systematically emphasized and encouraged in structure reports.

3. Where uncertainty arises in assignment, a given structure may be incorporated in both enantiomeric space groups but with half the weight (which takes care of the probability aspect and keeps the observed data set unaltered).

If these are acceptable it could raise a moot point whether or not it is desirable to include in case *B* two subdivisions such as $P2^+/P2^-$ where the +, − symbols refer to, for example, chirality at the molecular level where such a distinction is possible (such as known L- or D-amino acids). Since such prior distinction may not always be possible it is necessary to adopt a more specific and experimentally determinable physical attribute such as optical rotation in the solid state for the specific crystal used for X-ray studies. Although the latter may be difficult from the experimental point of view, the need for such an identification/characterization is felt to be highly desirable.

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Use of the Debye–Waller approximation in diffraction-pattern calculation.

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Abstract

A new method of diffraction-pattern calculation is proposed and tested on quasicrystals. With use of an appropriately defined reference lattice, a structure factor can be well approximated by a rapidly convergent series expansion of a variable u that describes nearest distances between atomic positions and points of the reference lattice. Only the first few terms are significant for diffraction-pattern calculation. The possibility of using the Debye-Waller approximation is discussed. In this case an appropriate shift of the reference structure is required. Calculations based on the Debye-Waller formula in real and phason spaces give similar results.

Introduction

A new approach to the calculation of diffraction patterns has recently been proposed (Wolny, 1991; Wolny & Pytlik, 1992). The diffraction intensity is calculated in real space using a distribution of atomic positions around a periodic reference lattice of points with period equal to the wavelength for a given scattering wave vector.

For each scattering vector $\mathbf{k}$, a one-dimensional reference lattice of points $\{\boldsymbol{\lambda}_l\}$ can be defined such that

$$\mathbf{k}\cdot\boldsymbol{\lambda}_l = k\lambda_l = 2\pi l, \tag{1}$$

where l is an integer. The vectors $\boldsymbol{\lambda}_l$ are parallel to the scattering vector $\mathbf{k}$ and their lengths are given by

$$\lambda_l = \lambda_0 l, \tag{2}$$

where $\lambda_0 = 2\pi/k$ is the wavelength for scattering vector $\mathbf{k}$. It should be noted that the vectors $\boldsymbol{\lambda}_l$ depend on $\mathbf{k}$, which can be expressed by writing $\boldsymbol{\lambda}_l = \boldsymbol{\lambda}_l(\mathbf{k})$. For any position vector $\mathbf{r}_n$ and its component $\mathbf{r}_n^k$ parallel to $\mathbf{k}$, one can choose a vector $\boldsymbol{\lambda}_l$ such that (Fig. 1)

$$\mathbf{r}_n^k = \boldsymbol{\lambda}_l + \mathbf{u}_n, \tag{3}$$

where the length of $\mathbf{u}_n$ is less than or equal to $\lambda_0/2$. Vectors $\mathbf{r}_n^k$, $\boldsymbol{\lambda}_l$ and $\mathbf{u}_n$ are all parallel. With use of (1) and (3), the structure factor for a finite arrangement of N particles at positions $\mathbf{r}_n$ and with form factor f_n can be written as

$$F(\mathbf{k}) = \sum_{n=1}^{N} f_n \exp(iku_n) = \sum_{n=1}^{N} f_n \sum_{m=0}^{\infty} (iku_n)^m/m!, \tag{4}$$

and since

$$ku_n \le \pi \tag{5}$$

this series expansion is rapidly convergent and the first few terms are dominant.

