Acta Cryst. (1993). A**49**, 709–721

Intensity Statistics and Normalized Structure Factors for Crystals with an Incommensurate One-Dimensional Modulation

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(*Received* 19 *August* 1992; *accepted* 18 *March* 1993)

Dedicated to Professor A. J. C. Wilson on the occasion of the fiftieth anniversary of the 'Wilson Statistics'

Abstract

An analytical expression is derived for the probability density function (p.d.f.) of X-ray structure-factor amplitudes of a crystal with an incommensurate one-dimensional modulation. The influence of the (3+1)-dimensional superspace symmetry is taken into account. It is shown that, in first-order approximation, this p.d.f. has the same functional form as the p.d.f. for a nonmodulated crystal, with a suitable modification of the atomic form factor. For main reflections and satellite reflections, an expression for the average intensity is derived. This leads to a definition of normalized structure factors for a crystal with an incommensurate one-dimensional modulation. In the same first-order approximation, the p.d.f. for the amplitudes of these normalized structure factors is identical to the p.d.f. for a nonmodulated crystal and does not distinguish between main reflections and satellite reflections. The theoretical p.d.f.s are compared to p.d.f.s obtained from X-ray diffraction data of some incommensurate one-dimensionally modulated crystals.

1. Introduction

An incommensurately modulated crystal can be described as a three-dimensional translationally symmetric structure (the basic structure), upon which a periodic deviation is superimposed. The wavelength of the deviation is incommensurate with respect to the lattice of the basic structure, thus destroying the three-dimensional lattice symmetry. The diffraction pattern of an incommensurately 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. The intensity of a main reflection is mainly determined by the presence of averaged atoms at their average positions in the basic structure, while the intensity of a satellite reflection essentially depends on the degree of deviation from this basic structure.

During the last two decades, there has been increasing interest in incommensurately modulated crystals. The structures of a few hundred of such compounds have been determined from single-crystal X-ray diffraction experiments. The standard procedure is first to determine the (nonmodulated) average structure by classical methods (direct methods and/or Patterson methods) and then to determine the modulation by trial and error by searching for anomalously large temperature factors in the average structure or from the higher-dimensional Patterson function (Steurer, 1987).

Direct methods have been applied to X-ray diffraction data in only one instance (Hao, Liu & Fan, 1987). A symbolic-addition procedure (Karle & Karle, 1966) and a modified Sayre-tangent formula were employed, with common structure factors substituted for normalized structure factors.

As a first step towards the application of statistical methods to modulated crystals, investigations have been carried out into X-ray diffraction intensity distributions as functions of $(\sin\theta)/\lambda$ and into the possibility of obtaining an overall modulation amplitude from the experimental data of crystals with an incommensurate one-dimensional displacive modulation (Lam, Beurskens & van Smaalen, 1992). In the present paper, the probability density function (p.d.f.) of the structure-factor amplitude is derived for crystals with an incommensurate one-dimensional displacive modulation and/or an occupancy-factor modulation. It is shown that this p.d.f. can be used to define normalized structure factors for modulated crystals.

2. The structure factor

Let the unit cell of the basic structure be spanned by 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 position of an atom μ is given by $\mathbf{r}_{0,\mathbf{L}}^{\mu} = \mathbf{L} + \mathbf{r}_0^{\mu}$, where $\mathbf{L}$ is a basic-structure

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lattice vector and $\mathbf{r}_0^\mu$ is the relative position of the atom in the unit cell. Each atom is further characterized by its form factor f_0^μ and temperature tensor B_0^μ.

The atomic modulation functions $\mathbf{u}^\mu(\mathbf{q}\cdot\mathbf{r}_{0,\mathrm{L}}^\mu)$ and $p^\mu(\mathbf{q}\cdot\mathbf{r}_{0,\mathrm{L}}^\mu)$ denote the deviations from the basic-structure position and occupancy factor, respectively. They are periodic functions with period 1. The modulation wave vector $\mathbf{q}$ is incommensurate with respect to the reciprocal lattice of the basic structure. The position and occupancy factor of an atom in the one-dimensionally modulated crystal are given by $\mathbf{r}_\mathrm{L}^\mu = \mathbf{r}_{0,\mathrm{L}}^\mu + \mathbf{u}^\mu(\mathbf{q}\cdot\mathbf{r}_{0,\mathrm{L}}^\mu)$ and $p_\mathrm{L}^\mu = p^\mu(\mathbf{q}\cdot\mathbf{r}_{0,\mathrm{L}}^\mu)$, respectively.

The modulated crystal is embedded in (3+1)-dimensional superspace, giving a four-dimensional translationally symmetric supercrystal. The argument $\mathbf{q}\cdot\mathbf{r}_{0,\mathrm{L}}^\mu$ of the atomic modulation functions is replaced by $\bar{x}_4^\mu \equiv \mathbf{q}\cdot\mathbf{r}_{0,\mathrm{L}}^\mu + t$, where t is a continuous parameter along the extra dimension spanned by $\mathbf{e}_4$. This vector is perpendicular to physical space. The position of an 'atom' in the supercrystal is given by the set of points $t \in \mathbb{R}$ at fixed $\mathbf{r}_{0,\mathrm{L}}^\mu$ having coordinates $(x_1^\mu, x_2^\mu, x_3^\mu, x_4^\mu)$, where $x_i^\mu = [\mathbf{r}_{0,\mathrm{L}}^\mu + \mathbf{u}^\mu(\bar{x}_4^\mu)]\cdot\mathbf{a}_i^*$ $(i = 1,2,3)$ and $x_4^\mu = \bar{x}_4^\mu + \mathbf{q}\cdot\mathbf{u}^\mu(\bar{x}_4^\mu)$, with respect to the basic translation vectors $\mathbf{b}_i = \mathbf{a}_i - (\mathbf{q}\cdot\mathbf{a}_i)\,\mathbf{e}_4$ $(i = 1,2,3)$ and $\mathbf{b}_4 = \mathbf{e}_4$ of the supercrystal. Thus, each 'atom' in the supercrystal is a 'string' along $\mathbf{e}_4$ with periodic bends and densifications caused by the atomic modulations. Physical space is obtained as an intersection of superspace at constant t. Different values for t lead to equivalent descriptions of physical space (de Wolff, 1974).

The symmetry of the supercrystal is described by a (3+1)-dimensional superspace group. A symmetry operator is denoted $(\mathsf{R}\,\varepsilon|v_1, v_2, v_3, v_4)$, where R is the three-dimensional part of the point-group operator, $\varepsilon = \pm 1$ and the numbers v_i are the components of a four-dimensional translation vector with respect to the basic vectors $\mathbf{b}_i$ of the supercrystal. The operators $(\mathsf{R}|\mathbf{v})$, with $\mathbf{v} = \sum_{i=1}^3 v_i\,\mathbf{a}_i$, are elements of the three-dimensional external space group of the superspace group. It is assumed here that the external space group is identical to the basic-structure space group, so that there is a one-to-one correspondence between symmetry-independent 'atoms' in the supercrystal and symmetry-independent atoms in the basic structure (de Wolff, Janssen & Janner, 1981; Janner, Janssen & de Wolff, 1983).

Because the modulation wave vector is incommensurate, there exists a one-to-one correspondence between reciprocal-lattice vectors in (3+1)-dimensional superspace and reciprocal-lattice vectors in three-dimensional reciprocal space. Diffraction vectors in three-dimensional reciprocal space are defined as $\mathbf{S} = \mathbf{H} + m\,\mathbf{q}$, where $\mathbf{H}$ is a reciprocal-lattice vector of the basic structure and m is the integer satellite index. For a given incommensurate modulation wave vector, this decomposition is unique. There are two kinds of reflections: main reflections $(m = 0)$ and satellite reflections $(m \neq 0)$. The order of a reflection is given by $|m|$.

The structure factor for X-ray scattering (de Wolff, 1974; Yamamoto, 1982) can be rewritten as

$$F(\mathbf{S},m) = \epsilon(\mathbf{S}) \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon(\mathbf{S})} |g^\mu(\mathbf{S}\cdot\mathsf{R}_k, \varepsilon_k m)| f^\mu(\mathbf{S}\cdot\mathsf{R}_k) \times \exp\left[2\pi i(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}_0^\mu + \mathbf{H}\cdot\mathbf{v}_k + m v_4^k) + i\theta^\mu(\mathbf{S}\cdot\mathsf{R}_k, \varepsilon_k m)\right], \quad (1)$$

with the real atomic scattering factor for vibrating atoms defined by

$$f^\mu(\mathbf{S}) = f_0^\mu(|\mathbf{S}|)\exp\left(-\mathbf{S}\cdot B_0^\mu\cdot\mathbf{S}\right) \quad (2)$$

and the atomic modulation factor $g^\mu(\mathbf{S},m) \equiv |g^\mu(\mathbf{S},m)|\exp[i\theta^\mu(\mathbf{S},m)]$ given by

$$g^\mu(\mathbf{S},m) = \int_0^1 p^\mu(\tau + \mathbf{q}\cdot\mathbf{r}_0^\mu)\exp\{2\pi i \times [\mathbf{S}\cdot\mathbf{u}^\mu(\tau + \mathbf{q}\cdot\mathbf{r}_0^\mu) + m\tau]\}\mathrm{d}\tau, \quad (3)$$

where the integration extends over one period along $\mathbf{e}_4$. Because the atomic scattering factor is a real function and because $g^\mu(-\mathbf{S},-m) = [g^\mu(\mathbf{S},m)]^*$, where * denotes the complex conjugate, Friedel's law applies to the structure factor.

