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Static fluctuation distributions and their influence on diffraction patterns

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Abstract. Probability distributions of fluctuations of atomic positions around scattering vector dependent reference lattice points have been calculated for various crystalline and quasicrystalline structures, and their influence on the diffraction pattern has been discussed. For incommensurate scattering vectors flat fluctuation distributions are found, which change drastically when the scattering vector approaches the diffraction peak position. Moments of these distributions have been used to calculate the diffraction pattern. Limitations of the Debye–Waller approximation are discussed and a new more accurate method of peak intensity estimation is proposed and tested for real space and phason space fluctuations.

1. Introduction

It is well known that spatial fluctuations have great influence on diffraction patterns. Whenever the atomic positions fluctuate around lattice points the Bragg peak intensities decrease and their reductions are commonly approximated by the Debye–Waller factor. Usually, these fluctuations are thermally excited and they are time dependent. To calculate the Debye–Waller correction one has to know the mean square value of the atomic displacements from the lattice positions. There are many structures, such as quasicrystals, random structures and microtwins (Wolny and Pytlik 1991), which are not periodic so no lattice exists. However, even for those structures fluctuations can be calculated. For this purpose a scattering vector dependent reference lattice (Wolny and Pytlik 1991, Wolny 1992) has been defined. The period of this lattice is equal to the wavelength corresponding to the actual scattering vector. The distribution of the shortest distances (described by the variable u) between atomic positions and the reference lattice points fully determines the intensity of the diffraction pattern. As was shown in the previously mentioned papers only the first few moments of this distribution are important for diffraction pattern calculation. In that case the static approximation, normalized to N^2 intensity of the diffraction pattern, is given by the formula (Wolny and Pytlik 1991)

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

where I is the diffraction pattern intensity, k is the length of the scattering vector, N the number of atoms, $\langle u^m\rangle$ is the mth moment of u

$$\langle u^m\rangle = \frac{1}{N}\sum_{n=1}^{N} f_n(u_n)^m \tag{2}$$

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and f_n is an atomic form factor. Both $\langle u^m \rangle$ and u_n are scattering vector dependent.

The reference lattice can be shifted with respect to the real structure and for a certain value of the shift the second term of equation (1) becomes zero (Wolny 1992). This means that the imaginary part of the structure factor vanishes and the second moment of variable u is the dominating one. For this particular shift the diffraction pattern can be calculated by an approximation of formula (1) which looks similar to the well known Debye–Waller factor

$$I/N^2 = \exp(-k^2\langle u^2 \rangle). \tag{3}$$

Usually, the Debye–Waller factor describes only the reduction of peak intensities caused by thermal vibrations of atoms, and the second moment of u does not depend on the scattering vector. Recently (Jarić 1986, Tang and Jarić 1990, Henley 1991, Wolny and Pytlik 1992), this factor written in phason space was used to estimate peak intensities for static quasicrystals. Using formula (3) with the scattering vector dependent second moment of u, after an appropriate shift of the reference lattice, one can calculate the full diffraction pattern, not only estimate the peak intensity reduction. However, one should remember that equation (3) is only an approximation of the strictly valid equation (1) and the error of this approximation increases with decreasing value of peak intensities.

It is clear from the above that the probability distributions of variable u are fundamental for the shape of the diffraction pattern. In this paper several such distributions for different crystalline and quasicrystalline structures are discussed. Diffraction patterns have been calculated for two-dimensional structures only; however, similar results are obtained for the real three-dimensional structures.

2. Definition of structures

Two different types of structure have been chosen for further calculations. The first type are periodic two-dimensional structures, based on a hexagonal lattice, with random displacements of atoms from the periodic positions. The orientation of the displacements is random and their absolute values are given by a Gaussian distribution with standard deviation (parameter sigma) equal to 0.15 (figure 1(a)) or 0.5 (figure 1(b)) in units of the lattice vector. For simplicity the value of the lattice vector was chosen as unity. If, after these random displacements, the distance between two atoms was less than 0.3 one of them was removed. By this procedure the mean concentration of atoms decreased with increasing value of displacements, resulting in various more or less disordered structures. For small displacements (figure 1(a)) periodic lines of atoms are easily observed; however, higher values of random displacements (figure 1(b)) completely destroy that periodicity and the obtained structures are reminiscent of an amorphous structure rather than a crystalline one.