The real and imaginary parts of the structure factor are given by

$$\mathrm{Re}[F(\mathbf{k})] = N(1 - k^2\langle u^2\rangle/2! + k^4\langle u^4\rangle/4! - k^6\langle u^6\rangle/6! + \ldots), \tag{6a}$$

$$\mathrm{Im}[F(\mathbf{k})] = N(k\langle u\rangle - k^3\langle u^3\rangle/3! + k^5\langle u^5\rangle/5! - \ldots), \tag{6b}$$

where

$$\langle u^m\rangle = (1/N)\sum_{n=1}^{N} f_n (u_n)^m \tag{7}$$

is an mth moment of variable u. Finally, the intensity of the diffraction pattern for a given scattering vector that is

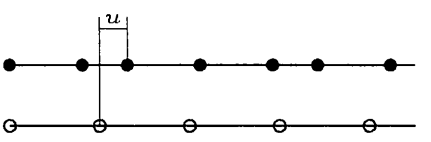

Fig. 1. The variable u describes the shortest distance of the projection of the atomic position (filled circles) from the reference lattice ('wave lattice' - open circles).

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normalized to N^2 can be expressed as

$$I(\mathbf{k})/N^2 = (1 - k^2\langle u^2\rangle/2! + k^4\langle u^4\rangle/4! - \ldots)^2 + (k\langle u\rangle - k^3\langle u^3\rangle/3! + \ldots)^2 \quad (8)$$

and it depends only on the length of scattering vector and moments of variable u. It should be noted here that the variable u and its moment distribution depend on the scattering vector.

Application to quasicrystals

The discussed method is quite general but for its presentation we choose the analysis of the diffraction pattern of a two-dimensional quasicrystal. We have also performed many tests for other structures, such as single crystals, twins and random and amorphous structures and we have found that quasicrystals are an instructive test of the method. Their diffraction pattern is rather complicated but, for peaks with $k_z = 0$ [k_z is the component of the five-dimensional scattering vector along the main diagonal of the five-dimensional cube (Jarić, 1986)] when Robinson triangles are used for tiling (Wolny & Pytlik, 1991), analytical expressions describing peak intensities can be obtained using a five-dimensional representation. This facilitates comparison of diffraction patterns obtained for different levels of the approximation to the diffraction pattern obtained by Fourier analysis.

The diffraction pattern of an ideal quasicrystal is well understood in higher-dimensional representation (Elser, 1985, 1986; Kalugin, Kitaev & Levitov, 1985; Duneau & Katz, 1985). For two-dimensional Penrose tiling, five-dimensional representation has been extensively used (de Bruijn, 1981; Jarić, 1986; Strandburg, 1989; Tang & Jarić, 1990; Wolny & Pytlik, 1991; Wolny, 1991). Higher-dimensional analysis allows calculation of the diffraction-peak intensities using Debye-Waller approximation and mean square fluctuations of phason-space coordinates. Diffraction for a one-dimensional Fibonacci chain has also been extensively studied (Jagodzinski, 1991).

The structure used for the diffraction calculations was a Penrose-like tiling obtained by the inflation method using Robinson triangles; it has been described by Wolny, Pytlik & Lebech (1988), (1990), Lebech, Wolny & Pytlik (1988) and Wolny & Pytlik (1991). A one-dimensional cut of the diffraction pattern along the y direction ($k_x = 0$) was calculated and is shown in Fig. 2. A logarithmic scale was used for the scattering vector as it allows convenient presentation of the first three series of peaks, which are periodic in this scale. These series of peaks are described by Jarić (1986) and Wolny & Pytlik (1991) as

$$k_y = k_0\tau^n, \qquad n = 0, 1, 2, \ldots \quad (9)$$

with different values of k_0 approximately equal to 2.955, 5.909 and 6.607 for the three series. The values of τ is about 1.618. Peak intensities of these series were linked by a solid line (Fig. 2) calculated according the formula (Wolny, 1991)

$$I(k_y)/N^2 = \exp(-0.4015k_0^4/k_y^2). \quad (10)$$

This is a Debye-Waller approximation that is calculated in phason space (Wolny & Pytlik, 1991). It is an analytical expression of the envelope function (Wolny, Pytlik & Lebech, 1988, 1990; Lebech, Wolny & Pytlik, 1988) that connects peak intensities of all peaks belonging to the same series (Fig. 2). It follows from this figure that the Debye-Waller formula is valid only for the most intense peaks and deviations from the envelope function of the low-intensity peaks are observed in Fig. 2. It has already been shown (Wolny, 1991; Wolny & Pytlik, 1992) that there are no visible differences between the diffraction patterns obtained directly from the Fourier transform and those obtained from (8) with use of at least the first eight moments of variable u.