Special attention is required for the appearance of the average atomic position $\mathbf{r}_0^\mu$ in (3), the expression for the atomic modulation factor $g^\mu(\mathbf{S},m)$. In agreement with common usage (de Wolff, 1974; Yamamoto, 1982), the atomic modulation functions $p^\mu(\bar{x}_4^\mu)$ and $\mathbf{u}^\mu(\bar{x}_4^\mu)$ are defined with respect to $\mathbf{r}_0^\mu$. Consequently, the definitions of these functions depend on $\mathbf{r}_0^\mu$. In contrast to common usage, the scalar product $\mathbf{q}\cdot\mathbf{r}_0^\mu$, which usually appears in the exponential part of the structure-factor expression, has been included in the expression for $g^\mu(\mathbf{S},m)$. If this had not been done, a variation of $\mathbf{r}_0^\mu$ would have caused a correlated change of the values of the atomic modulation functions (Fig. 1*a*), causing the phase of $g^\mu(\mathbf{S},m)$ to vary with $\mathbf{r}_0^\mu$. However, by including $\mathbf{q}\cdot\mathbf{r}_0^\mu$ in $g^\mu(\mathbf{S},m)$, a variation of $\mathbf{r}_0^\mu$ also introduces a shift in the arguments of the atomic modulation functions, which cancels the effect of the changes in their definitions. As a result, the values of the atomic modulation functions are independent of $\mathbf{r}_0^\mu$ (Fig. 1*b*). (See Appendix *A*.) It follows that $g^\mu(\mathbf{S},m)$ is an atomic property, independent of the average position $\mathbf{r}_0^\mu$ of the atom. Consequently, the average atomic positions $\mathbf{r}_0^\mu$ can be used as independent random variables (see § 3). Note that $g^\mu(\mathbf{S},m)$ is a property not of one single atom in the basic-structure unit cell but of the collection of all atoms in the modulated crystal having average positions related to one another by basic-structure lattice translations.

The set of K symmetry operators obtained from the superspace group by factoring out all four-dimensional lattice translations generates K different symmetry-equivalent positions. This set includes the lattice-centering operations. The symmetry-enhancement

factor $\epsilon(\mathbf{S})$ is defined, analogously to the case for non-modulated crystals (Giacovazzo, 1980), as the number of times the condition $\mathbf{S}\cdot\mathsf{R}_k = \mathbf{S}$ is satisfied for all symmetry operators in this set. For a nonsystematically absent reflection $\mathbf{S}$, it follows that, because of symmetry, each term in the structure-factor expression appears $\epsilon(\mathbf{S})$ times. Therefore, the second summation in (1) only counts those symmetry operators that generate $K/\epsilon(\mathbf{S})$ different diffraction vectors. The transformation rules for the atomic modulation functions were used to perform this symmetry-reduction procedure (Yamamoto, 1982).

The first summation in (1) counts the N/K symmetry-independent atoms in the modulated crystal, with N being the total number of atoms in the unit cell of the basic structure (none of which are on special positions).

For a phase-restricted reflection, there exists an operator $(\mathsf{R}_{k_0}\,\varepsilon_{k_0}|v_1^{k_0}, v_2^{k_0}, v_3^{k_0}, v_4^{k_0})$, in the second summation of (1), for which $\mathbf{S}\cdot\mathsf{R}_{k_0} = -\mathbf{S}$. This operator can be factored out of this summation so that the number of symmetry operators is further reduced by a factor of two and the structure factor becomes

$$\begin{aligned} F(\mathbf{S},m) &= 2\epsilon(\mathbf{S})\exp\left[i\varphi_1(\mathbf{S})\right] \\ &\quad\times \sum_{\mu=1}^{N/K}\sum_{k=1}^{K/[2\epsilon(\mathbf{S})]} |g^\mu(\mathbf{S}\cdot\mathsf{R}_k,\varepsilon_k m)|f^\mu(\mathbf{S}\cdot\mathsf{R}_k) \\ &\quad\times\cos\left[2\pi(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}_0^\mu + \mathbf{H}\cdot\mathbf{v}_k + mv_4^k)\right. \\ &\quad\left.+\,\theta^\mu(\mathbf{S}\cdot\mathsf{R}_k,\varepsilon_k m) - \varphi_1(\mathbf{S})\right], \end{aligned} \tag{4}$$

where, because Friedel's law applies, $\varphi_1(\mathbf{S})$ is given by

$$\varphi_1(\mathbf{S}) = \pi(\mathbf{H}\cdot\mathbf{v}_{k_0} + mv_4^{k_0}). \tag{5}$$

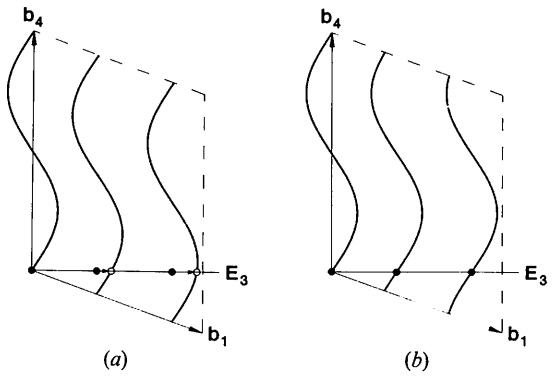


Fig 1. Dependency of the definition of the atomic modulation function on $\mathbf{r}_0^\mu$. Sections of superspace through $\mathbf{b}_1$ and $\mathbf{b}_4$ are shown. Physical space is denoted by the line E_3. A single superspace atom μ, having a displacive modulation only, is displayed at three different average positions $\mathbf{r}_0^\mu$ (denoted • in E_3). For each position, only one period of the atomic modulation function is shown. (*a*) In this example, the atomic modulation functions are defined by $\mathbf{u}^\mu(\bar{x}_4^\mu;\mathbf{r}_0^\mu) = \mathbf{U}^\mu\sin(2\pi\bar{x}_4^\mu)$, where $\bar{x}_4^\mu = \mathbf{q}\cdot\mathbf{r}_{0,\mathrm{L}}^\mu + t$ and $\mathbf{U}^\mu$ is a constant vector. Note that this choice is independent of the parameter $\mathbf{r}_0^\mu$. These functions are drawn for three different positions $\mathbf{r}_0^\mu$. The atomic displacements in E_3, denoted • → ∘, vary with $\mathbf{r}_0^\mu$. (*b*) The atomic modulation functions are defined by $\mathbf{u}^\mu(\bar{x}_4^\mu;\mathbf{r}_0^\mu) = \mathbf{U}^\mu\sin[2\pi(\bar{x}_4^\mu - \mathbf{q}\cdot\mathbf{r}_0^\mu)]$, where $\bar{x}_4^\mu$ and $\mathbf{U}^\mu$ are the same as in (*a*). The form of this function depends on $\mathbf{r}_0^\mu$ but the atomic displacements in E_3 are all the same (• = ∘).

The phase of the structure factor is now restricted to two values, $\varphi_1(\mathbf{S})$ and $\varphi_1(\mathbf{S})+\pi$. Phase-restricted reflections have p.d.f.s different from those of non-phase-restricted reflections (Wilson, 1949).

The following abbreviations are used in this paper: $F \equiv F(\mathbf{S},m)$, $\epsilon \equiv \epsilon(\mathbf{S})$, $f_k^\mu \equiv f^\mu(\mathsf{S}\mathsf{R}_k)$, $g_k^\mu \equiv g^\mu(\mathsf{S}\mathsf{R}_k,\varepsilon_k m)$, $\theta_k^\mu \equiv \theta^\mu(\mathsf{S}\mathsf{R}_k,\varepsilon_k m)$ and $\varphi_1 \equiv \varphi_1(\mathbf{S})$. Trivial arguments are omitted in some of the functions defined below, to shorten the corresponding equations.

3. The probability density function

The probability density function (p.d.f.), $P_{|F|,\varphi}$, for the amplitude $|F|$ and phase Φ of the structure factor measures the chance, $P_{|F|,\Phi}(R,\varphi)\,\mathrm{d}R\,\mathrm{d}\varphi$, of finding $|F|$ with a numerical value between R and $R+\mathrm{d}R$ and Φ with a value between φ and $\varphi+\mathrm{d}\varphi$. For crystals having three-dimensional lattice periodicity, the p.d.f. is obtained for a single diffraction vector by averaging over all configurations of symmetry-independent atoms in the unit cell, with the assumption that the positions of these atoms can be treated as independent random variables. The same assumption is made with respect to the average positions $\mathbf{r}_0^\mu$ of the symmetry-independent atoms in the basic-structure unit cell of the modulated crystal, but with unchanging atomic modulations.

It is also assumed that the symmetry-independent atoms are uniformly distributed throughout the basic-structure unit cell. As a consequence, the p.d.f. P_r for finding a configuration of symmetry-independent atoms must be a constant equal to $V^{-N/K}$, where V is the volume of the basic-structure unit cell (Hauptman & Karle, 1952, 1953; Karle & Hauptman, 1953).