The second type, a quasicrystalline structure, was a two-dimensional tiling obtained by applying an inflation method to Robinson triangles (Wolny and Pytlik 1991). The atomic positions of such a perfectly ordered quasicrystalline structure (figure 2(a)) were subject to similar random displacements as discussed above but with the standard deviation of the Gaussian distribution equal to 0.15 (figure 2(b)).

3. Diffraction patterns

Diffraction patterns of the hexagonal structures calculated along the y direction (i.e. for $k_x = 0$) are shown in figures 3 and 4 for different values of introduced displacements and

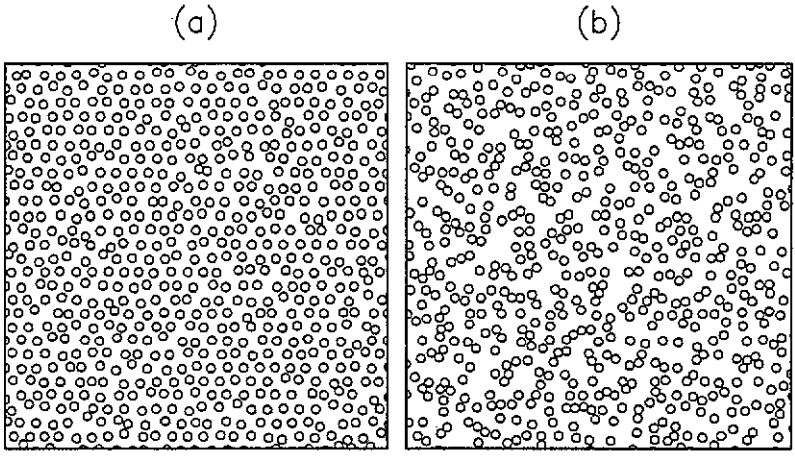

Figure 1. Hexagonal structures with different displacements of atoms from the lattice positions. The orientations of the displacements are random and their values are given by Gaussian distributions with the standard deviations (parameter sigma of the distribution) equal to 0.15 (*a*) and 0.5 (*b*). The value of the lattice vector is unity.

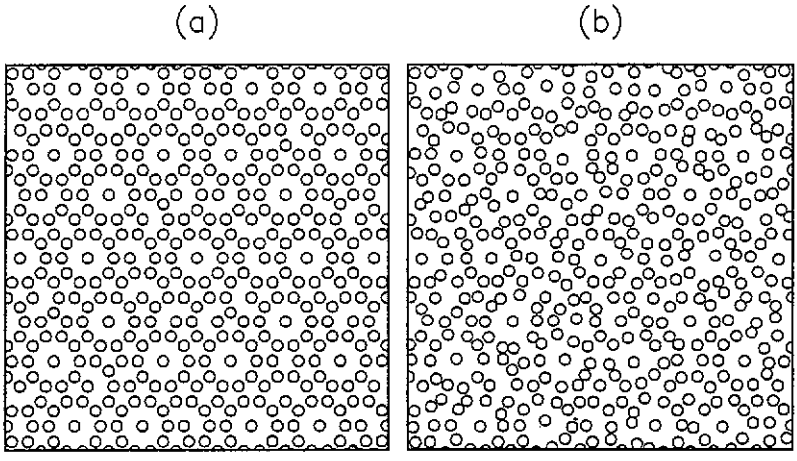

Figure 2. Quasicrystalline structures obtained by applying an inflation method to Robinson triangles: (*a*) perfect quasicrystal; (*b*) quasicrystal with random displacement of atoms given by a Gaussian distribution with the standard deviation equal to 0.15.

