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Structure-Factor Calculations in Refinement of a Modulated Crystal Structure

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Abstract

Problems concerning structural analysis of a one-dimensionally modulated structure using its $(3+1)$-dimensional symmetry are discussed. Simple modifications of the common structure-factor formula for occupational, displacive with small amplitudes and mixed modulation are obtained. The integral form of the structure factor known from literature is critically considered and an analytical form for harmonic displacive (not necessarily rectilinear) modulation has been found. Analytical corrections to the temperature factors have been introduced and generalized to cover the phase relationships of elliptic modulating waves. The results of this paper have been used to prepare a set of programs to refine modulated structures.

1. Introduction

As a result of many important works by de Wolff, Janssen & Janner (1981, and references therein), progress in the symmetry description of modulated structures by higher-dimensional crystallographic symmetry has been obtained. An alternative approach, based on the concept of wreath product, has been presented by Litvin (1980) and Koptsik (1978).

In the works by Yamamoto (1982*a, b, c*) a $(3+d)$-dimensional crystallographic symmetry approach has been applied to the structure refinement and the structure-factor formula (SFF) suitable for this purpose has been presented.

The form of the Debye-Waller factor for modulated structure has been discussed in papers by Overhauser (1971), Axe (1980) and Adlhart (1982) and applied by Steurer & Adlhart (1983) in the refinement of α-bis(N-methylsalicylideneiminato)nickel(II).

Although the SFF presented by Yamamoto covers practically all kinds of modulation, the necessity of numerical integration makes application unlikely in many cases for which much simpler formulae would be sufficient. There are also some questions still open concerning temperature-factor corrections, especially in relation to the treatment proposed by Overhauser and Axe. As will be discussed later, the approaches of Yamamoto and Adlhart can lead to different results.

The present work deals with structure factors of special as well as general (elliptical displacive waves included) cases of modulations. The compact analytical expression convenient for computing in the case of occupational, displacive with small amplitudes, mixed and general types of modulation in the harmonic approximation will be presented and their limitations discussed.

An extension of the temperature-factor corrections proposed by Axe is proposed for the case of general harmonic modulation with displacive wave.

Our considerations are restricted to the single-q modulated structures described by $(3+1)$-dimensional crystallographic groups.

The notation used in this paper is mostly adopted from original papers by de Wolff and Yamamoto in order to make the comparison easier.

2. Single-q modulated structure description

In the modulated structure the positional, occupational and thermal parameters can be written as periodic functions of a continuous parameter [or parameters in multidimensional modulation, see Yamamoto (1982*a*) for that more general case and the notation] as follows:

$$x_i^\mu(\bar{x}_4^\mu) = \bar{x}_i^\mu + \sum_n u_{i,n}^\mu \varepsilon_n + \text{c.c}, \quad i = 1, 2, 3,$$

$$y^\mu(\bar{x}_4^\mu) = \sum_n y_n^\mu \varepsilon_n + \text{c.c}, \quad y^\mu = P^\mu, B^\mu \text{ or } B_{ij}^\mu, \quad (2.1)$$

where $\varepsilon_n = \exp(2\pi i \bar{x}_4^\mu)$, μ enumerates the symmetry-independent atoms and c.c means the complex conjugate terms with coefficients denoted as $u_{t,-n}^\mu$ or y_{-n}^μ. Furthermore, the quantities with the subscripts 4 are related to those with the smaller subscripts by the following equations:

$$x_4^\mu = \mathbf{q} \mathbf{x}^\mu = \sum_{i=1}^3 q_i x_i^\mu$$

$$B_{i4}^\mu = B_{4i}^\mu = \sum_{j=1}^3 B_{ij}^\mu q_j \qquad (2.2)$$

$$B_{44}^\mu = \sum_{i,j=1}^3 q_i B_{ij}^\mu q_j.$$

The modulation vector $\mathbf{q}$ is related to the diffraction pattern as follows:

$$\mathbf{h}' = h_1 \mathbf{a}^* + h_2 \mathbf{b}^* + h_3 \mathbf{c}^* + h_4 \mathbf{q},$$

