chosen to meet this condition (see § 7). The contribution to Γ can then be written, using (29), as

$$\sum_{\mu=1}^N (Z_\mu^2 |p_m^\mu|^2 / 4\pi\sigma) \iint_{\Omega} \left\{ \prod_{k_u=1}^{K_u} J_0^2[2\pi C_{k_u}^\mu(\mathbf{S})] \right\} d\Omega. \quad (33)$$

With the assumption that the amplitudes $C_{k_u}^\mu$ are small, the multiple product in (33) can be approximated using the series expansion for Bessel functions [equation (8.440) of Gradshteyn & Ryzhik (1980)] and disregarding all terms of order higher than 2 in the amplitudes $C_{k_u}^\mu$. Subsequent substitution of (16) for $C_{k_u}^\mu$ results in the following expression for the integrand of (33):

$$1 - 8\pi^2 s^2 \sum_{k_u=1}^{K_u} \{ (U_{k_u}^{\mu,c})^2 \cos^2[\delta_{k_u}^{\mu,c}(\mathbf{S})] + (U_{k_u}^{\mu,s})^2 \cos^2[\delta_{k_u}^{\mu,s}(\mathbf{S})] \}. \quad (34)$$

Note that each of the terms in (34) can be integrated independently. Thus, the angles $\delta_{k_u}^{\mu,c}$ and $\delta_{k_u}^{\mu,s}$ can be replaced by a single integration variable δ and $d\Omega = \sin(\delta) d\delta d\xi$, where δ and ξ are polar angles, with $\delta \in [0, \pi]$ and $\xi \in [0, 2\pi]$, describing the orientation of the diffraction vector. Expression (34) can then be replaced by

$$1 - 8\pi^2 s^2 \left[\sum_{k_u=1}^{K_u} (U_{k_u}^\mu)^2 \right] \cos^2(\delta), \quad (35)$$

where the atomic modulation amplitudes $U_{k_u}^\mu$ are given by

$$U_{k_u}^\mu = [(U_{k_u}^{\mu,c})^2 + (U_{k_u}^{\mu,s})^2]^{1/2}. \quad (36)$$

By substitution of (35) for the integrand and by use of the transformation $x = \cos(\delta)$, (33) becomes

$$P_m^2 \int_0^1 \{ 1 - [4\pi s (V_m/P_m) x]^2 / 2 \} dx, \quad (37)$$

with overall modulation amplitudes defined by

$$P_{k_p} = \left[(1/\sigma) \sum_{\mu=1}^N Z_\mu^2 |p_{k_p}^\mu|^2 \right]^{1/2}, \quad (38)$$

$$V_{k_p} = \left(\sum_{k_u=1}^{K_u} V_{k_p, k_u}^2 \right)^{1/2} \quad (39)$$

and

$$V_{k_p, k_u} = \left[(1/\sigma) \sum_{\mu=1}^N Z_\mu^2 |p_{k_p}^\mu|^2 (U_{k_u}^\mu)^2 \right]^{1/2}. \quad (40)$$

Note that the amplitudes V_{k_p, k_u} are a mixture of the modulation amplitudes of the $|k_p|$ th harmonic of the density modulation and those of the k_u th harmonic of the displacive modulation.

Expression (37) is not a very good approximation to (33). Especially at larger s values and larger displacive modulations, the integrand of (37) may even become negative. In contrast, the integrand of (33) is positive or zero. To improve the behavior of the present approximation, (37) is written as

$$P_m^2 \prod_{k_u=1}^{K_u} \int_0^1 \{ 1 - [4\pi s (V_{m, k_u}/P_m) x]^2 / 2 \} dx, \quad (41)$$

which is correct up to second order in the amplitudes of the displacive modulation. By use of the series expansion for Bessel functions, the integrand of (41) can be replaced by

$$J_0^2[4\pi s (V_{m, k_u}/P_m) x]. \quad (42)$$

From a strictly mathematical point of view, the replacement of a truncated series expansion by a special function is, in general, not a unique operation. Of course, the main reason to use (42) for the integrand of (41) is that squared Bessel functions are also involved in (33). In addition, squared Bessel functions show a more desirable behavior at larger values of their arguments. This is in contrast to, for example, approximations based on exponential functions. Furthermore, for a special case of displacive modulation, it can be shown that, for main reflections ($m=0$), (33) can be evaluated to correspond exactly to equation (12) of Lam, Beurskens & van Smaalen (1992a). This also suggests the use of Bessel functions for incorporating effects of higher-order terms in the series expansion. By use of (42) for the

integrand of (41),* the contribution to Γ for terms of type 1 can finally be written as

$$P_m^2 \prod_{k_u=1}^{K_u} Z(s; 0, V_{m,k_u}/P_m), \quad (44)$$

where the function Z is defined by [equation (12) of Lam, Beurskens & van Smaalen (1992a)]

$$Z(s; n, u) = \int_0^1 J_n^2(4\pi s u x) dx. \quad (45)$$

For terms of type 2(a), combination of conditions (19) and (31) results in the extra condition $k = k_p + m$. Therefore, the summation with respect to k_p in (22) is now restricted to those terms that fulfil the condition $1 \leq k_p + m \leq K_u$. The contribution to Γ can then be written, using (29), as

$$\sum_{\mu=1}^N \sum_{\substack{k_p=-K_p \\ 1 \leq k_p+m \leq K_u}}^{K_p} (Z_{\mu}^2 |p_{k_p}^{\mu}|^2 / 4\pi\sigma) \\ \times \iint_{\Omega} \left\{ J_1^2[2\pi C_{k_p+m}^{\mu}(\mathbf{S})] \right. \\ \left. \times \prod_{\substack{k_u=1 \\ k_u \neq k_p+m}}^{K_u} J_0^2[2\pi C_{k_u}^{\mu}(\mathbf{S})] \right\} d\Omega. \quad (46)$$