two different sizes of the structures used for calculations. For a structure with a small value of atomic displacements (figure 3) the diffraction patterns are dominated by Bragg peaks for both radii (i.e. $R = 5$ or 40) of the structure. The intensities of these peaks decrease with increasing value of scattering vector which can be described in the first approximation by the Debye–Waller factor (broken curve) for the mean square displacements from the periodic positions. Unfortunately, for higher values of scattering vector this approach fails and the peak intensities are much higher than those predicted by the Debye–Waller approximation. However, the accuracy of peak intensity estimation can be improved by using equation (1) written for the moments of u calculated in a special way. In this approach the moments

of the variable u, which in general depend on the scattering vector, are approximated by constant values, calculated for the scattering vector, corresponding to the first Bragg peak. These particular values of the moments are used to estimate all the other diffraction peak intensities along the same direction as the scattering vector. The results of this approach have been shown in figures 3 and 4 by dotted curves. From these figures one can easily notice that the discussed approximation estimates quite well the most intensive Bragg peaks, much better than can be obtained from the Debye–Waller formula. The diffraction pattern (figure 4) of the more disordered structure consists only of very weak peaks with intensities that would not be described by the Debye–Waller formula. The use of higher moments allows correct estimation of Bragg peaks even though the dotted curve obtained looks very unusual.

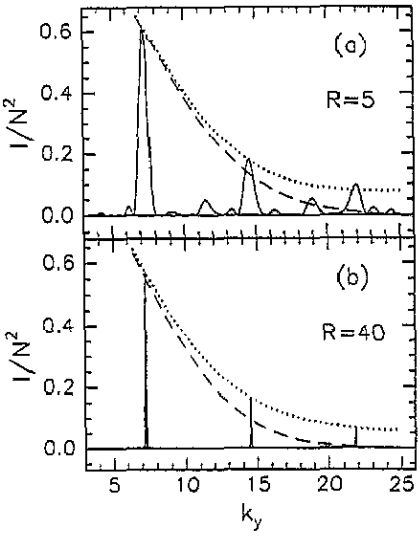

Figure 3. Diffraction patterns obtained by Fourier transformation of the structure presented in figure 1(*a*) ($\sigma = 0.15$) and calculated along the y direction ($k_x = 0$) for two radii of the structure: (*a*) $R = 5$ and (*b*) $R = 40$. The broken curves describe the peak intensities calculated in the Debye–Waller approximation, and the dotted curves those calculated by appropriate use of equation (1) for fluctuations calculated for the scattering vector describing the first Bragg peak position.

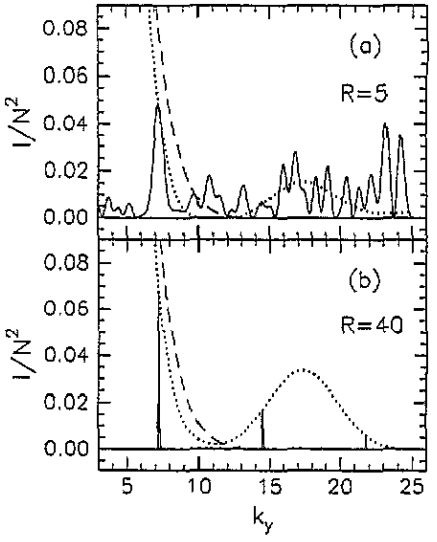

Figure 4. Diffraction patterns obtained from Fourier transformation of the structure presented in figure 1(*b*) ($\sigma = 0.5$) for two different radii of the structure: (*a*) $R = 5$ and (*b*) $R = 40$. The broken and dotted curves have been calculated in a similar way as in figure 3.

The maximum intensities of observed Bragg peaks normalized to N^2 do not depend on the size of the structure and/or number of atoms taken into account in the calculation. The above is true only for samples which are large enough to suppress the concentration fluctuations. The full width at half maximum (FWHM) of the peaks decreases continuously with increasing radius of the structure, similarly to what is observed for perfect crystals. A linear plot of FWHM versus the reciprocal of the structure dimension is obtained. Diffuse scattering easily observed in the diffraction pattern for $R = 5$ is hardly noticed for $R = 40$. This type of scattering scales as N and for higher numbers of atoms its contribution to the diffraction pattern compared to the Bragg peaks decreases. The diffuse scattering is

especially significant for structures with higher values of atomic displacements (figure 4). For smaller radius (e.g. $R = 5$) the diffuse peaks are as strong as the Bragg ones; however, when the radius of the structure increases the Bragg peaks start to dominate in the diffraction pattern.