$h_1, \ldots, h_4$ are integers, where $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ are basic-structure reciprocal-lattice vectors. The vector $\mathbf{h}'$ can be regarded as a projection of the four-dimensional vector $\mathbf{h} = \sum_{i=1}^4 h_i \mathbf{b}_i$, $\mathbf{b}_1 = (\mathbf{a}^*, 0)$, $\mathbf{b}_2 = (\mathbf{b}^*, 0)$, $\mathbf{b}_3 = (\mathbf{c}^*, 0)$, $\mathbf{b}_4 = (\mathbf{q}, 1)$. In the incommensurate case the correspondence between $\mathbf{h}$ and $\mathbf{h}'$ is one to one.

In real space the atomic coordinates can be regarded as projections of vectors in four-dimensional space with the basic vectors $\mathbf{a}_1 = (\mathbf{a}, -q_1)$, $\mathbf{a}_2 = (\mathbf{b}, -q_2)$, $\mathbf{a}_3 = (\mathbf{c}, -q_3)$, $\mathbf{a}_4 = (0, 1)$. The $\bar{x}_4^\mu$ component is a continuous parameter corresponding to the phase of the modulating function. In the basis introduced above, the action of the four-dimensional crystallographic symmetry operation $(R|\tau)$ on the positional, occupational and thermal parameters of atom μ can be defined as follows:

$$\bar{x}_i^\lambda = \sum_{j=1}^4 R_{ij} \bar{x}_j^\mu + \tau_i$$

$$x_i^\lambda(\bar{x}_4^\lambda) = \sum_{j=1}^4 R_{ij} x_j^\mu(\bar{x}_4^\mu) + \tau_i$$

$$B_{ij}^\lambda(\bar{x}_4^\lambda) = \sum_{k,l=1}^4 R_{ik} B_{kl}^\mu(\bar{x}_4^\mu) R_{jl} \qquad (2.3)$$

$$B^\lambda(\bar{x}_4^\lambda)[\text{or } P^\lambda(\bar{x}_4^\lambda)] = B^\mu(\bar{x}_4^\mu)[\text{or } P^\mu(\bar{x}_4^\mu)]$$

$$i, j = 1, \ldots, 4.$$

For these equations, the parameters of the symmetry-equivalent atom λ can be generated from the parameters of the atom μ. It is very important that the crystallographic symmetry introduced in this way is higher than the actual three-dimensional one.

During the structure refinement of structure-factor calculations it may be useful to define the action of the rotations on reflection indices rather than positional or anisotropic thermal parameters as follows

(see Rollet, 1965):

$$h_i^s = \sum_{j=1}^4 R_{ji}^s h_j, \quad i = 1, \ldots, 4$$

$$H_i^s = h_i^s + h_4^s q_i, \quad i = 1, 2, 3, \qquad (2.4)$$

where s counts the symmetry elements. The SFF has the following form:

$$F(\mathbf{h}) = \sum_{\mu,s} M^\mu f^\mu(\mathbf{h}') \int_0^1 d\bar{x}_4^\mu P^\mu(\bar{x}_4^\mu)$$

$$\times \exp\left\{ - \sum_{i,j=1}^3 H_i^s B_{ij}^\mu(\bar{x}_4^\mu) H_j^s \right.$$

$$\left. + 2\pi i \sum_{i=1}^4 [h_i^s x_i^\mu(\bar{x}_4^\mu) + h_i \tau_i^s] \right\}, \qquad (2.5)$$

where μ counts the symmetry-independent atoms, M^μ is the multiplicity and $f^\mu(\mathbf{h}')$ is the atomic scattering factor of the μth atom. The relationship between three- and four-dimensional notations can be discussed by the following equations:

$$\sum_{i,j=1}^4 h_i^s B_{ij}^\mu(\bar{x}^\mu) h_j^s = \sum_{i,j=1}^3 H_i^s B_{ij}^\mu(\bar{x}_4^\mu) H_j^s$$

$$\sum_{i=1}^4 h_i^s u_i^\mu(\bar{x}_4^\mu) = \sum_{i=1}^3 H_i^s u_i^\mu(\bar{x}_4^\mu). \qquad (2.6)$$

As will be discussed below, in some cases important for applications (2.5) can be significantly simplified, because the integration can be performed analytically rather than numerically. However, (2.5) is suitable for more complicated modulations (e.g. anharmonic).