Non-phase-restricted reflections

The derivation of the p.d.f. for the structure-factor amplitude of non-phase-restricted reflections is performed analogously to a procedure given by Castleden (1987) for X-ray structure factors of nonmodulated crystals.† The structure factor F given by (1) is a function of the average atomic positions $\mathbf{r}_0^\mu$, which are assumed to be independent random variables. Because $F = A + iB$, the p.d.f. $P_{A,B}$ for (A,B) having the numerical values (a,b) is given by

$$\begin{aligned} P_{A,B}(a,b) &= (2\pi)^{-2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left[-i(au+bv)\right] \\ &\quad\times Q(u,v)\,\mathrm{d}u\,\mathrm{d}v, \end{aligned} \tag{6}$$

where $Q(u,v) \equiv \langle\exp\left[i(Au+Bv)\right]\rangle$ is, by definition, the characteristic function of $P_{A,B}$. Because A and B

† For phase-restricted reflections, the phase of the structure factor is not a continuous random variable, as for non-phase-restricted reflections, but is a discrete random variable. Therefore, the p.d.f. for phase-restricted reflections [(16)] contains only one Fourier integral and not two, as is the case for non-phase-restricted reflections [(6) and (8)]. This means that the p.d.f. presented by Castleden (1987) is not valid for phase-restricted reflections.

are functions of the independent random variables $\mathbf{r}_0^\mu$, the characteristic function can also be written as an expectation value with respect to the p.d.f. $P_\mathbf{r}$ for the configurations of symmetry-independent atoms in the basic-structure unit cell:

$$Q(u,v) = \int_V \dots \int_V \exp\left[i(Au+Bv)\right] \times P_\mathbf{r}(\mathbf{r}_0^1,\dots,\mathbf{r}_0^{N/K})\mathrm{d}\mathbf{r}_0^1\dots\mathrm{d}\mathbf{r}_0^{N/K}, \quad (7)$$

where the integrals are over the volume of the basic-structure unit cell.

Because $F = |F|\exp(i\Phi)$, the p.d.f. $P_{|F|,\Phi}$ for $(|F|,\Phi)$ having the numerical values (R,φ) can be derived. By the introduction of polar coordinates $a = R\cos\varphi$, $b = R\sin\varphi$, $u = \rho\cos\xi$ and $v = \rho\sin\xi$, and using $P_{|F|,\Phi}(R,\varphi)\,\mathrm{d}R\,\mathrm{d}\varphi = P_{A,B}(a,b)\,\mathrm{d}a\,\mathrm{d}b$, it follows from (6) that the p.d.f. for the structure factor can be written as

$$P_{|F|,\Phi}(R,\varphi) = (2\pi)^{-2}R\int_0^\infty\int_0^{2\pi}\exp\left[-iR\rho\cos(\xi-\varphi)\right] \times Q(\rho\cos\xi,\rho\sin\xi)\rho\,\mathrm{d}\rho\,\mathrm{d}\xi. \quad (8)$$

By the same procedure as given by Castleden (1987), the exponent in (7) can be evaluated as an N/ϵ-tuple product over integers $n_{\mu,k}$, of the form

$$\sum_{n_{1,1}=-\infty}^{\infty}\dots\sum_{n_{N/K,K/\epsilon}=-\infty}^{\infty}\left[\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/\epsilon}J_{n_{\mu,k}}(\rho\epsilon|g_k^\mu|f_k^\mu)\right] \times\exp\left\{i\sum_{\mu=1}^{N/K}\sum_{k=1}^{K/\epsilon}n_{\mu,k}[2\pi(\mathbf{S}\cdot\mathsf{R}_k\cdot\mathbf{r}_0^\mu+\mathbf{H}\cdot\mathbf{v}_k + mv_4^k)+\theta_k^\mu-\xi+\pi/2]\right\}, \quad (9)$$

with J_n the nth-order Bessel function of the first kind.

By substitution of (9) for the exponent in (7) and with the *a priori* assumption of uniformly distributed atoms, the characteristic function can be evaluated. When performing the integration with respect to the average atomic positions, one should be aware that, for main reflections, the components of $\mathbf{S}$ are all integers while, for satellite reflections, at least one of the components of $\mathbf{S}$ is not an integer. Then, the expression for the characteristic function becomes

$$Q(\rho\cos\xi,\rho\sin\xi) = \sum_{n_{1,1}=-\infty}^{\infty}\dots\sum_{n_{N/K,K/\epsilon}=-\infty}^{\infty}\left[\prod_{\mu=1}^{N/K}\prod_{j=1}^{3}h(\alpha_{\mu,j}^c) \times\exp(i\pi\alpha_{\mu,j}^c)\right]\left[\prod_{\mu=1}^{N/K}\prod_{k=1}^{K/\epsilon}J_{n_{\mu,k}}(\rho\epsilon|g_k^\mu|f_k^\mu)\right] \times\exp\left\{i\sum_{\mu=1}^{N/K}\sum_{k=1}^{K/\epsilon}n_{\mu,k}[2\pi(\mathbf{H}\cdot\mathbf{v}_k+mv_4^k) + \theta_k^\mu-\xi+\pi/2]\right\}, \quad (10)$$

where

$$h(z) = \begin{cases}1 & (z=0)\\ (\pi z)^{-1}\sin(\pi z) & (z\neq 0)\end{cases} \quad (11)$$

and

$$\alpha_{\mu,j}^c = \sum_{k=1}^{K/\epsilon}n_{\mu,k}\left(\sum_{i=1}^{3}S_iR_{ij}^k\right). \quad (12)$$

Here, S_i is the ith component of the diffraction vector with respect to the reciprocal-lattice vectors $\mathbf{a}_i^*$ of the basic structure and R_{ij}^k is the ijth component of the matrix R_k.

For each term in the multiple summation of (10), the $\alpha_{\mu,j}^c$ form a set of $3N/K$ numbers. A term will not contribute to the multiple summation if there is an $\alpha_{\mu,j}^c$ in the set with a nonzero integer value. Note that, for main reflections, a term only contributes to the multiple summation if the condition $\alpha_{\mu,j}^c = 0$ is fulfilled for all μ and j. [This is in agreement with condition (2) given by Castleden (1987).] For satellite reflections, there is no such condition because at least one of the coordinates of the diffraction vector is not an integer. However, terms in the multiple summation with some of the $\alpha_{\mu,j}^c$ not integers and all others zero decrease rapidly in magnitude.

Following Castleden (1987), the p.d.f. $P_{|F|,\Phi}$ for the structure factor is evaluated. The characteristic function (10) is substituted in (8) and the integral with respect to ξ is calculated by means of an integral equation for Bessel functions. It is noticed that, for each term with given integers $n_{\mu,k}$ in the resulting formula for $P_{|F|,\Phi}$, there exists a corresponding term with all the integers reversed in sign, being its complex conjugate. Therefore, the imaginary parts of all terms cancel and $P_{|F|,\Phi}$ is a real function. The phase of the structure factor is now integrated out so that the p.d.f. $P_{|F|}$ for the structure-factor amplitude is obtained as

$$P_{|F|}(R) = R\sum_{n_{1,1}=-\infty}^{\infty}\dots\sum_{n_{N/K,K/\epsilon}=-\infty}^{\infty}G^c(R) \times\left[\prod_{\mu=1}^{N/K}\prod_{j=1}^{3}h(\alpha_{\mu,j}^c)\right]\cos\left(\sum_{\mu=1}^{N/K}\left\{\pi\sum_{j=1}^{3}\alpha_{\mu,j}^c + \sum_{k=1}^{K/\epsilon}n_{\mu,k}[2\pi(\mathbf{H}\cdot\mathbf{v}_k+mv_4^k)+\theta_k^\mu]\right\}\right), \quad (13)$$

where

$$G^c(R) = \int_0^\infty \left(\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/\epsilon} J_{n_{\mu,k}}(\rho\epsilon|g_k^\mu|f_k^\mu) \right) \times J_0(\rho R)\rho\,\mathrm{d}\rho \quad (14)$$

is an integral containing multiple products of Bessel functions and the condition exists that

$$\sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} n_{\mu,k} = 0, \quad (15)$$

resulting from the integration with respect to φ and further reducing the number of terms contributing to the multiple summation.

Phase-restricted reflections

The p.d.f. for the structure-factor amplitude of a phase-restricted reflection is evaluated following a procedure indicated by Peschar (1987). From the actual structure factor F' of the phase-restricted reflection, given by (4), a new structure factor $F = F' \exp(-i\varphi_1)$ can be obtained. Because $|F| = |F'|$, the p.d.f. for the structure-factor amplitude is the same for both structure factors. The new structure factor F is a real function dependent on the average atomic positions $\mathbf{r}_0^\mu$, which are assumed to be independent random variables. The p.d.f. P_F for F having the numerical value c is given by

$$P_F(c) = (2\pi)^{-1} \int_{-\infty}^{\infty} \exp(-icw) Q(w)\,\mathrm{d}w, \quad (16)$$

where $Q(w) \equiv \langle \exp(iFw) \rangle$ is by definition the characteristic function of P_F. Because F can be positive as well as negative, the p.d.f. $P_{|F|}$ for $|F|$ having the numerical value R is obtained from (16) as

$$P_{|F|}(R) = \pi^{-1} \int_{-\infty}^{\infty} \cos(wR) Q(w)\,\mathrm{d}w. \quad (17)$$

The characteristic function can also be written as the expectation value with respect to the p.d.f. P_r of the configurations of symmetry-independent atoms in the basic-structure unit cell:

$$Q(w) = \int_V \cdots \int_V \exp(iFw) \times P_\mathrm{r}(\mathbf{r}_0^1, \ldots, \mathbf{r}_0^{N/K})\,\mathrm{d}\mathbf{r}_0^1 \ldots \mathrm{d}\mathbf{r}_0^{N/K}, \quad (18)$$

where the integrals are over the volume of the basic-structure unit cell.