The diffraction pattern of the quasicrystalline structure (figure 5(*a*)) was discussed in the previous paper (Wolny and Pytlik 1991) both in real space and phason space. It was shown (see also Jarić 1986) that the diffraction pattern is aperiodic in a linear scale of scattering vector but can be divided into a periodic series of peaks in a logarithmic scale of scattering vector (with a period equal to $\ln(\tau)$), such that

$$k_n = k_0 \tau^n \tag{4a}$$

and

$$k_n^{\text{perp}} = k_0(-\tau)^{-n} \qquad (n = 0, 1, 2, 3, \ldots) \tag{4b}$$

where k_n^{perp} is a perpendicular space (perp-space or phason space) component of the scattering vector, k_0 is a constant and τ is an irrational number equal to about 1.618. The first three series of peaks calculated along the y direction for structures built up with Robinson triangles are described by $k_0 \simeq 2.9545$, 5.9091 or 6.6065. An increase of peak intensities belonging to the same series with increasing value of scattering vector is observed and can be described analytically by the Debye–Waller factor in phason space (Wolny and Pytlik 1991). In this approach the intensities of diffraction peaks belonging to the same series can be described by the formula

$$I(k_y)/N^2 = \exp[-(k_0)^4\langle h^2\rangle/(k_y)^2] \tag{5}$$

where $\langle h^2\rangle$ is a mean square value of phason fluctuations. The broken curves shown in figure 5 have been calculated according to (5) for the three different values of k_0 given above. In a similar way to real-space fluctuations the Debye–Waller approximation in phason space fails for lower-intensity diffraction peaks. This means that higher-order moments of phason fluctuations cannot be neglected for these peaks. Equation (1) written for phason fluctuations is

$$I(k_y)/N^2 = (1 - k_0^4\langle h^2\rangle/(2!k_y^2) + k_0^8\langle h^4\rangle/(4!k_y^4) - \ldots)^2 + (k_0^2\langle h\rangle/k_y - k_0^6\langle h^3\rangle/(3!k_y^3) + \ldots)^2 \tag{6}$$

and this has been plotted in figure 5 as dotted curves for appropriate values of k_0. The moments of the phason fluctuations were calculated for a given structure as described by Wolny and Pytlik (1991). In principle, only even moments have been used and the contribution of odd moments has been neglected. It can be seen from figure 5 that formula (6) essentially improves the approximation of peak intensities, especially the weakest peaks at higher values of scattering vector.

The diffraction pattern of the quasicrystalline structure with random displacement of atoms is shown in figure 5(*b*). Bragg peaks appear for the same scattering vector as given by (4); however, their intensities are governed, in the first approximation, by a product of two Debye–Waller factors (broken curve): one in phason space (5) and the other written for random displacements of atoms from ideal quasicrystalline positions in real space (equation (3) written for the second moment of these displacements). The Debye–Waller factor written

in phason space increases the intensities of the diffraction peaks belonging to the same series with increasing value of scattering vector (similar to the case for perfect quasicrystals). On the other hand the Debye–Waller factor written for random displacements in real space reduces the peak intensities with increasing value of scattering vector. As a final result of these two factors, peak intensities belonging to the same series pass through a maximum for a certain scattering vector as observed in figure 5(*b*). Also in this case the higher-order moments of fluctuations in both spaces, real and phason, are essential for Bragg peaks with small intensities. The peaks are much better described by the dotted curves which have been calculated as a product of equations (1) and (6) written for the moments of the real-space displacements from the ideal quasicrystalline positions and the appropriate moments of perp-space fluctuations.

4. Probability distributions of fluctuations

Probability distributions of fluctuations of atomic positions around the points of the reference lattice depend on scattering vector. The range of the variable u describing the fluctuations is from $-\lambda/2$ to $+\lambda/2$, where λ is the wavelength for the wave vector k ($\lambda = 2\pi/k$). In units of λ all the fluctuations are bounded to the range from -0.5 to 0.5 and the Debye–Waller type formula (3) can be written as

$$I(k)/N^2 = \exp[-4\pi^2\langle(u/\lambda)^2\rangle]. \tag{7}$$

When fluctuations are given in units of λ the intensity of the diffraction pattern calculated by (7) depends only on the second moment of the probability distribution of this new variable, and explicit dependence on the scattering vector vanishes. The above applies not only to the Debye–Waller type factor but also to formula (1) written for the related variable (u/λ)

$$\begin{aligned} I(k)/N^2 = {} & [1 - (2\pi)^2\langle(u/\lambda)^2\rangle/2! + (2\pi)^4\langle(u/\lambda)^4\rangle/4! - \ldots]^2 \\ & + [2\pi\langle(u/\lambda)\rangle - (2\pi)^3\langle(u/\lambda)^3\rangle/3! + \ldots]^2. \end{aligned} \tag{8}$$