3. Small-displacive-modulation-amplitude approximation

Throughout this and the next sections the assumption is made that the temperature factors are not modulated, $B_{ij,n}^\mu = 0$ for $n \neq 0$. This is not a strong restriction. As will be discussed later, the refinement procedure based on the zero-order terms $B_{ij,0}^\mu$ partially covers the anomalous thermal vibrations due to structural modulation.

To simplify the notation the following quantity can be extracted from SFF (2.5):

$$W_s^\mu(\mathbf{h}) = M^\mu f^\mu(\mathbf{h}') \exp\left\{ - \sum_{i,j=1}^3 H_i^s B_{ij,0}^\mu H_j^s \right.$$

$$\left. + 2\pi i \sum_{i=1}^3 [(h_i^s \bar{x}_i^\mu + h_i \tau_i^s) + h_4 \tau_4^s] \right\}. \qquad (3.1)$$

In addition, the new notation for satellite indices h_4 and h_4^s is used: $h_4 = m$, $h_4^s = m(s)$.

If all displacive modulation amplitudes are equal to zero the modulation is purely occupational. Using the notation introduced, the SFF can be written in

the following form:

$$F(\mathbf{h}) = \sum_{s,\mu} W_s^\mu(\mathbf{h}) P_{-m(s)}^\mu. \qquad (3.2)$$

As pointed out by Yamamoto, this type of modulation leads to serious phase problems during structure refinement, but this problem will not be discussed here.

The next simple case is the pure displacive modulation with small amplitudes. In this case the expansion $\exp(x) \simeq 1 + x + \ldots$ can be used and the SFF reads

$$F(\mathbf{h}) = \sum_{s,\mu} W_s^\mu(\mathbf{h}) P_0^\mu \left(\delta_{m(s),0} + 2\pi i \sum_{i=1}^{3} H_i^s u_{i,-m(s)}^\mu \right), \qquad (3.3)$$

where $\delta_{m,n}$ is the Kronecker delta function and $u_{i,0}^\mu = 0$ according to the assumption that the average displacement is zero. It is easy to see that the range of harmonics taken into account should be greater than or equal to that of satellite reflections. Furthermore, in both cases discussed above the main reflections are not affected by the modulation functions. Strictly, this is not true for the mixed displacive and occupational modulation leading to the SFF in the form

$$F(\mathbf{h}) = \sum_{s,\mu} W_s^\mu(\mathbf{h}) \left(P_{-m(s)}^\mu + 2\pi i \sum_{n=N}^{M} P_n^\mu \sum_{i=1}^{3} H_i^s u_{i,-m(s)-n}^\mu \right), \qquad (3.4)$$

where $N = N_{max} - m(s)$, $M = -N_{max}$ for $m(s) \geq 0$ and $N = N_{max}$, $M = -N_{max} - m(s)$ for $m(s) < 0$ and N_{max} is the maximal range of the harmonics included (it is assumed that $N_{max} \geq |m(s)|$ for each satellite reflection). However, the terms with $n \neq 0$ lead to corrections smaller than the error caused by the approximation $J_0(x) \simeq 1$ for the zero-order Bessel function (see next section), and can be neglected.

4. Harmonic approximation for displacive modulation

To analyse the harmonic approximation for displacive modulation it is convenient to change the parametrization of the modulating functions as follows:

$$u_{i,1}^\mu \varepsilon_1 + \text{c.c} = \alpha_i^\mu \sin\left[2\pi(\bar{x}_4^\mu + \varphi_i^\mu)\right], \quad i = 1, 2, 3, \quad (4.1)$$

and $u_{i,n}^\mu = 0$ for $n \neq 1$. This type of structural modulation has been discussed in the literature under additional restrictions on the parameters α_i^μ and φ_i^μ. Such models include pure longitudinal and transverse modulations (see e.g. Böhm, 1975) or, more generally, rectilinear modulation ($\varphi_i^\mu = \varphi^\mu$, $i = 1, 2, 3$). We will discuss the general modulation of the harmonic type (see van Aalst, den Hollander, Peterse & de Wolff, 1976), taking into account its $(3 + 1)$-dimensional symmetry.