The characteristic function is evaluated, using a procedure similar to the one given above, as

$$Q(w) = \sum_{n_{1,1}=-\infty}^{\infty} \cdots \sum_{n_{N/K,K/(2\epsilon)}=-\infty}^{\infty} \times \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha_{\mu,j}^d) \exp(i\pi\alpha_{\mu,j}^d) \right] \times \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/(2\epsilon)} J_{n_{\mu,k}}(2w\epsilon|g_k^\mu|f_k^\mu) \right] \times \exp\left\{ i \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/(2\epsilon)} n_{\mu,k}[2\pi(\mathbf{H}\cdot\mathbf{v}_k + mv_4^k) + \theta_k^\mu - \varphi_1 + \pi/2] \right\}, \quad (19)$$

with the function h defined by (11) and the numbers

$$\alpha_{\mu,j}^d = \sum_{k=1}^{K/(2\epsilon)} n_{\mu,k} \left(\sum_{i=1}^{3} S_i R_{ij}^k \right) \quad (20)$$

having the same meanings as the numbers $\alpha_{\mu,j}^c$ given by (12).

In order to evaluate the p.d.f. of the structure-factor amplitude, the integral in (17) is split into two parts, *i.e.* $\int_{-\infty}^{\infty} \ldots \mathrm{d}w \to \int_0^\infty \ldots \mathrm{d}w + \int_{-\infty}^0 \ldots \mathrm{d}w$. After substitution of (19) into both integrals, the second integral is transformed by replacing all numbers $n_{\mu,k}$ by $-n_{\mu,k}$, because the summations may be reversed, and changing w into $-w$. Thus, the second integral becomes the complex conjugate of the first integral. The p.d.f. $P_{|F|}$ for the structure-factor amplitude then becomes

$$P_{|F|}(R) = 2\pi^{-1} \sum_{n_{1,1}=-\infty}^{\infty} \cdots \sum_{n_{N/K,K/(2\epsilon)}=-\infty}^{\infty} G^d(R) \times \left[\prod_{\mu=1}^{N/K} \prod_{j=1}^{3} h(\alpha_{\mu,j}^d) \right] \cos\left(\sum_{\mu=1}^{N/K} \left\{ \pi \sum_{j=1}^{3} \alpha_{\mu,j}^d + \sum_{k=1}^{K/(2\epsilon)} n_{\mu,k}[2\pi(\mathbf{H}\cdot\mathbf{v}_k + mv_4^k) + \theta_k^\mu - \varphi_1 + \pi/2] \right\} \right), \quad (21)$$

where

$$G^d(R) = \int_0^\infty \left[\prod_{\mu=1}^{N/K} \prod_{k=1}^{K/(2\epsilon)} J_{n_{\mu,k}}(2w\epsilon|g_k^\mu|f_k^\mu) \right] \times \cos(wR)\,\mathrm{d}w \quad (22)$$

is an integral containing multiple products of Bessel functions.

4. Approximated probability density functions

Exact evaluation of the integrals (14) and (22) is only possible for a few simple cases. For the general case, analytical expressions can be derived, but cannot be simplified. It is possible, however, to obtain a first-order approximation for p.d.f.s (13) and (21) by only considering the term in the series expansion with $n_{\mu,k} = 0$ for all μ and k. Then, the multiple products in the integrals (14) and (22) contain zero-order Bessel functions (J_0). For large N, the integrands only give a significant contribution to the integrals if the argument of J_0 is small. Therefore, the approximation $J_0(z) \simeq \exp(-z^2/4)$ can be used.

In addition, let $\mathcal{S}_n$ be defined as

$$\mathcal{S}_n \equiv \sum_{\mu=1}^{N} |g^\mu f^\mu|^n, \tag{23}$$

where the summation extends over all atoms in the basic-structure unit cell. If the symmetry operators are factored out as in § 2 and the transformation rules for atomic modulation functions (Yamamoto, 1982) are used, it can be shown that (23) is identical to

$$\mathcal{S}_n = \begin{cases} \epsilon \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/\epsilon} |g_k^\mu f_k^\mu|^n \\ \qquad \text{(non-phase-restricted reflections)} \\ 2\epsilon \sum_{\mu=1}^{N/K} \sum_{k=1}^{K/(2\epsilon)} |g_k^\mu f_k^\mu|^n \\ \qquad \text{(phase-restricted reflections).} \end{cases} \tag{24}$$

In first-order approximation, the p.d.f. $P_{|F|}$ for a non-phase-restricted reflection (13) is written as

$$P_{|F|}(R) = R \int_0^\infty \rho \exp\left(-\tfrac{1}{4}\rho^2 \epsilon \mathcal{S}_2\right) J_0(\rho R)\, \mathrm{d}\rho, \tag{25}$$

with $\mathcal{S}_2$ defined by (23). This integral can be evaluated [equation (6.631-4) of Gradshteyn & Ryzhik (1980)] to obtain:

$$P_{|F|}(R) = (2R/\epsilon\mathcal{S}_2) \exp\left(-R^2/\epsilon\mathcal{S}_2\right). \tag{26}$$

The p.d.f. $P_{|F|}$ for a phase-restricted reflection (21) can be written in first-order approximation as

$$P_{|F|}(R) = 2\pi^{-1} \int_0^\infty \exp\left(-\tfrac{1}{2}w^2 \epsilon \mathcal{S}_2\right) \cos(wR)\mathrm{d}w, \tag{27}$$

with $\mathcal{S}_2$ defined by (23). Evaluation of this integral [equation (3.869-4) of Gradshteyn & Ryzhik (1980)] gives

$$P_{|F|}(R) = (2/\pi\epsilon\mathcal{S}_2)^{1/2} \exp\left(-R^2/2\epsilon\mathcal{S}_2\right). \tag{28}$$

Note that, for both (26) and (28), the condition $\mathcal{S}_2 > 0$ must be fulfilled.

P.d.f.s (26) and (28) show a close resemblance to p.d.f.s for nonmodulated crystals (Wilson, 1949, 1950). In fact, they can be obtained from the latter by replacement of the atomic form factors f^μ with $|g^\mu| f^\mu$, where $|g^\mu|$ is the amplitude of the atomic modulation factor [(3)]. The effect of the superspace symmetry is taken into account by the symmetry-enhancement factor ϵ, which is defined similarly as for nonmodulated crystals.

In the limit of diminishing modulation ($\mathbf{u}^\mu \to 0$, $p^\mu \to 1$), p.d.f.s (26) and (28) reduce to those for nonmodulated crystals. For main reflections ($m = 0$), $|g^\mu| \to 1$, $\mathcal{S}_2 \to \sum_{\mu=1}^{N} (f^\mu)^2$ and $P_{|F|}(R)$ becomes identical to the p.d.f. for a nonmodulated crystal. For satellite reflections ($m \neq 0$), $|g^\mu| \to 0$, $\mathcal{S}_2 \to 0$ and $P_{|F|}(R) \to 0$ for $R \neq 0$, *i.e.* the satellite reflections disappear.

5. Normalized structure factors

For nonmodulated crystals, normalized structure factors are defined by $E \equiv F\langle|F|^2\rangle^{-1/2}$, where (in first-order approximation) $\langle|F|^2\rangle = \epsilon \sum_{\mu=1}^{N} (f^\mu)^2$, with $\langle\ \rangle$ denoting an average over all configurations of symmetry-independent atoms in the unit cell. The same definition can be used for modulated crystals but with $\langle|F|^2\rangle \equiv \int_0^\infty R^2 P_{|F|}(R)\, \mathrm{d}R = \epsilon\mathcal{S}_2$, where $P_{|F|}$ is given by either (26) or (28). Thus, the following expression is obtained for normalized structure factors of modulated crystals:

$$E = F(\epsilon\mathcal{S}_2)^{-1/2}. \tag{29}$$

From (29), the p.d.f.s $P_{|E|}$ for a normalized structure-factor amplitude $|E|$ of a modulated crystal having a numerical value X can be derived. Introducing the transformation $X = R(\epsilon\mathcal{S}_2)^{-1/2}$ and using $P_{|E|}(X)\,\mathrm{d}X = P_{|F|}(R)\,\mathrm{d}R$, one can write the p.d.f. $P_{|E|}$ for non-phase-restricted reflections as

$$P_{|E|}(X) = 2X \exp\left(-X^2\right), \tag{30}$$

while for phase-restricted reflections it becomes

$$P_{|E|}(X) = (2/\pi)^{1/2} \exp\left(-X^2/2\right). \tag{31}$$

Note that (30) and (31) are independent of specific properties of the modulated crystal, as for nonmodulated crystals. Also note that these p.d.f.s are independent of the diffraction vector $\mathbf{S}$, in contrast to p.d.f.s derived in previous sections.