Through the same procedure as is used for terms of type 1, this expression can be approximated by

$$\sum_{\substack{k_p=-K_p \\ 1 \leq k_p+m \leq K_u}}^{K_p} P_{k_p}^2 \int_0^1 \{ [4\pi s (V_{k_p,k_p+m}/P_{k_p}) x]^2 / 4 \} dx, \quad (47)$$

where the overall modulation amplitudes P_{k_p} and V_{k_p,k_p+m} are given by (38) and (40), respectively. Note that the integrand of (47) only contains a contribution from the factor J_1^2 in (46). In the present low-order approximation, neglect of the higher-order terms has effectively the same result as if all factors J_0^2 in (46) had been replaced by 1.

* Instead of the integrand of (41), one can also replace the integrand of (37) by a squared Bessel function. Expression (44) can then be replaced by

$$P_m^2 Z(s; 0, V_m/P_m). \quad (43)$$

Although this is a less complicated expression than (44), it has a serious disadvantage. For crystals with large displacive modulations, the overall modulation amplitudes V_{k_p} will be considerably larger than the amplitudes V_{k_p,k_u} . However, the present approximations are based on small modulation amplitudes. Therefore, (44) is expected to be a better approximation. Numerical tests show that this is indeed true. Especially for main reflections, where Γ is mainly determined by the contribution from terms of type 1, and at higher s values, severe deviation from the true intensity distribution occurred when (43) was used to estimate the X-ray diffraction intensities.

By use of the series expansion for Bessel functions, the factor between braces in the integrand of (47) can be replaced by a factor J_1^2 . The contribution to Γ for terms of type 2(a) can then finally be written as

$$\sum_{\substack{k_p=-K_p \\ 1 \leq k_p+m \leq K_u}}^{K_p} P_{k_p}^2 Z(s; 1, V_{k_p,k_p+m}/P_{k_p}), \quad (48)$$

with the function Z given by (45).

For terms of type 2(b), conditions (19) and (32) lead to the extra condition $k = -(k_p + m)$ and the summation with respect to k_p in (22) is restricted to those terms that fulfil the condition $1 \leq -(k_p + m) \leq K_u$. Because the contribution to Γ for these terms can be derived in exactly the same way as described for terms of type 2(a), it can also be obtained from (48) by replacement of every occurrence of $k_p + m$ by $-(k_p + m)$.

As a further simplification, one can assume that, for the $|k_p|$ th harmonic of the density modulation, the amplitudes $|p_{k_p}^{\mu}|$ are approximately the same for all atoms. One can then use the approximation

$$V_{k_p,k_u}/P_{k_p} \approx U_{k_u} = \left[(1/\sigma) \sum_{\mu=1}^N Z_{\mu}^2 (U_{k_u}^{\mu})^2 \right]^{1/2}. \quad (49)$$

While, for given K_p and K_u , (44) and (48) require a total number of $(K_p + 1)(K_u + 1)$ overall modulation amplitudes, with approximation (49), only $K_p + 1 + K_u$ amplitudes are needed. This reduction of the total number of overall modulation amplitudes is very important for the development of a fitting procedure. It will not only improve the convergence of the procedure, but the fit parameters can also be obtained more accurately. In fact, preliminary tests showed that, without (49), a successful fitting procedure could not be developed because of dependencies between the fit parameters, as is discussed in § 7. Also, note that the new overall modulation amplitudes U_{k_u} depend only on the displacive modulation, whereas the amplitudes V_{k_p,k_u} also depend on the density modulation. This means that, with (49), density modulation and displacive modulation have been 'decoupled', *i.e.* each type of modulation now has its own overall modulation amplitudes. This will make it easier to interpret the parameters obtained from the fitting procedure.

With the expressions [(44), (48)] for the terms of type 1 and types 2(a) and 2(b), using approximation (49), and with zero for other terms, (22) leads to the following result for Γ :

$$\Gamma(s; m) = P_m^2 \prod_{k_u=1}^{K_u} Z(s; 0, U_{k_u}) \\ + \sum_{\substack{k_p=-K_p \\ 1 \leq |k_p+m| \leq K_u}}^{K_p} P_{k_p}^2 Z(s; 1, U_{|k_p+m|}). \quad (50)$$

To show that approximation (50) is independent of the sign of the satellite index m , one should note that from (7) it follows that $|p_{k_p}^\mu| = |p_{-k_p}^\mu|$ for all μ and k_p . Consequently, the amplitudes P_k are independent of the sign of k_p . As a direct result, the first term of (50) is independent of the sign of m . Further, the second term of (50) does not change if both m and k_p are reversed in sign. Hence, $\Gamma[(50)]$ is independent of the sign of the satellite index.

Before a discussion of which overall modulation amplitudes can be estimated from a fitting procedure employing (50), two special cases for Γ are considered.

6. Special cases for Γ

While (50) describes the effect of combined density and displacive modulations on the average X-ray diffraction intensities, one can also consider crystals where only one of these two types of modulation occurs.

For crystals with only density modulation [$U_{k_u,i}^\mu = 0$ for all μ , k_u and i ; see equation (1)], one can easily show that $U_{k_u} = 0$, so that (50) reduces to

$$\Gamma(s; m) = P_m^2 \quad (51)$$

(assuming that K_p is large enough; see § 7). It follows that, for each reflection order $|m|$, $G_c(s; |m|)$ has the same functional form as the corresponding expression for nonmodulated crystals (Wilson, 1942). This means that, for this special case, average intensities can be estimated from a Wilson plot, which can be made separately for each reflection order (although this is not a recommended procedure).