Using the Anger–Jacobi generating function and the Graff summation theorem for Bessel functions the SFF (2.5) can be transformed by the following substitution:

$$\exp\left\{ 2\pi i \sum_{i=1}^{3} H_i^s \alpha_i^\mu \sin\left[2\pi(\bar{x}_4^\mu + \varphi_i^\mu)\right] \right\}$$

$$= \prod_{i=1}^{3} \sum_{n(i)=-\infty}^{\infty} J_{n(i)}(2\pi H_i^s \alpha_i^\mu)$$

$$\times \exp\left[2\pi i n(i)(\bar{x}_4^\mu + \varphi_i^\mu)\right]$$

$$= \sum_{n=-\infty}^{\infty} J_n[\kappa_s^\mu(\mathbf{h})] \exp\left\{2\pi i n[\bar{x}_4^\mu + \varphi_s^\mu(\mathbf{h})]\right\}, \quad (4.2)$$

where $\kappa_s^\mu(\mathbf{h})$ and $\varphi_s^\mu(\mathbf{h})$ are defined by the equation

$$\kappa_s^\mu(\mathbf{h}) \exp\left[2\pi i \varphi_s^\mu(\mathbf{h})\right] = 2\pi \sum_{i=1}^{3} H_i^s \alpha_i^\mu \exp\left(2\pi i \varphi_i^\mu\right). \qquad (4.3)$$

The SFF can then be transformed to the form

$$F(\mathbf{h}) = \sum_{s,\mu} W_s^\mu(\mathbf{h}) P_0^\mu J_{-m(s)}[\kappa_s^\mu(\mathbf{h})]$$

$$\times \exp\left[-2\pi i m(s)\varphi_s^\mu(\mathbf{h})\right]. \qquad (4.4)$$

Although the SFF obtained has a form quite similar to that known from literature, all the restrictions on modulating parameters mentioned above have been removed. Furthermore, the $(3 + 1)$-dimensional symmetry has been introduced to the formula in the form suitable for calculations.

Contrary to the approximation discussed in § 3, in the currently discussed modulation described by the first-order harmonics only, an arbitrary order of satellite reflections can be observed in the diffraction pattern. The scattering amplitude $F(\mathbf{h})$ contains the terms proportional to the Bessel functions of order equal to the order of the satellite reflection. This is not true for mixed modulation described by the following SFF:

$$F(\mathbf{h}) = \sum_{s,\mu} W_s^\mu(\mathbf{h}) \sum_n P_n^\mu J_{-m(s)-n}[\kappa_s^\mu(\mathbf{h})]$$

$$\times \exp\left\{-2\pi i [m(s)+n]\varphi_s^\mu(\mathbf{h})\right\}. \qquad (4.5)$$

In that case the satellite reflection of order m is also affected by the Bessel functions of order different from m. A similar effect of mixing the different order terms can also be caused by the temperature-factor modulation, as will be discussed in the next section. The range of the summation over n is limited by the occupational modulation harmonics range only [see (3.4)]. Each reflection is affected by all harmonics of both occupational and displacive modulating functions, but the main contribution to the structure factor is the harmonic of the satellite reflection order.

5. Modulation and temperature factors

The modification of the temperature (Debye–Waller) factor due to the structural modulation has been discussed by Overhauser (1971), Axe (1980) and Adlhart (1982) from the physical point of view. A phenomenological description of the temperature factors in the form of the modulating function, analogously to the other parameters, has been introduced by Yamamoto (1982a).

The difficulties in the description of the thermal vibrations of the modulated structure are caused by the complicated relationships between the displacive wave parameters and the parameters introduced on the temperature factor (e.g. the mean-square fluctuations of the phases or amplitudes).