With the present definition of normalized structure factors [(29)], neither the acentric p.d.f. [(30)] nor the centric p.d.f. [(31)] distinguishes between main reflections and satellite reflections. These p.d.f.s are identical to p.d.f.s for normalized structure-factor amplitudes of nonmodulated crystals, also in first-order approximation (Giacovazzo, 1980). The difference between the

approach for nonmodulated crystals and the present approach for modulated crystals is in the definition and evaluation of $\mathcal{S}_2$ [(23)]. It follows that, with the present definition of normalized structure factors [(29)], the structure-factor statistics of modulated crystals are the same for both main and satellite reflections and are, in addition, identical to the structure-factor statistics of nonmodulated crystals.

As with nonmodulated crystals, normalized structure factors (29) can be associated with structure factors due to point atoms in a modulated crystal. Consequently, averaging over reciprocal space instead of physical space provides an equivalent method of obtaining p.d.f.s and expectation values. In particular, for any large set of reflections (general, zone, row), $\langle |E|^2 \rangle = 1$, regardless of whether or not this set contains main reflections, satellite reflections or main and satellite reflections. This can be derived by a straightforward calculation from (30) and (31).

For nonmodulated crystals, treated in the same approximation, $\langle |F|^2 \rangle$ can be estimated from experimental X-ray intensities with no prior knowledge of the crystal structure other than the unit-cell contents (Wilson, 1942). In the present case, exact evaluation of $\langle |F|^2 \rangle$, and likewise of $\mathcal{S}_2$ [(23)], also requires knowledge of the complete atomic modulation functions. To obtain an *a priori* estimate of the normalized structure-factor amplitudes, further approximations are necessary.

For crystals with an incommensurate one-dimensional displacive modulation, $\langle |F|^2 \rangle$ can be estimated if an overall modulation amplitude is introduced that simulates the effect of the atomic displacements. Experimental $|E|$ values estimated from measured X-ray intensities (I) on a relative scale (corrected for Lorentz and polarization effects and absorption) are then defined by [equations (18) and (19) of Lam, Beurskens & van Smaalen (1992)]

$$|E_b|^2 = I \left\{ \epsilon G(s; |m|) \sum_{\mu=1}^{N} [f_0^\mu(s)]^2 \right\}^{-1}, \qquad (32)$$

where f_0^μ is the form factor for atoms at rest and $s = (\sin\theta)/\lambda$. The function $G(s; |m|)$,

$$G(s; |m|) = K^{-2} \exp(-2Bs^2) \int_0^1 J_{|m|}^2(4\pi s U x) \mathrm{d}x, \qquad (33)$$

only depends on the scale factor K, the overall isotropic temperature parameter B and the overall modulation amplitude U. These parameters can be obtained by fitting† this function against (seminormalized) average intensities *versus* s^2.

† The fitting procedure (Lam, Beurskens & van Smaalen, 1992) was modified to perform a logarithmic fit. This automatically assigns a larger weight to weak intensity data and generally results in a better fit.

6. Numerical evaluation

The validity of the approximate expressions (30) and (31) has been tested by calculating $|E_b|$ and $P_{|E_b|}$ from X-ray structure-factor data for several structures with an incommensurate one-dimensional displacive modulation. 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. A first test for the theory was provided by fictitious structures devised to fulfil these requirements as closely as possible. In addition, the effect of special atomic modulations on the p.d.f.s is examined. In the last part of this section, p.d.f.s for some real modulated crystals are shown.

Normalized structure-factor amplitudes $|E_b|$ were estimated from (32) using the previously defined fitting procedure to determine K, B and U (Lam, Beurskens & van Smaalen, 1992). The p.d.f. $P_{|E_b|}$ for the normalized structure-factor amplitudes was then calculated by counting the number of reflections within suitable $|E_b|$ intervals and then multiplying this number by an appropriate normalization constant.

All the model structures created have superspace group $P1(q_1, q_2, q_3)1$ (models $A1$–$A4$) or superspace group $P\bar{1}(q_1, q_2, q_3)\bar{1}$ (models $C1$–$C4$). Each model structure has a realistic density ($\sim$18 Å^3 atom^{-1}) and realistic atomic modulations. The basic-structure unit cell contains 50 carbon atoms, with the symmetry-independent atoms randomly positioned and not occupying any special positions. For each symmetry-independent atom, the modulation function is given by $\mathbf{u}^\mu(\bar{x}_4^\mu) = \mathbf{U}_s^\mu \cos(2\pi\bar{x}_4^\mu) + \mathbf{U}_c^\mu \sin(2\pi\bar{x}_4^\mu)$, where the directions of the vectors $\mathbf{U}_s^\mu$ and $\mathbf{U}_c^\mu$ were chosen at random. The atomic modulation amplitude U_μ, defined by $U_\mu^2 = (U_s^\mu)^2 + (U_c^\mu)^2$ with U_s^μ and U_c^μ representing the lengths of the vectors $\mathbf{U}_s^\mu$ and $\mathbf{U}_c^\mu$, respectively, fluctuates around the overall modulation amplitude U. The latter is given by $U^2 = \sigma^{-1} \sum_{\mu=1}^{N} Z_\mu^2 U_\mu^2$, where $\sigma = \sum_{\mu=1}^{N} Z_\mu^2$ and Z_μ is the atomic number. To examine the effect of nonrandom atomic modulations, additional model structures were devised, having the same characteristics as those mentioned above but with a different type of atomic modulation. For one type of atomic modulation, the directions of the vectors $\mathbf{U}_s^\mu$ and $\mathbf{U}_c^\mu$ were chosen arbitrarily for each symmetry-independent atom but all atoms have identical modulation amplitudes. Another type of atomic modulation is the rigid-body displacement. For each symmetry-independent atom, the modulation function is given by $\mathbf{u}^\mu(\bar{x}_4^\mu) = (U_\mu/a_2)\sin(2\pi t)\,\mathbf{a}_2$, where $t = \bar{x}_4^\mu - \mathbf{q}\cdot\mathbf{r}_{0,\mathrm{L}}^\mu$, *i.e.* the modulation is a sinusoidal translation along the $\mathbf{a}_2$ axis of the basic-structure unit cell, with all atoms having the same starting phase and modulation amplitudes. Characteristics of the model

Table 1. *Model structure characteristics*

Compounds: Ai, noncentrosymmetric superspace group $P1(q_1, q_2, q_3)1$; Ci, centrosymmetric superspace group $P\bar{1}(q_1, q_2, q_3)\bar{1}$ (see text for explanation).

Model structure	U (Å)	U_μ (Å) min./max.	Atomic modulation functions
$A1$	0.04	0.012/0.055	Random amplitudes and directions
$A2$	0.2	0.057/0.276	Random amplitudes and directions
$A3$	0.2	0.2/0.2	Identical amplitudes and random directions
$A4$	0.2	0.2/0.2	Rigid-body displacement
$C1$	0.04	0.019/0.051	Random amplitudes and directions
$C2$	0.2	0.097/0.255	Random amplitudes and directions
$C3$	0.2	0.2/0.2	Identical amplitudes and random directions
$C4$	0.2	0.2/0.2	Rigid-body displacement

Table 2. *Values of K, B, U and $\langle|E_b|^2\rangle$*

Parameters K, B and U were obtained from a fitting procedure applied to main reflections and $|m| = 1$ satellites. Values of $\langle|E_b|^2\rangle$ were calculated from the normalized structure-factor amplitudes $|E_b|$ [equation (32)] for (I) main reflections, (II) $|m| = 1$ satellites and (III) main reflections plus $|m| = 1$ satellites. These values must be compared to the input values $K = 1$, $B = 2$ and U as given in Table 1, while $\langle|E_b|^2\rangle = 1$.

Model structure	K	B (Å^2)	U (Å)	$\langle\|E_b\|^2\rangle$ (I)	(II)	(III)
$A1$	1.00	1.99	0.040	0.991	1.003	0.994
$A2$	1.01	1.98	0.198	0.985	1.005	0.993
$A3$	1.04	1.91	0.214	0.973	1.011	0.994
$A4$	1.01	1.98	0.200	0.986	1.004	0.993
$C1$	0.99	2.00	0.040	0.994	1.002	0.995
$C2$	1.01	1.98	0.203	0.987	1.004	0.994
$C3$	1.02	1.94	0.212	0.987	1.008	0.994
$C4$	1.01	1.97	0.199	0.989	1.012	1.000

structures together with details of all atomic modulations are given in Table 1. For all model structures, structure factors were calculated for main reflections and first-order satellites, up to $s = 1$ Å^{-1}, using $K = 1$ and $B = 2$ Å^2.

The values of the parameters K, B and U obtained from the fitting procedure are given in Table 2. For both small and medium-size atomic modulations, they are in excellent agreement with the values input to the structure-factor calculations. The largest deviations occur for the U values of structures $A3$ and $C3$. Also shown in Table 2 are the values of $\langle|E_b|^2\rangle$ calculated from the normalized structure-factor amplitudes $|E_b|$. For both main reflections and first-order satellites, these values are all close to 1, as they should be with the present definition of normalized structure factors [(29)]. Note that nonrandom atomic modulations do not apparently cause serious deviations from the ideal values. Figs. 2(*a*) and (*b*) show the results of the fitting procedure for the noncentrosymmetric structure $A2$ and the centrosymmetric structure $C2$, respectively. One can see that the intensity distributions are accurately reproduced. For the structures $A3$ and $C3$, the quality of the fitted intensity distributions for the main reflections (not shown here) is somewhat less. The intensity distributions given in Figs. 2(*a*) and (*b*) correspond well with the intensity distributions of all other noncentrosymmetric and centrosymmetric model structures, respectively.