If only displacive modulation occurs [for all atoms μ , $P_0^\mu \neq 0$ and $P_{|k_p|}^\mu = 0$ for $k_p \neq 0$; see (5)], it follows that $P_0 \neq 0$ and $P_{k_p} = 0$ for $k_p \neq 0$. Consequently, (50) reduces to

$$\Gamma(s; m) = \begin{cases} P_0^2 \prod_{k_u=1}^{K_u} Z(s; 0, U_{k_u}) & m = 0 \\ P_0^2 Z(s; 1, U_{|m|}) & m \neq 0 \end{cases} \quad (52)$$

(assuming that K_u is large enough; see § 7). For small displacive modulations, $\prod_{k_u=1}^{K_u} Z(s; 0, U_{k_u})$ can be approximated by $\exp(-8\pi^2 s^2 U^2/3)$, where U is defined by (58) in Appendix A. This means that $\Gamma(s; 0)$ resembles an isotropic temperature factor, causing $G_c(s; 0)$ to have the same functional form as the corresponding expression for nonmodulated crystals. Hence, for this special case, only the average intensities of main reflections can be used in a conventional Wilson plot. For satellite reflections, this is not possible because $Z(s; 1, U_{|m|})$ first increases with increasing s and then decreases, which is not the behavior of a temperature factor. (See Appendix A for a relation between temperature parameters and displacive

modulation.) Note that, if the displacive modulation only contains a first-order harmonic ($K_u = 1$), (52) combined with (21) corresponds to equation (13) of Lam, Beurskens & van Smaalen (1992a).

7. Estimating overall modulation amplitudes

The atomic modulation functions (u^μ and p^μ) are represented by truncated Fourier series [(1) and (5)], whereas the true series expansions of these functions may contain an infinite number of harmonics, which also implies an infinite number of modulation amplitudes. However, a fitting procedure, employing (50), (51) or (52), can only estimate a few modulation parameters from the collected intensity data. This also limits the number of terms of the truncated Fourier series, given by K_p and K_u , and gives an impression of the number of harmonics that can be used to develop a model of the incommensurately modulated structure.

To estimate overall modulation amplitudes from a fitting procedure, it is assumed that, for each reflection order $|m|$, up to a maximum order m_{\max} , the data set contains enough reflections to draw a plot of $\ln G_0(s; |m|)$ versus s^2 . For modulated crystals, this plot may be considered as the analog of the Wilson plot for nonmodulated crystals.

One problem is that a fitting procedure will not be able to separate the scale factor K from the amplitudes P_{k_p} . When (27) is combined with (50), (51) or (52), the scale factor always appears in the factors P_{k_p}/K . To solve this problem, one can either fix the value of the scale factor or the value of the amplitude P_0 . A reasonable estimate for the scale factor can be obtained from a conventional Wilson plot applied only to the intensities of the main reflections. On the other hand, an *a priori* chemical analysis of the contents of the basic-structure unit cell may result in an estimate for the overall amplitude P_0 . In the following, it is assumed that a reasonable estimate for the scale factor is available, which is kept fixed. Estimates for the overall modulation amplitudes can then be obtained as follows.

For the special cases mentioned in § 6, the situation is fairly simple. If only density modulation occurs, $K_u \equiv 0$ and Γ is given by (51), extrapolation of the plots towards $s = 0$ results in estimates for amplitudes P_{k_p} with $0 \leq |k_p| \leq m_{\max}$. The slope of each plot gives an estimate for the isotropic temperature parameter B . [With expression (51) for Γ , the plots must be straight lines, parallel to one another.] Note that the Fourier series for the density modulation functions has to be restricted to $K_p = m_{\max}$.

For the case where only displacive modulation occurs, $K_p \equiv 0$ and Γ is given by (52). It is evident that B and U cannot be obtained separately from a fitting procedure if only main reflections are

involved. The reason is that, for main reflections, the displacive modulation simulates a temperature effect that adds to the true temperature parameter B , leading to the (pseudo)temperature parameter $B_u = B + 4\pi^2 U^2/3$ of the average structure (see § 6 and Appendix A). However, the dependency of $Z(s; 0, u)$ on s is entirely different from that of $Z(s; 1, u)$. One can therefore use main reflections together with satellites, in a single fitting procedure, to separate all amplitudes U_{k_u} with $1 \leq k_u \leq m_{\max}$ from the temperature parameter B (Lam, Beurskens & van Smaalen, 1992a). The Fourier series for the displacive modulation functions can then be restricted to $K_u = m_{\max}$. Amplitudes U_{k_u} corresponding to higher-order harmonics ($k_u > m_{\max}$) cannot be separated from the temperature parameter B and may be given a zero value. The amplitude P_0 can be determined by extrapolation of the intensity distribution for the main reflections towards $s = 0$.

For the general case, with Γ given by (50), extrapolation towards $s = 0$ results in estimates for amplitudes P_{k_p} with $0 \leq |k_p| \leq m_{\max}$. To find out which of the amplitudes U_{k_u} can be determined from a fitting procedure, one should remember that (50) is derived using the assumption of small displacive modulations and series are only expanded up to second order in the amplitudes of the displacive modulation. A similar series expansion of (50), up to second order in the amplitudes U_{k_u} , would lead to a first-order polynomial in s^2 . Consequently, in the present low-order approximations, the $m_{\max} + 1$ intensity distributions allow at most $2(m_{\max} + 1)$ fit parameters. Because the temperature parameter B and the amplitudes P_{k_p} already require $m_{\max} + 2$ fit parameters, there can be at most m_{\max} fit parameters associated with the amplitudes U_{k_u} . On the assumption that lower-order harmonics are the most important ones, one can only estimate amplitudes U_{k_u} with $1 \leq k_u \leq m_{\max}$. The Fourier series for the displacive modulation can then be restricted to $K_u = m_{\max}$.