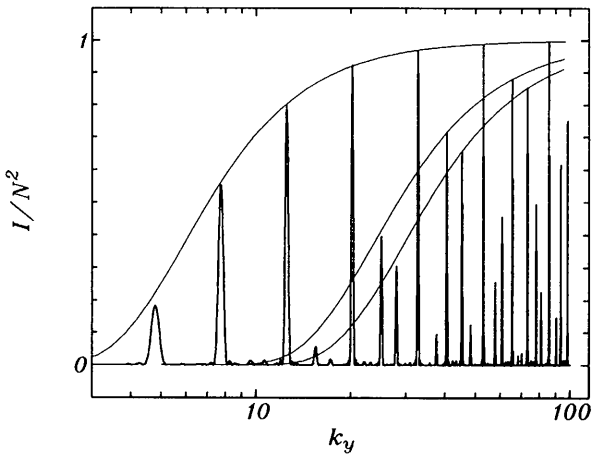

Fig. 2. Diffraction pattern obtained for a Penrose-like tiling and calculated along the k_y direction for $k_x = 0$. The diffraction pattern consists of a series of peaks that are periodic in the logarithmic scale of the scattering vector. Peak intensities belonging to the first three series of peaks, with k_0 approximately equal to 2.955, 5.909 and 6.607, have been connected by solid lines calculated according to the Debye-Waller approximation in phason space [equation (10)].

Debye–Waller approximation

The Debye-Waller approximation was used to describe the reduction of peak intensity caused by the thermal vibration of atoms around lattice positions. In this case, if the origin is chosen at a lattice point and the scattering vector corresponds to the reciprocal-lattice vector, the imaginary part of the structure factor is equal to zero and the first two terms of the expansion of the real part (6a) become dominant. The diffraction intensity can then be approximated by the well known Debye-Waller formula for a one-dimensional variable u,

$$I/N^2 = \exp(-k^2\langle u^2\rangle). \quad (11)$$

The series expansion of (11) is

$$I/N^2 = 1 - k^2\langle u^2\rangle + k^4\langle u^2\rangle^2/2! - k^6\langle u^2\rangle^3/3! + \ldots \quad (12)$$

and the first two terms of this expansion are similar to the first two terms of (8) after squaring,

$$I/N^2 \simeq (1 - k^2\langle u^2\rangle/2)^2 = 1 - k^2\langle u^2\rangle + (k^2\langle u^2\rangle/2)^2 \simeq 1 - k^2\langle u^2\rangle. \quad (13)$$

To calculate a diffraction pattern using (11), one should check first that the imaginary part of the structure factor is negligible. For centrosymmetric distributions this is automatically fulfilled (all odd moments of variable u are

equal to zero) if the center is chosen as the origin. In general, the above requirement can be achieved by an appropriate adjustment of a reference lattice to the real structure (a shift of the reference lattice along the direction of the scattering vector). In Fig. 3 the first four moments were plotted against the shift y_0 of the structure along the y direction and for three different scattering vectors. When the scattering vector approaches any peak position (in the case of Fig. 3 the peak considered is at $k_y \simeq 20.25$) the values of all the moments start to oscillate with increasing amplitude of oscillation. For calculation of the diffraction pattern according to (11) one can use this shift value, indicated by arrows in Fig. 3, which corresponds to the first moment being zero and the second moment being minimum. For this particular shift the third moment (Fig. 3*c*) is very close to zero and the fourth moment (Fig. 3*d*) is close to its minimum value. Analysis of other peaks fully supports the choice of the shift corresponding to the first moment being zero for the Debye-Waller approximation. However, it should be noted that the appropriate shifts may be different for different peaks observed in the diffraction pattern.