P.d.f.s $P_{|E_b|}$ for structures $A2$ and $C2$ are given in Fig. 3. The p.d.f.s for main reflections and first-order satellites are nearly identical for each structure. Furthermore, the p.d.f.s for structures $A2$ and $C2$ are in excellent agreement with the theoretical p.d.f.s for noncenstrosymmetric [(30)] and centrosymmetric [(31)] structures, respectively. A similar good agreement was observed for the p.d.f.s of the structures $A1$, $A3$, $C1$ and $C3$ (not shown here). This shows that, with the present definition of normalized structure factors [(29)], the structure-factor statistics do not distinguish between main and satellite reflections and are identical to the structure-factor statistics for nonmodulated crystals.

For the structures $A4$ and $C4$ (rigid-body modulations), the resulting p.d.f.s $P_{|E_b|}$ show entirely different behavior. For the noncentrosymmetric structure $A4$, the p.d.f. for main reflections is between acentric and centric (Fig. 4*a*), while the p.d.f. for first-order satellites follows

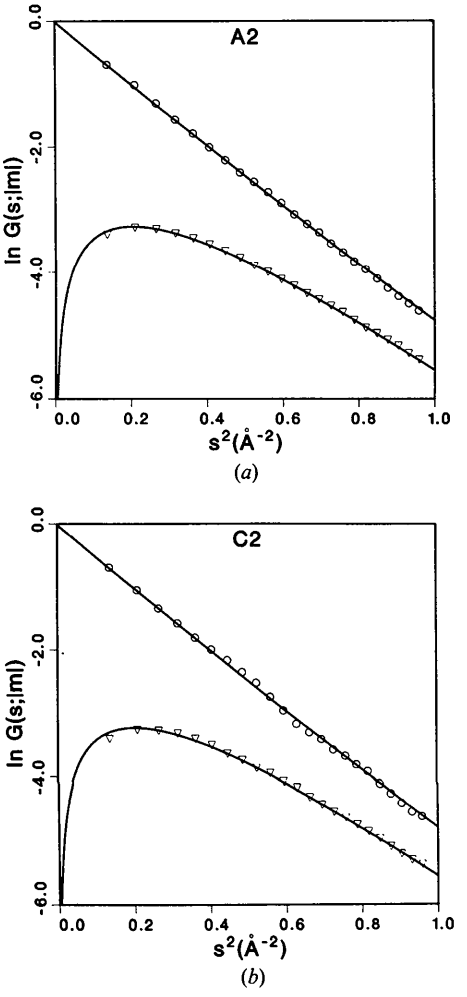


Fig. 2. Natural logarithm of the (seminormalized) average intensity $G(s;|m|)$ as a function of s^2, for main reflections (circles) and $|m| = 1$ satellite reflections (triangles). The solid lines represent the curves obtained from the fitting procedure: (*a*) for structure $A2$; (*b*) for structure $C2$.

the theoretical p.d.f. for centrosymmmetric structures (Fig. 4*b*). For the centrosymmetric structure *C*4, the p.d.f.s show severe deviations from the theoretical p.d.f., especially for low and intermediate $|E_b|$ values, indicating an excess of weak reflections. In fact, the p.d.f.s $P_{|E_b|}$ shown in Figs. 4(*c*) and (*d*) show remarkable resemblances to hypercentric distributions as known for nonmodulated crystals (Shmueli, Weiss & Kiefer, 1985). Note that, for structures *A*4 and *C*4, the p.d.f.s tend to be more centric than expected. This effect is larger for first-order satellites than for main reflections, presumably because the intensities of satellite reflections are much more sensitive to the modulation than the intensities of main reflections.

In summary, restriction of the atomic displacements to having the same modulation amplitude for all atoms does not have much influence on the p.d.f.s. Also, restriction of the directions of the atomic displacement vectors introduces pseudosymmetry, causing the p.d.f.s to become more centric than they are expected to be. This effect is more severe for satellites than for main reflections. An acentric p.d.f. can even be changed into a centric p.d.f. Although a rigorous mathematical treatment is not yet available, it seems that a special type of displacive modulation can introduce effects similar to hypersymmetry effects for nonmodulated crystals.

For three real compounds with displacively modulated structures, intensity distributions and p.d.f.s were calculated. For Na_2CO_3 (van Aalst, den Hollander, Peterse & de Wolff, 1976) and for $K_{0.3}MoO_3$ (Schutte, 1990), both the set of $|F|$ values derived from experiment and the more complete set of $|F|$ values derived from the published structure models were used. For $C_{12}D_{10}$ (deuterated biphenyl; Baudour & Sanquer, 1983), only the calculated $|F|$ values were available, as the structure was determined by neutron diffraction. For each

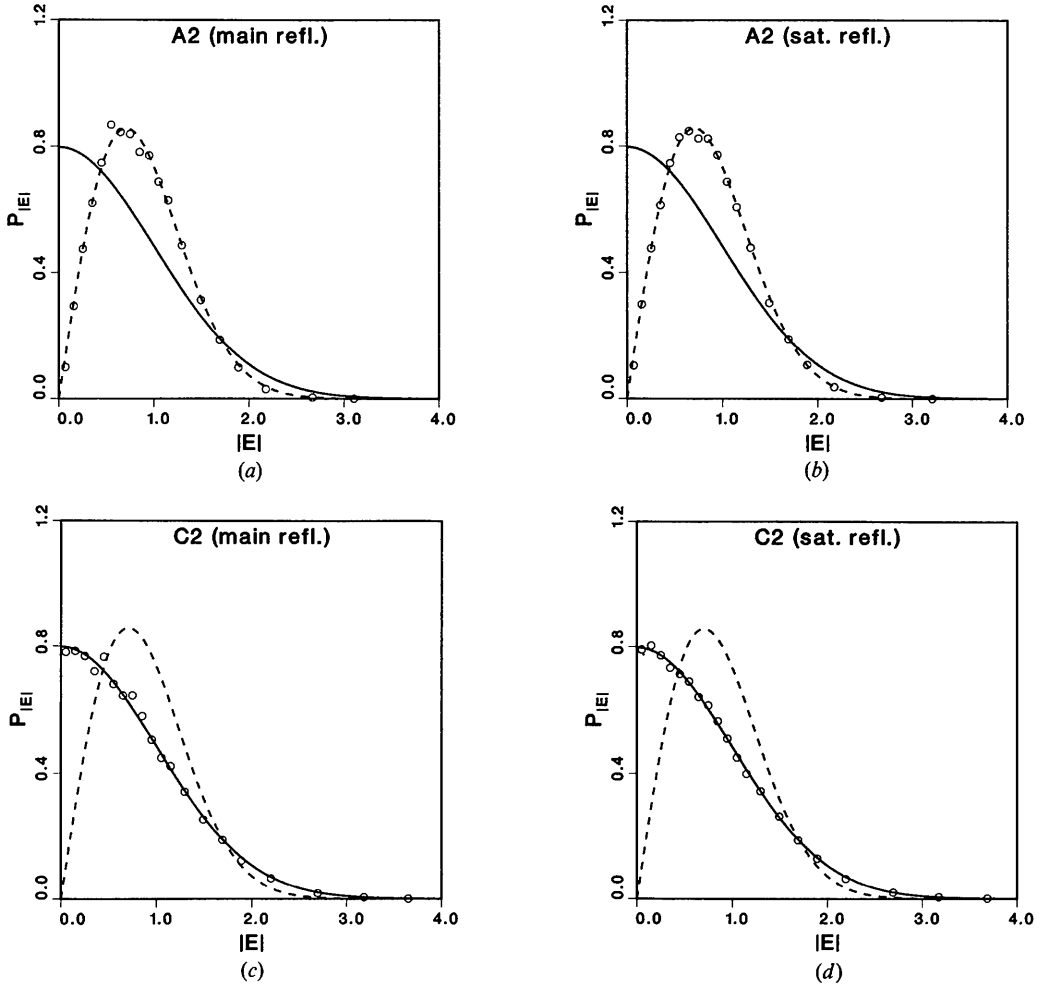


Fig. 3. P.d.f.s for model structures with random atomic modulations. The solid line represents the theoretical p.d.f. for normalized structure-factor amplitudes of centrosymmetric structures [(31)]. The dashed line represents the p.d.f. for normalized structure-factor amplitudes of noncentrosymmetric structures [(30)]. Circles represent the p.d.f. $P_{|E_b|}$ derived from the $|E_b|$ values [(32)], calculated for the various structures: (*a*) for main reflections of structure *A*2; (*b*) for $|m| = 1$ satellites of structure *A*2; (*c*) for main reflections of structure *C*2; (*d*) for $|m| = 1$ satellites of structure *C*2.

compound, the published structural model was used to calculate the overall modulation amplitude U and, similarly, the overall isotropic temperature parameter B (Hamilton, 1959). For both main reflections and first-order satellites, structure factors were calculated with scale factor $K = 1$ and up to $s = 1$ Å^{-1}.