Note that, in practical situations, *e.g.* the refinement of real structure with an incommensurate one-dimensional modulation, the Fourier series for the modulation functions are usually restricted to $K_p = K_u = m_{\max}$ because, if satellite reflections with $|m| > m_{\max}$ are too weak to be observed, one may assume that harmonics with $|k_p| > m_{\max}$ or $k_u > m_{\max}$ are insignificant. However, this is not always the case.

One should be aware that (50), (51) and (52) are only approximations to (22). Therefore, the rules given above should not be applied blindly. For example, consider a crystal where only displacive modulation occurs and assume that the atomic modulation functions only contain first-order harmonics, *e.g.* sine waves. If the amplitudes of the atomic displacements are large enough, nonzero

average X-ray diffraction intensities may be obtained not only for main reflections and first-order satellites but also for second-order satellites. Estimation of overall modulation amplitudes, by use of expression (52) for Γ , will then result in nonzero values for the amplitudes U_1 and U_2 . However, from the atomic modulation functions, it follows that $U_{k_u} \equiv 0$ for $k_u > 1$. The discrepancy lies in the fact that, in the derivation of (50), only a few low-order terms in the multiple summation of (22) have been considered [terms of type 1 and types 2(a) and 2(b)]. But the first-order harmonics also contribute to second- and higher-order reflections through the higher-order terms in the multiple summation of (22). This discrepancy especially occurs for large atomic displacements.

On the other hand, consider a crystal with large anharmonic displacive modulations, where higher-order harmonics are very important, *e.g.* a 'sawtooth' modulation. Special structural effects that also occur for nonmodulated crystals, *e.g.* molecules with a noncrystallographic center of symmetry, and special types of modulation, *e.g.* 'rigid-body' modulation, may result in an excess of weak X-ray diffraction intensities (Lam, Beurkens & van Smaalen, 1993). Consequently, it may not be possible to measure satellite reflections of order higher than 1 because these reflections are too weak to become observed. One may then easily conclude from the available intensity distributions that higher-order harmonics are not important.

Note that, for crystals with only density modulation, the rule described above is correct because the $|k_p|$ th-order harmonics only contribute to reflections of order $|k_p|$.

8. Numerical evaluation

The validity of approximation (50) for Γ has been tested by calculating intensity distributions from the simulated X-ray diffraction data of several model structures with different incommensurate one-dimensional modulations. As for nonmodulated crystals, the assumptions underlying the approximations require a structure with many symmetry-independent equal atoms that are randomly distributed throughout the basic-structure unit cell. Here, also, a random distribution of the components of the atomic modulation functions is required. The model structures were devised to fulfil these requirements as closely as possible. As a first test for the theory, expectation values for average X-ray diffraction intensities were estimated using overall modulation amplitudes calculated directly from the atomic modulation parameters of the structural model. For a subsequent test, overall modulation amplitudes obtained from a fitting procedure were used.

Characteristics of the model structures together with details of all atomic modulations are given in Table 1. All model structures (denoted P , D and DP) created have superspace group $P\bar{1}(q_1, q_2, q_3)$, with a realistic modulation wave vector. The basic-structure unit cell has realistic cell dimensions and contains 50 C atoms, with the symmetry-independent atoms randomly distributed throughout the cell and not occupying any special positions. The model structures come with different types of modulation; structure P with displacive modulation, structure D with density modulation and structure DP with a combination of density modulation and displacive modulation. The maximum numbers of harmonics contributing to the atomic modulation functions [(1) and (5)] are restricted to $K_p = K_u = 2$. Amplitudes and phases of the atomic modulation functions were chosen at random but the atomic modulation amplitudes $P_{|k_p|}^\mu$ and $U_{k_u}^\mu$ [(36)] fluctuate within reasonable limits around the overall modulation amplitudes P_{k_p} and U_{k_u} , given by (38) and (49), respectively. For an atom of structure DP , the modulation was obtained by combining the displacive modulation of the corresponding atom in structure P with the density modulation of the same atom in structure D . Furthermore, for each reflection order $|m|$, reflections of structure D have approximately the same average intensity as reflections of structure P . Consequently, structure DP is not dominated by a particular type of modulation. Overall modulation amplitudes calculated directly from the atomic modulation parameters of the structural model are given in lines m of Table 2. For all model structures, structure factors were calculated (Yamamoto, 1985) for main reflections and first- and second-order satellites ($m_{\max} = 2$), up to $s = 1 \text{ \AA}^{-1}$, using $K = 1$ and $B = 2 \text{ \AA}^2$. (These calculated reflection intensities are denoted 'reflection data'.)

For each model structure, the intensity distributions (26) were obtained from the reflection data as follows. First, suitable s intervals were created by dividing reciprocal space into spherical shells of equal volume. Then, for each reflection order $|m|$, reflections were partially normalized and sorted into these intervals. Thus, each interval contains approximately the same number of reflections. In a progressive averaging procedure, each interval was combined with its two neighboring intervals. Finally, for each reflection order, the resulting data points were plotted as graphs of $\ln G_o(s; |m|)$ versus s^2 .