To test the hypothesis that the choice of the shifts corresponding to the first moment of variable u being zero is sufficient to allow use of the Debye-Waller approximation, the following calculations have been made. The biggest difference between the shifts, corresponding to the first and third moments being zero, was observed for lower-intensity peaks and it approached zero for higher-intensity peaks. For example, the peak observed at $k_y \simeq 4.78$ has normalized intensity of about 0.18 and it is the lowest-intensity peak observed for the first series of peaks (Fig. 2). For this peak, the zero of the first moment is at a shift of 0.4053 and the zero of the third moment corresponds to a shift of 0.4088. The zero of the fifth moment is at 0.4090. Use of the shift of 0.4053 gives values of the third and fifth moments, multiplied by $k^3/3!$ and $k^5/5!$ respectively, which are less than 0.5% of the second moment multiplied by $k^2/2$. All higher moments can be neglected.

Choice of the correct shift is essential, as otherwise the Debye-Waller approximation gives completely unreliable results for the diffraction intensity. The diffraction pattern of the discussed structure, calculated according to the Debye-Waller approximation (11), is shown in Fig. 4. It appears to be similar to the diffraction pattern calculated by the Fourier transform (Fig. 2); however, some essential differences can easily be noticed. The background is constant and equal to 0.037, the value expected for a uniform distribution of variable u. The higher-intensity peaks are equal for the Fourier transform and the Debye-Waller approximation. Peaks of lower intensity start to differ;

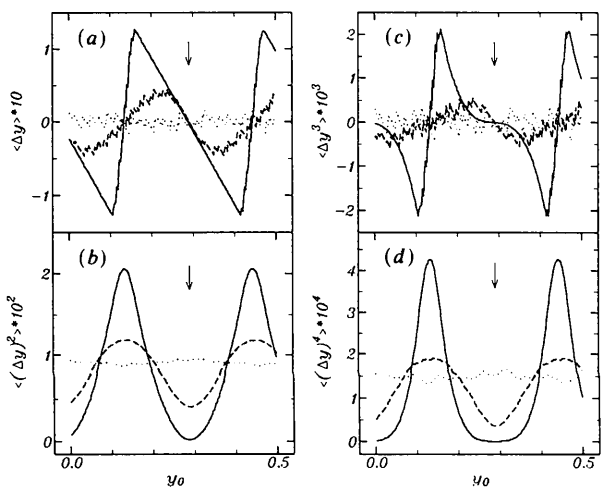

Fig. 3. Values of the first four moments of the variable $\Delta y \equiv u$ *vs* the shift y_0 of the real structure for different scattering vectors: $k_y = 19.0$ (· · · ·); $k_y = 20.0$ (– – –); $k_y = 20.25066$ - peak position (——); (*a*) first moment, (*b*) second moment, (*c*) third moment, (*d*) fourth moment. The arrows indicate the value of the shift used for diffraction-pattern calculations according to the Debye-Waller formula (Fig. 4) at which the first moment is zero and the second moment is at its minimum.

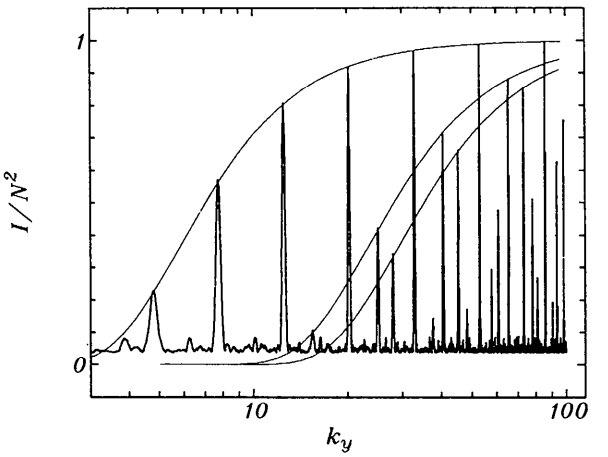

Fig. 4. Diffraction pattern obtained for a Penrose-like structure and calculated using the Debye-Waller approximation in real space [equation (11)]. An appropriate shift of the real structure was used to obtain this pattern (see text). Solid lines connecting the maxima of the peaks are the same as in Fig. 2 and describe the Debye-Waller approximation in phason space.