Results obtained from the fitting procedure together with the values of $\langle |E_b|^2 \rangle$ are summarized in Table 3. Apparently, all scale factors for the calculated structure factors are overestimated. The scale factors for the observed X-ray intensities were not reported in the literature and cannot be compared to the scale factors input to the structure-factor calculations. The fitted values for B and U are in reasonable agreement with *a priori* calculated values. Note that the values of B and U obtained from the fitting procedure applied to calculated structure factors compare very well with those obtained from observed X-ray intensities, which shows that the deviations between calculated and fitted parameters are intrinsic to the structures and not a result of experimental errors. The values of $\langle |E_b|^2 \rangle$ are close to 1 for calculated structure factors as well as observed X-ray intensities.

From Fig. 5, it can be seen that the experimental intensity distributions are reasonably well reproduced for all three modulated crystals. The p.d.f.s for Na_2CO_3 (Figs. 6*a* and *b*) and $K_{0.3}MoO_3$ (Figs. 6*c* and *d*) obtained from calculated structure-factor amplitudes are essentially centric, as expected from their superspace groups, but show hypercentric behavior. This is likely to be caused by atoms on special positions, the nonrandom arrangement of atoms in the basic-structure unit cells and the nonrandom character of the atomic modulation; for Na_2CO_3, the atomic displacements are parallel to the $\mathbf{a}_2$ axis for most of the atoms. The same deviations were also observed for p.d.f.s of main reflections, using $|E|$ values obtained through a conventional Wilson plot (Wilson, 1942). This indicates that these anomalies are intrinsic to the structure. The behavior of the p.d.f.s obtained from calculated structure factors is smoother than that of those obtained from the experimental X-ray

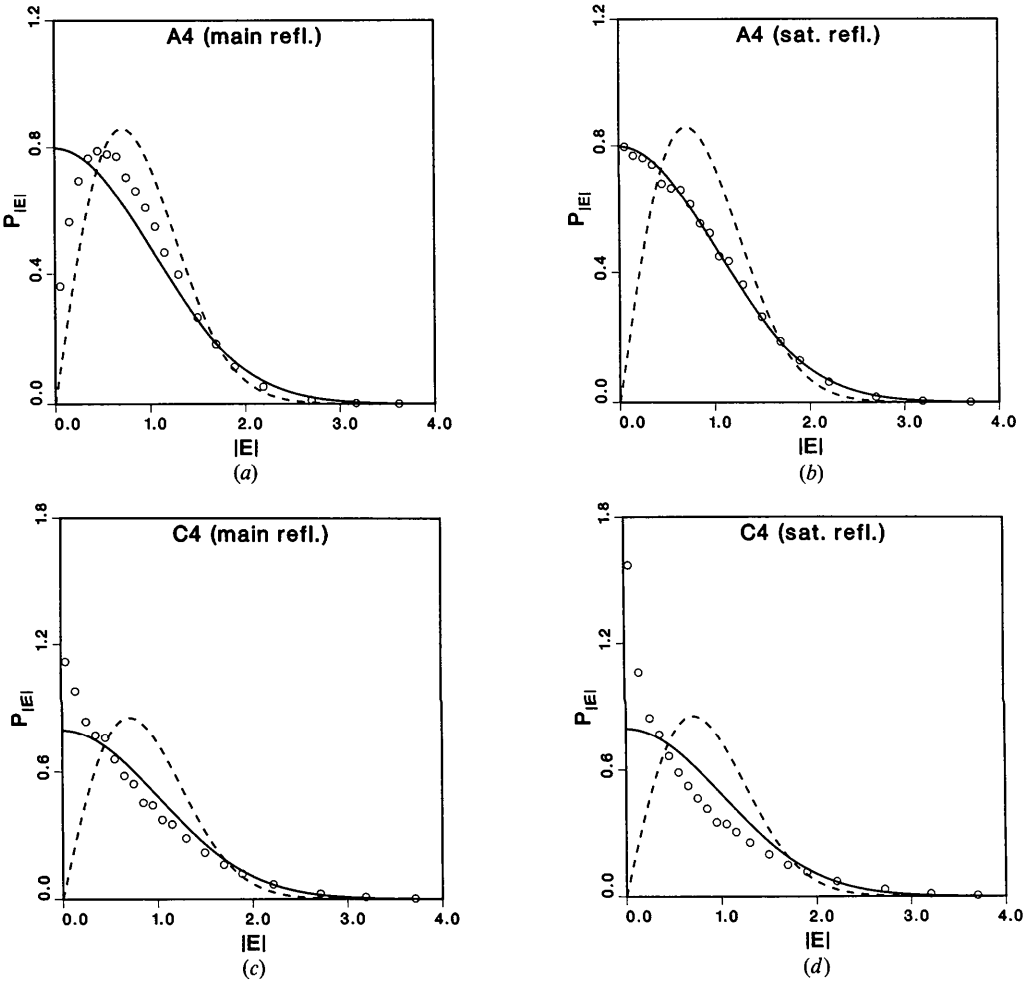


Fig. 4. P.d.f.s for structures with rigid-body modulations (see Fig. 3 for definitions): (*a*) for main reflections of structure *A*4; (*b*) for $|m| = 1$ satellites of structure *A*4; (*c*) for main reflections of structure *C*4; (*d*) for $|m| = 1$ satellites of structure *C*4.

Table 3. *Values of K, B, U and* $\langle |E_b|^2 \rangle$

Parameters K, B and U were obtained from a fitting procedure applied to main reflections and $|m| = 1$ satellites. Values of $\langle |E_b|^2 \rangle$ were calculated from the normalized structure-factor amplitudes $|E_b|$ [equation (32)] for (I) main reflections, (II) $|m| = 1$ satellites and (III) main reflections plus $|m| = 1$ satellites. For each compound, line *pp* contains B and U calculated from published parameters and the expected values of $\langle |E_b|^2 \rangle$; for calculated data, $K = 1$. For experimental data, K is unknown. Lines f_c and f_o show the results obtained from calculated data and experimental X-ray data, respectively. The values of K for experimental data cannot be compared to those for calculated data.

Model structure		K	B (Å^2)	U (Å)	$\langle \lvert E_b \rvert^2 \rangle$ (I)	(II)	(III)
	pp	1	1.42	0.386	1	1	1
Na_2CO_3	f_c	1.07	1.10	0.422	1.007	1.007	1.007
	f_o	0.60	1.16	0.461	0.997	1.009	1.005
	pp	1	0.22	0.033	1	1	1
$K_{0.3}MoO_3$	f_c	1.04	0.15	0.035	0.995	1.001	0.999
	f_o	3.18	0.17	0.035	0.993	0.994	0.993
	pp	1	0.99	0.112	1	1	1
$C_{12}D_{10}$	f_c	1.05	0.70	0.110	0.998	1.008	1.005

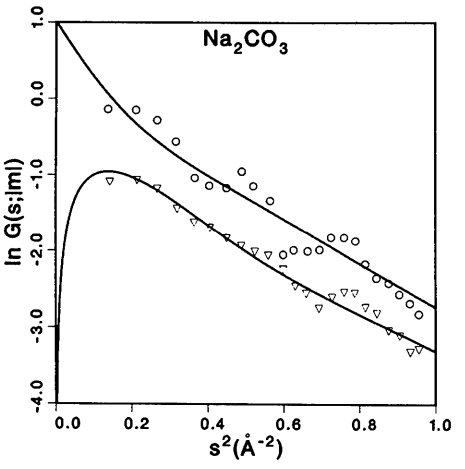
data. This is a result of the large number of reflections with intensities less than or equal to a few standard deviations. Note that the p.d.f.s have the same shape for main reflections and first-order satellites.

The p.d.f.s for $C_{12}D_{10}$ obtained from calculated structure factors show behavior that is more centric than acentric (Figs. 6*e* and *f*), although the superspace group is noncentrosymmetric. This is a typical example of a modulated crystal with pseudosymmetry. In the basic structure (space group $P2_1/a$), there is an inversion center at the center of the molecule. This inversion center is destroyed by the displacive modulation (specifically, by the torsion around the long molecular axis). This means that the superspace group is noncentrosymmetric (external space group *Pa*), but half of the symmetry-independent atoms have average positions $\mathbf{r}_0^\mu$ related to those of the other symmetry-independent atoms by an inversion center. This causes the p.d.f.s to deviate from the theoretical p.d.f. [(30)].

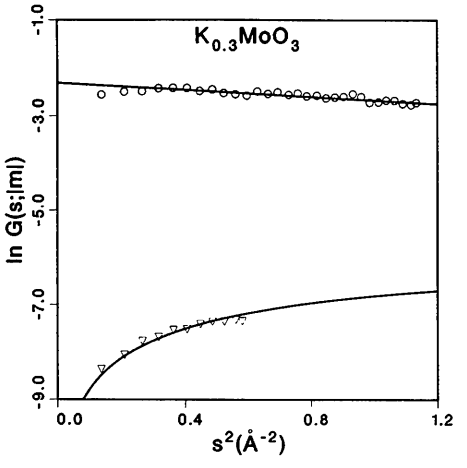
7. Concluding remarks

A definition has been presented for normalized structure factors in X-ray diffraction for main reflections and satellite reflections of incommensurate one-dimensionally modulated crystals. For displacively modulated crystals, the normalized structure-factor amplitudes can be estimated from experimental X-ray intensity data using the previously defined fit of (seminormalized) average intensity *versus* $(\sin^2 \theta)/\lambda^2$ (Lam, Beurskens & van Smaalen, 1992).