Equation (8) means that the full diffraction pattern can be calculated from the probability distributions of this new variable. In principle, only the first few moments of these distributions are important and, as has been discussed above, for the Debye–Waller approximation preceded by an appropriate shift of the reference lattice, only the second moment is used for diffraction pattern calculation. For uniform distribution (i.e. when $P(u/\lambda)$ is a constant equal to unity) the value of the second moment is equal to $\frac{1}{12}$ and according to (7) the intensity of the diffraction pattern is about 0.037. This value estimates the background of the diffraction pattern calculated according to the Debye–Waller approximation (Wolny 1992). Several probability distributions calculated for the hexagonal structure with small displacements of atoms from their periodic positions are shown in figure 6 for different values of the scattering vector along the y direction, with $k_x = 0$. For a scattering vector corresponding to the position of the first diffraction peak (i.e. $k = k_y = 2\pi/\sin(\pi/3) \simeq 7.26$) the probability distribution of related fluctuations (u/λ) is an almost symmetrical function having a maximum at the zero value of the fluctuations. The distribution is rather sharp with a small value of the second moment which, according to (7), corresponds to relatively high diffraction peak intensity. For the next peaks the distributions become broader and the second moment increases, which reduces the diffraction peak intensities. For perfect crystalline structures (i.e. without any atomic displacements),

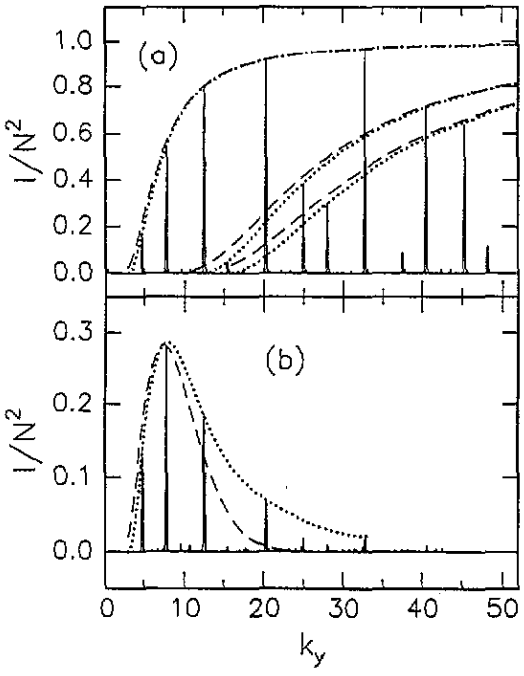

Figure 5. Diffraction patterns calculated along the y direction for the quasicrystalline structures shown in figure 2: (*a*) perfect quasicrystal; (*b*) quasicrystal with random displacement of atoms. The radius of the structure was equal to 20. The broken curves represent a product of two Debye–Waller factors calculated in real space and phason space. The dotted curves have been calculated as a product of two equations: (1) (for frozen phonons) and (6) (for frozen phasons)—see text.

with a primitive unit cell, the fluctuation distributions calculated for scattering vectors at diffraction peak positions are delta functions with the second moment equal to zero. This gives the diffraction pattern normalized to N^2 with all peak intensities equal to unity.