As a first test, for each reflection order, expectation values G_c were estimated by use of (27), combined with expression (50) for Γ , and compared with the intensity distributions (26) obtained from the reflection data. Here, Γ was evaluated using overall modulation amplitudes calculated directly from the atomic modulation parameters of the structural

Table 1. *Model structure characteristics*

Minimum (min.) and maximum (max.) values for the atomic modulation amplitudes $P_{|k_p|}^\mu$ ($0 \leq |k_p| \leq K_p = 2$) and $U_{k_u}^\mu$ ($1 \leq k_u \leq K_u = 2$) of the following model structures: structure P , with displacive modulation; structure D , with density modulation; structure DP , with density modulation and displacive modulation (see text for explanation). The overall modulation amplitudes corresponding to the atomic modulation amplitudes are given in Table 2.

Model structure	P_0^μ min./max.	P_1^μ min./max.	P_2^μ min./max.	U_1^μ (Å) min./max.	U_2^μ (Å) min./max.
P	1/1	0/0	0/0	0.095/0.256	0.019/0.123
D	0.781/0.979	0.401/0.591	0.147/0.337	0/0	0/0
DP	0.781/0.979	0.401/0.591	0.147/0.337	0.095/0.256	0.019/0.123

Table 2. *Overall modulation amplitudes*

For each model structure, line m contains the values of the overall isotropic temperature parameter B and the overall modulation amplitudes P_{k_p} ($0 \leq k_p \leq K_p = 2$) and U_{k_u} ($1 \leq k_u \leq K_u = 2$) calculated directly from the atomic parameters of the structural model. Similarly, line f contains the values of the same parameters, but obtained from a fitting procedure employing (26) and (27) with (50). For comparison, line W contains the values of the parameters B and P_0 obtained from a conventional Wilson plot applied only to the intensities of the main reflections.

Model structure		B (Å ²)	P_0	P_1	P_2	U_1 (Å)	U_2 (Å)
P	m	2	1	0	0	0.200	0.080
	f	2.00	0.999	0.001	0.000	0.195	0.081
	W	2.45	0.965				
D	m	2	0.900	0.250	0.125	0	0
	f	1.99	0.897	0.248	0.124	0.000	0.000
	W	1.98	0.895				
DP	m	2	0.900	0.250	0.125	0.200	0.080
	f	2.01	0.914	0.243	0.123	0.199	0.084
	W	2.41	0.867				

model (see lines m of Table 2). Figs. 1(a), (c) and (e) show that, for all model structures, the true intensity distributions are accurately reproduced, although a small deviation at higher s values can be observed for the intensity distribution of the second-order satellites of structure DP .

As a next step, for each model structure, the modulation parameters were estimated by use of a fitting procedure employing (26), (27) and (50). Fitting was done with the Marquardt nonlinear least-squares method (Kowalik & Osborne, 1968; Bevington, 1969). With the highest reflection order m_{\max} equal to 2, the following fit parameters were used: the overall isotropic temperature parameter B and the overall modulation amplitudes P_{k_p} ($0 \leq k_p \leq K_p = 2$) and U_{k_u} ($1 \leq k_u \leq K_u = 2$). The scale factor K was fixed to have the value 1 (see discussion in § 7). Starting values for B and P_0 were obtained from a conventional Wilson plot applied only to the intensities of the main reflections. (The amplitude P_0 was assigned the value of K_w^{-1} , where K_w is the scale factor of the Wilson plot.) The starting values for the

amplitudes P_1 and P_2 were set to 0.001 while the amplitudes U_1 and U_2 were assigned starting values of 0.001 \AA . The fitting procedure minimized the function

$$\chi_r^2 = \sum_{i=1}^{n_o} w_i (y_i^o - y_i^c)^2 / (n_o - n_p), \quad (53)$$

where, for each model structure, the summation with respect to i counts the number of data points up to a total number of n_o data points in all intensity distributions together, n_p is the number of fit parameters and w_i is a weight factor that counts the total number of reflections in each s interval. Further, y_i^o is equal to $\ln G_o(s; |m|)$ calculated from the reflection