For both phase-restricted and non-phase-restricted reflections, theoretical expressions have been derived for centric and acentric p.d.f.s, respectively, of normalized structure-factor amplitudes. These p.d.f.s make no distinction between main reflections and satellite reflections and, in addition, are identical to p.d.f.s for normalized structure-factor amplitudes of nonmodulated crystals.



(*a*)



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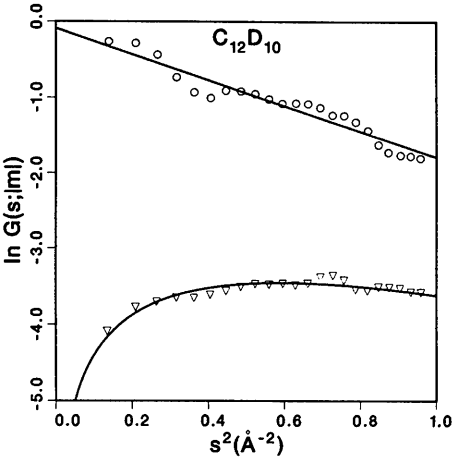

(*c*)

Fig. 5. Natural logarithm of the (seminormalized) average intensity $G(s, |m|)$ as a function of s^2 (see Fig. 2 for definitions): (*a*) Na_2CO_3; (*b*) $K_{0.3}MoO_3$; (*c*) deuterated biphenyl.

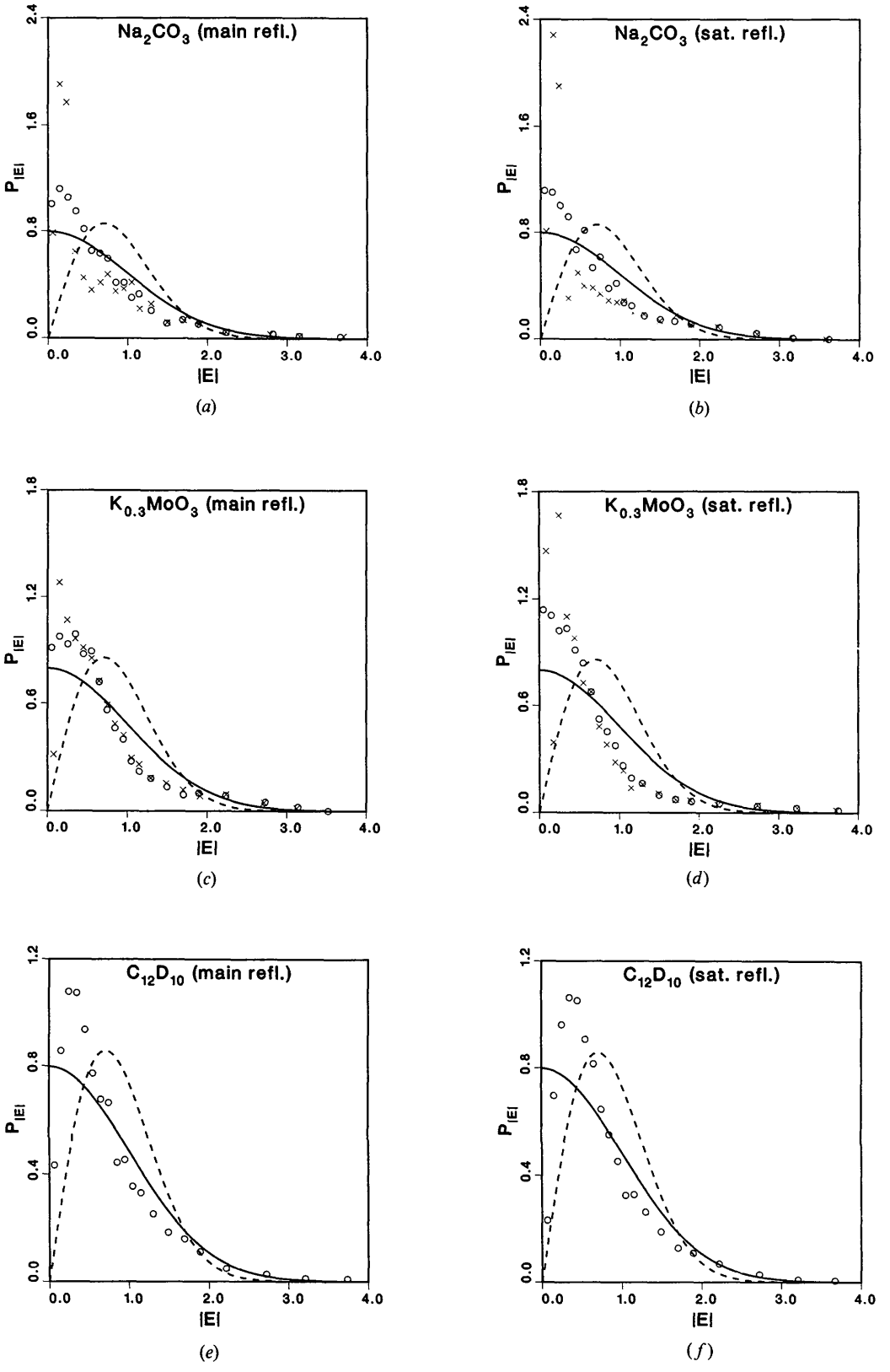

Fig. 6. P.d.f.s for several real structures with a displacive modulation (see Fig. 2 for definitions); circles are obtained from calculated structure factors and crosses are obtained from experimental X-ray data: (*a*) for main reflections of Na_2CO_3; (*b*) for $|m| = 1$ satellites of Na_2CO_3; (*c*) for main reflections of $K_{0.3}MoO_3$; (*d*) for $|m| = 1$ satellites of $K_{0.3}MoO_3$; (*e*) for main reflections of $C_{12}D_{10}$; (*f*) for $|m| = 1$ satellites of $C_{12}D_{10}$.

The theoretical p.d.f.s are in excellent agreement with p.d.f.s obtained from normalized structure-factor amplitudes of idealized model structures having many equal atoms randomly distributed throughout the basic-structure unit cell, none of them occupying special positions, with random atomic displacements. Model structures with special displacive modulations cause the p.d.f.s derived from X-ray intensities to deviate severely from the theoretical p.d.f.s. This is especially true for rigid-body displacements, which cause the experimental p.d.f.s to be more centric than the theoretical p.d.f.s and which can even change an acentric p.d.f. into a centric one.

For real modulated crystals, there is reasonable agreement between practical p.d.f.s and theoretical p.d.f.s, although various effects that also exist for nonmodulated crystals (Srinivasan & Parthasarathy, 1976) cause deviation from the theoretical p.d.f.s; for example, nonrandom atomic distribution and atoms on special positions. Deviations are also caused by special atomic modulations and by the destruction of symmetry elements by modulation, leading to pseudosymmetry.

The results obtained from the idealized model structures show the present definition of normalized structure factors to provide correct structure-factor statistics for incommensurately modulated crystals. Additional tests are in progress, investigating the reliability of the triplet phase relation and the tangent formula, using only large normalized structure-factor amplitudes. It is expected that, eventually, statistics of this kind will be used by direct-method procedures applied to incommensurately modulated crystals.

The authors thank A. Janner (University of Nijmegen) for many stimulating discussions and F. Tuinstra (Delft University of Technology) for supplying the experimental data on Na_2CO_3. 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*

The contribution of atom μ, having electron density ρ_μ, in basic-structure unit cell $\mathbf{L}$, to the electron density of the modulated crystal is

$$p^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^\mu)]\rho_\mu\{|\mathbf{r}-\mathbf{r}^\mu_{0,\mathbf{L}}-\mathbf{u}^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^\mu)]|\}. \quad (34)$$

The atomic modulation functions depend on the choice of the phase-reference point $\mathbf{g}^\mu$. This can be chosen arbitrarily for each atom (Petříček, Coppens & Becker, 1985). Therefore, the contribution (34) can also be written as

$$p'^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}'^\mu)]\rho_\mu\{|\mathbf{r}-\mathbf{r}^\mu_{0,\mathbf{L}}-\mathbf{u}'^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}'^\mu)]|\}, \quad (35)$$

with the atomic modulations described by functions p'^μ and $\mathbf{u}'^\mu$, defined with respect to another phase-reference point $\mathbf{g}'^\mu$.

Because (34) and (35) must describe the same electron density, they must be equal, which leads to

$$p^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^\mu)] = p'^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}'^\mu)], \quad (36)$$

$$\mathbf{u}^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^\mu)] = \mathbf{u}'^\mu[\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}'^\mu)]. \quad (37)$$

Because the phase-reference points $\mathbf{g}^\mu$ and $\mathbf{g}'^\mu$ are independent of one another, the left- and right-hand sides of (36) and, similarly, of (37) must be independent of these phase-reference points. Therefore, although the atomic modulation functions p^μ and $\mathbf{u}^\mu$, as well as their argument $\mathbf{q}\cdot(\mathbf{L}+\mathbf{g}^\mu)$, depend on the choice of the phase-reference point $\mathbf{g}^\mu$, the values of the atomic modulations are independent of this choice.

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