For scattering vectors which are incommensurate with the reciprocal lattice of the structure the probability distributions are constant and equal to unity. When the scattering vector approaches commensurate values the distribution fluctuations start to oscillate (figure 6(*b*)). For example, if the scattering vector is half of the reciprocal lattice vector the discussed distribution function has two maxima. In figure 6(*b*) these maxima (full curve) occur for u/λ corresponding to 0 and 0.5 respectively (the value -0.5 of related fluctuations is symmetry equivalent to 0.5). In general, if the scattering vector k is commensurate with the reciprocal vector k_0 with the relation $k = k_0/n$, the distribution function has n maxima. Usually, for such scattering vectors and a Debye–Waller type approximation (3), one has to shift the reference lattice appropriately (Wolny 1992) to decrease the higher-order moment contribution to the diffraction pattern. However, even then a weak artificial peak is observed in the calculated diffraction pattern for $k = k_0/2$, with a maximum intensity of about 8% of the corresponding peak at $k = k_0$. The intensities of higher-order peaks ($k = k_0/n$, with $n = 3, 4, 5, \ldots$) can be neglected. These artificial peaks are present in diffraction patterns calculated according to formula (3), but they do not appear if only higher-order moments are considered (equation (1)).

For the hexagonal structure with a higher value of atomic displacements (figure 1(*b*))

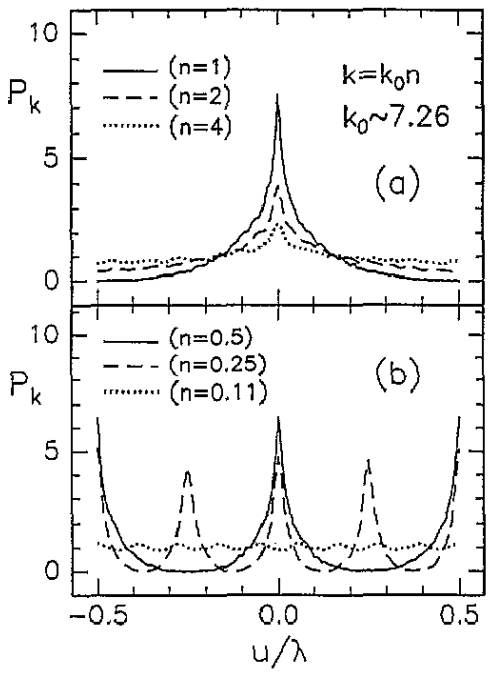

Figure 6. Probability distributions of reduced fluctuations (u/λ) for the hexagonal structure with small deviations from lattice positions (figure 1(*a*)). Calculations have been performed for scattering vectors corresponding to (*a*) the first, second and fourth peaks observed in diffraction patterns (figure 2), and (*b*) some rational fractions (0.5, 0.25, and 0.11) of the value of the first diffraction peak.

the probability distributions shown in figure 7 are similar to that presented in figure 6(*a*). However, the distributions are much broader, which corresponds to the higher values of the second moments and lower diffraction peak intensities. In principle, for such broad distributions the Debye–Waller type formula (3) gives the correct value of peak position but an incorrect value of the peak intensity (see also the discussion in the previous section). The corrections originating from higher moments are as important as the value of the second moment itself and to calculate the diffraction pattern the full series expansion (formula (1)) should be used.

For perfect quasicrystals the probability distributions of fluctuations around points of the reference lattice behave differently than previously discussed. Distributions corresponding to the first series of diffraction peaks described by (4) are shown both for the perfect quasicrystal (figure 8(*a*)) and the quasicrystalline structure with random displacements of atoms (figure 8(*b*)). These diffraction peak intensities increase with increasing value of scattering vector, which is connected with the narrowing of the appropriate distributions of fluctuations (in real space). When the value of the scattering vector approaches infinity the distributions corresponding to scattering vectors given by (4) become a delta function and the intensities of the appropriate diffraction peaks are equal to unity. The same behaviour of diffraction peaks is also observed for other tilings (twins, random or precipitated, see Wolny and Pytlik 1991); however, for these structures probability distributions of fluctuations as well as peak intensities depend on the number of scattering atoms and/or the size of the structure.

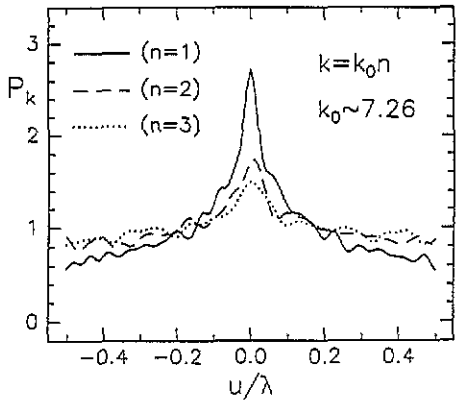

Figure 7. Probability distributions of reduced fluctuations (u/λ) for the hexagonal structure shown in figure 1(b) ($\sigma = 0.5$) calculated for scattering vectors corresponding to the first three diffraction peaks.