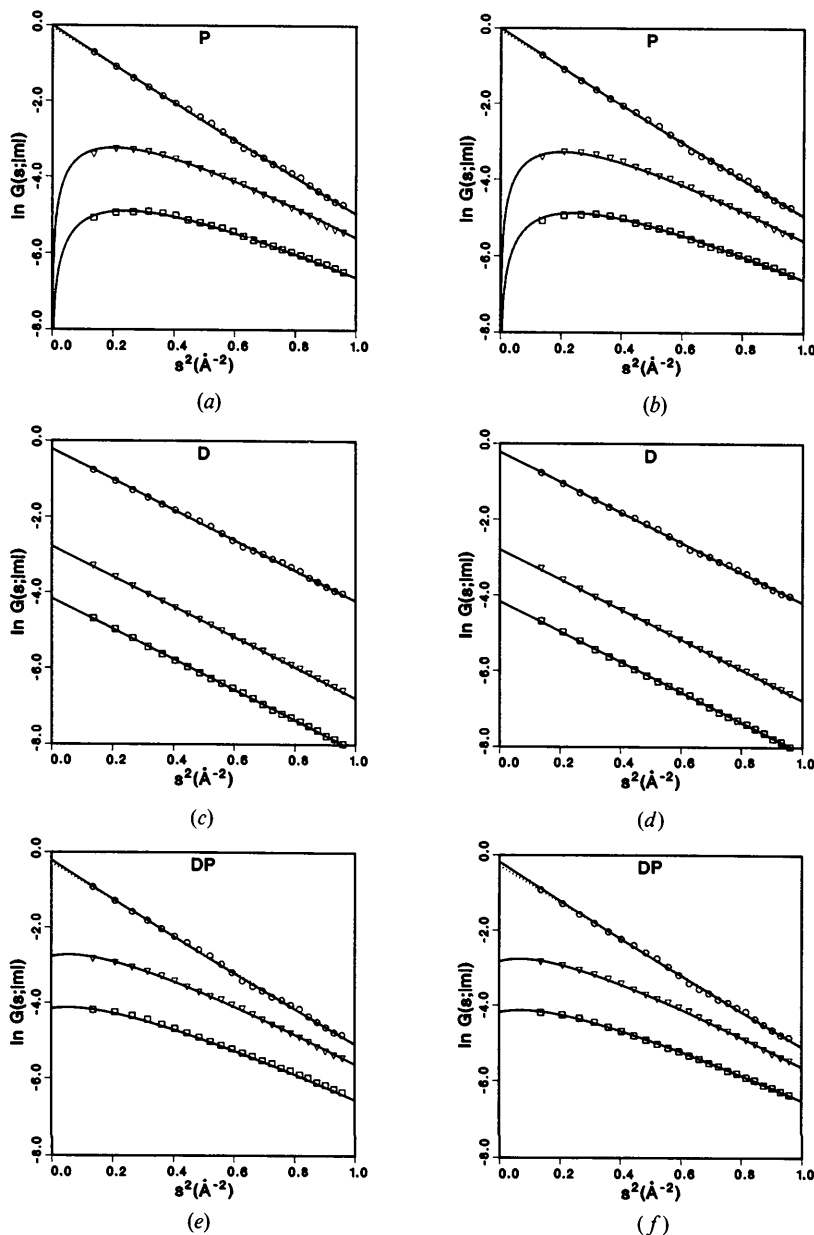


Fig. 1. Natural logarithm of the partially normalized average intensity $G_o(s; |m|)$, as a function of s^2 , for main reflections (circles), $|m|=1$ satellites (triangles) and $|m|=2$ satellites (squares). The dotted lines are conventional Wilson plots applied only to the intensities of the main reflections. The solid lines represent $G_c(s; |m|)$ calculated by use of (27), combined with expression (50) for Γ and with overall modulation amplitudes that are either calculated directly from the structural model or obtained from the fitting procedure. (a) Structure P with amplitudes from the model. (b) Structure P with amplitudes from the fit. (c) Structure D with amplitudes from the model. (d) Structure D with amplitudes from the fit. (e) Structure DP with amplitudes from the model. (f) Structure DP with amplitudes from the fit.

data and y_i^f , which is a function of the fit parameters, is equal to $\ln G_c(s; |m|)$. Refinement of the fit parameters was stopped when the decrease of χ_r^2 became less than 0.1% of the previous χ_r^2 value.

For all model structures, the parameters obtained from the fitting procedure (see lines f of Table 2) are in good agreement with the parameters calculated *a priori* from the atomic parameters of the structural model (see lines m of Table 2). The starting parameters for B and P_0 , obtained from the Wilson plot, are given by lines W of Table 2. Note that, for structures P and DP, where displacive modulation occurs, the B values obtained from the Wilson plot are significantly larger than the B values obtained from the fitting procedure. This is caused by the large correlation between displacive modulation and thermal motion (see Appendix A). For structure D , where only density modulation occurs, the values of the parameters B and P_0 obtained from the Wilson plot are in good agreement with the values obtained from the fitting procedure.

Figs. 1(b), (d) and (f) show that, for all model structures, the intensity distributions (26) calculated from the simulated reflection data are accurately reproduced by the intensity distributions estimated from the parameters obtained by the fitting procedure. Also, note that the Wilson plot, used to estimate the starting values for B and P_0 , indicated by a dotted line in each figure, coincides largely with the intensity distribution estimated for the main reflections.

The convergence of the fitting procedure turned out to be reasonably fast (only a few minutes on a PC with an 80486 processor). For structure P (displacive modulation), approximately three times as many cycles were needed before the stopping criterion was fulfilled. This slower convergence was probably caused by the amplitudes P_1 and P_2 , which behaved somewhat unstably during the refinement process. This is explained as follows. As mentioned earlier, each amplitude P_{k_p} ($k_p \neq 0$) is estimated by extrapolation of the intensity distribution for the $|k_p|$ th-order satellites towards $s = 0$. This is also seen from equation (50) for Γ , where the first term, which is important at the lower s values, depends heavily on the amplitudes P_{k_p} ($k_p \neq 0$), whereas the second term, which is important at the higher s values, depends only weakly on these amplitudes. However, there are some problems regarding this extrapolation. First of all, the s intervals at lower s values are much larger than those at higher s values, so there are few data points near $s = 0$. Of course, one can use smaller intervals, but this does not solve the problem because the weight of the data points, which is the number of reflections in each interval, must be adjusted accordingly. In addition, as for non-modulated crystals, one of the assumptions that

leads to (50) is not valid for $s = 0$ (Wilson, 1949). Thus, the few data points near $s = 0$ are unreliable and should be excluded from the fitting procedure. Second, for crystals where only displacive modulation occurs, the intensity distribution for the satellite reflections show asymptotic behavior at $s = 0$, *i.e.* $\ln G_c(s; |m|) \rightarrow -\infty$ for $s \rightarrow 0$ and $m \neq 0$ (see Figs. 1a and b). For these two reasons, determination of the amplitudes P_{k_p} ($k_p \neq 0$), by extrapolation of the intensity distributions for the satellite reflections towards $s = 0$ will be less straightforward. In fact, the refinement of these amplitudes depends heavily on the second term of (50), which depends only weakly on these amplitudes. As a result, convergence of the amplitudes P_{k_p} ($k_p \neq 0$) will be slower but the values obtained from the fitting procedure will be correct, as is seen in Table 2. This slower convergence will occur for any crystal for which displacive modulation is the dominant type of modulation.