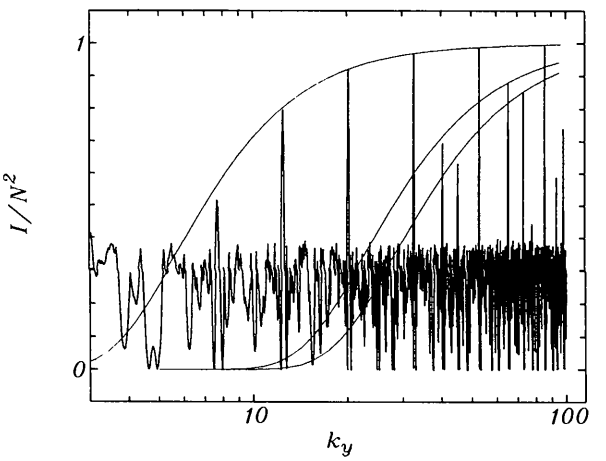

Fig. 5. Diffraction pattern for a Penrose-like structure calculated by the formula $I/N^2 = (1 - k^2\langle u^2\rangle/2)^2$, which is derived from the series expansion [equation (8)] limited to the second moment of variable u together with the shifting procedure (see text) to reduce the imaginary part of the structure factor.

however, excellent correlation is observed between the peak intensities obtained from the Debye–Waller approximations in real and phason spaces.

Finally, one further property of the Debye–Waller approximation should be emphasized. This approximation is valid to the order of the second moment of variable u. However, the series expansion (8), limited to the second moment, together with the shift procedure discussed above, gives the diffraction pattern shown in Fig. 5. In this case, the higher-intensity peaks are calculated correctly, but the background is extremely high. This comes from the fact that for the background calculation the higher moments are as important as the second (compare the second and the fourth moments in Fig. 3 for $k_y = 19$, *i.e.* for a scattering vector that is far from the peak position). The Debye–Waller approximation (Fig. 4) suppresses the background oscillations observed in Fig. 5 for diffraction patterns calculated according to (8) with a series expansion limited to the second moment only.

Concluding remarks

A method of diffraction-pattern calculation based on a series expansion of structure factors is discussed. If the moments of the u distribution are constant (*i.e.* they do not depend on the number of atoms and/or on the dimensions of the sample), the calculated diffraction pattern consists of well defined Bragg peaks that scale as N^2. This conclusion is very important for noncrystalline structures and especially for quasicrystals. Of course, one can obtain similar results for the original Penrose tiling by performing the higher-dimensional analysis. However, there are quasicrystals that are perfectly ordered but which cannot be fully analyzed in higher dimensions. For example, the structures obtained by the inflation method using two Robinson triangles have their h_z components undetermined (Wolny & Pytlik, 1991), where h_z is a perpendicular-space position component (Jarić, 1986), and only certain peaks (with corresponding $k_z = 0$) can be analyzed in five dimensions.

The possibilities of using the Debye–Waller approximation in real and phason spaces have been discussed. In real space, the Debye–Waller approximation requires the calculation of the second moment of the u distribution. This moment depends on the relative shift of the real structure and reference lattices, showing large oscillations for the scattering vectors approaching peak positions. The second moment is dominant for a certain shift, where the first moment is zero and the imaginary part of the structure factor is negligibly small. Use of the above analysis allows calculation of the diffraction pattern according to the Debye–Waller formula. Similar results for the intensities were obtained from analysis in real and phason spaces for quasicrystals.

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