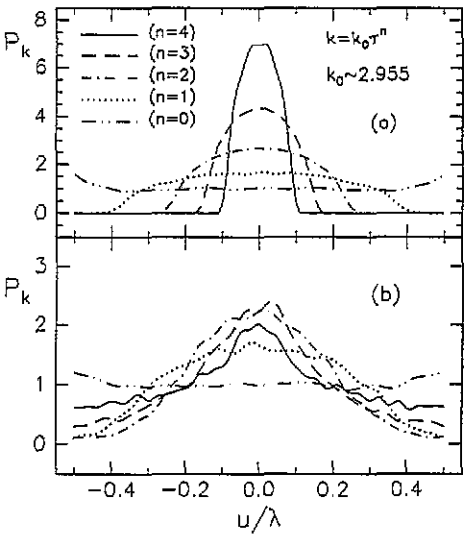

Figure 8. Probability distributions of reduced fluctuations (u/λ) calculated for the first series of peaks of quasicrystalline structures: (a) the perfect quasicrystal shown in figure 2(a); (b) the quasicrystal with random displacements of atoms from figure 2(b).

5. Summary

The intensity of the diffraction pattern depends on the moments of the probability distributions of the variable (u/λ), which describes the related shortest distance between atomic positions and points of the reference lattice. Several such distributions have been calculated for two-dimensional structures: hexagonal and quasicrystalline ones. For the hexagonal structure the positions of atoms have been subject to some additional displacements from their lattice points. These random displacements reduce the intensity of Bragg peaks (in the first approximation according to the Debye–Waller type formula) and increase the contribution of diffuse scattering. Different scaling with number of atoms separates these two components of the diffraction pattern. For a high enough number of atoms the Bragg peaks dominate in the diffraction pattern even for a disordered structure such as that shown in figure 1(b). Probability distributions of fluctuations around the points of the reference lattice have been calculated for different values of scattering vector. Whenever the scattering vector describes the position of any peak in the diffraction pattern, the corresponding distribution of reduced fluctuations (u/λ) has a maximum, which goes to infinity as the value of the diffraction peak intensity approaches unity. For lower-intensity diffraction peaks the corresponding distributions become broader. When the scattering vector is incommensurate to any vectors describing diffraction peak positions, the probability distribution is a flat function of (u/λ) with the value of the second moments equal to $\frac{1}{12}$. According to (7) this gives a diffraction intensity equal to about 0.037, which is the value of the background in the Debye–Waller type approximation. For a commensurate value of the scattering vector several maxima can be observed in the fluctuation distributions. For example, when the scattering vector is half of the diffraction peak vector, one obtains a two-state distribution. In this case, the Debye–Waller type formula can be used after an

appropriate shift of the reference lattice. However, even then a weak artificial peak is still left in the calculated diffraction pattern.

Diffraction peaks of quasicrystals are also strictly connected with the distributions of spatial fluctuations around reference lattice points. For the series of peaks given by (4) the corresponding fluctuation distributions become sharper for higher values of scattering vector. This gives an increasing value of the higher-order diffraction peak intensities in the same series. Diffraction patterns of quasicrystals can also be calculated using the Debye–Waller approximation to fluctuations of perpendicular space components. However, in this approach only maxima of diffraction peak intensities can be estimated in the limit of validity of the Debye–Waller approximation. For the quasicrystalline structure with random displacement of atoms, diffraction peak intensities can be estimated by a product of two Debye–Waller factors calculated in perpendicular (phason) and real spaces.

It has been shown that the Debye–Waller approximation in phason space gives incorrect results for lower-intensity peaks, especially at higher values of scattering vector. For these peaks higher-order moments of fluctuation distribution are not negligible and should be taken into account by using formula (1). This formula can be modified to also include phason fluctuations and quite satisfactory results have been obtained for the perfect quasicrystalline structure (i.e. with only phason distribution) as well as for the quasicrystalline structure with random displacement of atoms (i.e. with frozen distributions of phasons and phonons).

Acknowledgments

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