9. Concluding remarks

A theoretical expression is derived for the average X-ray diffraction intensity, as a function of $(\sin\theta)/\lambda$, of main reflections and low-order satellite reflections of crystals with an incommensurate one-dimensional modulation. The atomic modulation functions for displacive and density modulations contain harmonics up to any order. The modulation of individual atoms is taken into account by the introduction of overall modulation amplitudes. The theoretical average intensity is equal to the average X-ray diffraction intensity of nonmodulated crystals (Wilson, 1942), multiplied by a modification factor that depends on $(\sin\theta)/\lambda$, the reflection order $|m|$ and the overall modulation amplitudes.

Tests performed on three idealized model structures show that the theoretical intensity distributions (27), employing approximation (50), are in excellent agreement with the simulated intensity distributions. A fitting procedure is presented that enables the estimation of the scale factor, the overall isotropic temperature parameter and the overall modulation parameters from the experimental intensity distributions (26). The estimated parameters again are in excellent agreement with the parameters calculated directly from the structural parameters [(38), (49)].

As is expected for the present idealized test structures, the theoretical intensity distributions evaluated by use of estimated parameters compare slightly better with the simulated intensity distributions than those evaluated by use of calculated parameters. This is more prominently observed for the second-order satellites.

The values of the overall modulation amplitudes estimated from the fitting procedure can be used to obtain information about the type of modulation

and the importance of the various harmonics involved in the atomic modulation functions

The first applications of direct methods to incommensurately modulated structures employed $|F|$ values instead of normalized structure factors (Hao, Liu & Fan, 1987; Xiang, Fan, Wu & Li, 1990), as a definition for the latter was not yet available. Recently, preliminary definitions for normalized structure factors have been proposed (Lam, Beurskens & van Smaalen, 1992a,b, 1993) with atomic modulation functions that contain only a first-order harmonic. A more general definition for normalized structure factors of crystals with an incommensurate one-dimensional modulation has now been given in (28). These normalized structure factors can be used for the computerization of various direct-methods procedures. Experiments regarding the use of these normalized structure factors in the triplet phase relationship and the tangent formula (Karle & Karle, 1966) are in progress (Lam *et al.*, 1994).

In situations where the displacive modulation gives large anisotropic effects in reciprocal space, (14) may be the basis for a more accurate definition of normalized structure factors for crystals with an incommensurate one-dimensional modulation.

The authors thank A. Janner (University of Nijmegen) for many stimulating discussions. Part of this work was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for the Advancement of Pure Research (NWO).

APPENDIX A

For crystals with displacive modulation, it is well known that the temperature parameters of an atom in the average structure (*i.e.* the structure obtained from main reflections only) are usually larger than those of the same atom in the basic structure because the displacive modulation simulates a temperature effect (Pérez-Mato, Madariaga & Tello, 1986). The relation between these temperature parameters and the displacive modulation of the atom is shown as follows. The correction to the atomic scattering factor as a result of the anisotropic thermal vibration of an atom is given by

$$\exp \left[-\frac{1}{4} \sum_{i,j=1}^3 (\mathbf{B}^\mu)_{ij} S_i S_j a_i^* a_j^* \right], \quad (54)$$

where $(\mathbf{B}^\mu)_{ij}$ is the ij th component of the temperature tensor \mathbf{B}^μ and a_i^* is the length of \mathbf{a}_i^* . Further, the components of the temperature tensor of an atom in the basic structure are denoted $(\mathbf{B}_b^\mu)_{ij}$ while the components of the temperature tensor of the same atom

in the average structure are denoted $(\mathbf{B}_a^\mu)_{ij}$. For small amplitudes $C_{k_u}^\mu$ [(14)] and in a low-order approximation [see condition (30)], one can easily show, by use of (54) for the temperature factor and (20) for the atomic modulation factor, that the relation between these components can be written as

$$(\mathbf{B}_a^\mu)_{ij} = (\mathbf{B}_b^\mu)_{ij} + 4\pi^2 \sum_{k_u=1}^{K_u} (\mathbf{U}_{k_u}^\mu)_{ij} (a_i^* a_j^*)^{-1}, \quad (55)$$

where the $(\mathbf{U}_{k_u}^\mu)_{ij}$, defined in (15), are the components of the K_u symmetric tensors $\mathbf{U}_{k_u}^\mu$. This clearly shows that the displacive modulation of an atom introduces an extra temperature factor. Note that, as long as the multiple summation in (20) can be approximated by the term given by condition (30), (55) can also be used for structures where displacive modulation occurs together with density modulation.

As for nonmodulated crystals, the temperature tensors \mathbf{B}_b^μ and \mathbf{B}_a^μ can be reduced to the effective isotropic temperature parameters $B_{b,\text{eff}}^\mu$ and $B_{a,\text{eff}}^\mu$, respectively (Hamilton, 1959). Then, by use of (3), (4), (15) and (36), the relation between these parameters can be obtained from (55) as

$$B_{a,\text{eff}}^\mu = B_{b,\text{eff}}^\mu + (4\pi^2/3) \sum_{k_u=1}^{K_u} (U_{k_u}^\mu)^2. \quad (56)$$

One can now write down a relation between the overall isotropic temperature parameters $B_{b,\text{eff}}^\mu$ of the basic structure and $B_{a,\text{eff}}^\mu$ of the average structure. If, as usual, overall temperature parameters are defined as weighted averages over atomic temperature parameters, then it follows from (56) that

$$B_{a,\text{eff}}^\mu = B_{b,\text{eff}}^\mu + (4\pi^2/3)U^2, \quad (57)$$

where the effect of the displacive modulation is accounted for by the overall modulation amplitude U defined by

$$U = \left(\sum_{k_u=1}^{K_u} U_{k_u}^2 \right)^{1/2}, \quad (58)$$

with the amplitudes U_{k_u} given by (49).

References

- BEVINGTON, P. R. (1969). *Data Reduction and Error Analysis for the Physical Sciences*. New York: McGraw-Hill.
- GIACOVAZZO, C. (1980). *Direct Methods in Crystallography*. London: Academic.
- GRADSHTEYN, I. S. & RYZHIK, M. (1980). *Table of Integrals, Series, and Products*. London: Academic.
- HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.
- HAO, Q., LIU, Y.-W. & FAN, H.-F. (1987). *Acta Cryst.* **A43**, 820–824.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.
- KOWALIK, J. & OSBORNE, M. R. (1968). *Methods of Unconstrained Optimization Problems*. New York: Elsevier.
- LAM, E. J. W., BEURSKENS, P. T. & VAN SMAALEN, S. (1992a). *Solid State Commun.* **82**, 345–349.
- LAM, E. J. W., BEURSKENS, P. T. & VAN SMAALEN, S. (1992b). *Z. Kristallogr. Supplement Issue No. 6*, p. 349.

- LAM, E. J. W., BEURSKENS, P. T. & VAN SMAALEN, S. (1993). *Acta Cryst.* **A49**, 709–721.
- LAM, E. J. W., DE GELDER, R., BEURSKENS, P. T., VAN SMAALEN, S., FAN, H.-F. & LI, F.-H. (1994). In preparation.
- PÉREZ-MATO, J. M., MADARIAGA, G. & TELLO, M. J. (1986). *J. Phys. C*, **19**, 2613–2622.
- PETŘÍČEK, V. & COPPENS, P. (1988). *Acta Cryst.* **A44**, 235–239.
- PETŘÍČEK, V., COPPENS, P. & BECKER, P. (1985). *Acta Cryst.* **A41**, 478–483.
- WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.
- WILSON, A. J. C. (1949). *Acta Cryst.* **2**, 318–321.
- WILSON, A. J. C. (1950). *Acta Cryst.* **3**, 258–261.
- WOLFF, P. M. DE (1974). *Acta Cryst.* **A30**, 777–785.
- XIANG, S.-B., FAN, H.-F., WU, X.-J. & LI, F.-H. (1990). *Acta Cryst.* **A46**, 929–934.
- YAMAMOTO, A. (1982). *Acta Cryst.* **A38**, 87–92.
- YAMAMOTO, A. (1985). *REMOS85, Computer Program for the Refinement of Modulated Structures*. National Institute for Research in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 305, Japan.

Acta Cryst. (1994). **A50**, 703–714

A Bayesian Approach to Extracting Structure-Factor Amplitudes from Powder Diffraction Data

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(Received 25 October 1993; accepted 25 March 1994)

Abstract

This paper presents a method for the reliable extraction of structure-factor amplitude information from the least-squares integrated-intensity refinement of powder diffraction data. The inevitable overlap of Bragg reflections can lead to strongly correlated reflection intensities that can, in turn, produce unrealistic negative intensity estimates. A Bayesian method is presented that tackles the problem of highly correlated positive and negative intensities. The results indicate that accurate structure-factor amplitudes may be recovered even in regions of a powder diffraction pattern where overlap is almost complete.

1. Introduction

Structure determination from powder diffraction data alone is a substantial crystallographic challenge. Powder diffraction data are, in general, of poorer statistical quality than single-crystal data. More significantly, however, the collapse of three dimensions of diffraction data on to the one dimension of a powder diffraction pattern leads to inevitable peak overlap. Much attention has been given to the problems of overlapping integrated intensities (David, 1987, 1990; Jansen, Peschar & Schenk, 1992; Estermann, McCusker & Baerlocher, 1992; Bricogne, 1991; Gilmore, Henderson & Bricogne, 1991). It is, however, clear that a poor evaluation of the integrated intensities in a powder diffraction pattern will always lead to poor results no matter how good

the algorithms used in the analysis of overlapped reflections. In this paper, attention is focused on the reliable extraction of structure-factor amplitudes. It is assumed that the unit cell has already been derived using, for example, auto-indexing techniques and that, therefore, the Bragg-peak positions can be accurately determined. The approach is based upon the Pawley (1981) method and involves the least-squares fitting of the diffraction pattern to separate integrated intensities. The parameters that are usually varied in such a procedure include background parameters, cell parameters (determining peak positions), peak-width parameters (determining peak shape) and the integrated intensities (which are directly proportional to peak area). The procedure works extremely well if peak overlap is either non-existent or exact (in the case, for example, of 511 and 333 cubic Bragg reflections). When substantial overlap occurs, intensity values can become highly correlated. Although the summed area of a group of Bragg peaks will be well determined, the individual intensities can vary wildly between negative and positive values that are substantially larger in magnitude than the overall 'clump' intensity itself. This is clearly wrong and has been taken to represent a fundamental weakness of the least-squares method. Pawley (1981) was aware of the problem and ingeniously introduced into the least-squares analysis additional slack constraint terms that had the tendency to force individual intensities to be close to the mean value of a 'clump' of intensities. In practice, this approach does not completely obviate the problem of highly varying intensity values. An elegant tech-