Let us discuss the Overhauser approach. In our notation the corrected temperature factor has the form:

$$T_s^\mu = \exp\left[-\sum_{i,j=1}^{4} h_i^s B_{ij,0}^\mu h_j^s - (h_4^s)^2 \langle \varphi_\mu^2 \rangle / 2 \right], \quad (5.1)$$

where $\langle \varphi_\mu^2 \rangle$ is the mean-square phase fluctuation of the displacive modulating wave of the atom μ. The term $\exp[-(h_4^s)^2 \langle \varphi_\mu^2 \rangle / 2]$ is known as the Overhauser correction. Note that $(h_4^s)^2$ is the order of the satellite reflection squared. It is easy to see that the simplest way to introduce such a correction during the structure refinement is to take the $B_{44,0}^\mu$ parameters as refined quantities [the corresponding (2.6) is not valid in that case]. However, as a result, the displacive amplitudes obtained in this way are higher and can be regarded as parameters not affected by the phase fluctuations.

As was pointed out by Axe, the Overhauser correction can be modified to the form $\exp[-m(m-1)\times\langle \varphi_\mu^2 \rangle / 2]$, where $m = |h_4^s|$. In that case the resulting displacive amplitudes are the effective quantities, affected by the phase fluctuations, and they are smaller than in the previous case. This effect has been observed by Steurer & Adlhart (1983). Furthermore, it is seen that no correction is needed when only the first-order satellites are observed.

In a more detailed analysis both phase and amplitude fluctuations are taken into account. As a result the corrections to the temperature factors contain two parts: the first one affects the (ordinary) $B_{ij,0}^\mu$ terms and the second one is described by the modulated temperature factor with the amplitudes $B_{ij,2}^\mu$ only. The correction of the first type cannot be separated from the normal temperature factors during the structure refinement. In addition, both types of corrections contain partially both amplitude and phase fluctuations.

To analyse the $\bar{x}_4^\mu$-dependent terms the temperature-factor modulating waves should be transformed to the form:

$$B_{ij,n}^\mu \varepsilon_n + \text{c.c} = \beta_{ij,n}^\mu \cos\left[2\pi n(\bar{x}_4^\mu + \psi_{ij}^\mu) \right]. \quad (5.2)$$

With a similar procedure as in §4 [see (4.2)], the temperature-factor part of the SFF can be written as follows:

$$\exp\left\{ -\sum_{i,j=1}^{3} H_i^s \beta_{ij,n}^\mu H_j^s \cos\left[2\pi n(\bar{x}_4^\mu + \psi_{ij}^\mu) \right] \right\}$$

$$= \sum_{m=-\infty}^{\infty} I_m[\chi_s^\mu(\mathbf{h})] \exp\{2\pi i n m[\bar{x}_4^\mu + \psi_s^\mu(\mathbf{h})]\},$$

$$(5.3)$$

where [similar to (4.3)]:

$$\chi_s^\mu(\mathbf{h}) \exp[2\pi i n \psi_s^\mu(\mathbf{h})]$$

$$= -\sum_{i,j=1}^{3} H_i^s \beta_{ij,n}^\mu H_j^s \exp(2\pi i n \psi_{ij}^\mu) \quad (5.4)$$

and $I_m(x)$ is the modified Bessel function. Combining this result with (4.4), one can get the SFF in the form close to that derived by Axe (1980) and Adlhart (1982) under the assumption $n = 2$. In the pure displacive case the SFF has the form

$$F(\mathbf{h}) = \sum_{s,\mu} W_s^\mu P_0^\mu \exp\left[-m(s)\varphi_s^\mu(\mathbf{h}) \right]$$

$$\times \sum_{n=-\infty}^{\infty} J_{-m(s)-2n}[\kappa_s^\mu(\mathbf{h})] I_n[\chi_s^\mu(\mathbf{h})]$$

$$\times \exp\{4\pi i n[\psi_s^\mu(\mathbf{h}) - \varphi_s^\mu(\mathbf{h})]\}. \quad (5.5)$$

As shown in the Appendix,* our result is an extension of their results to cover more general phase relationships introduced in the displacive modulating functions. In addition the following relation holds:

$$\psi_{ij}^\mu = (\varphi_i^\mu + \varphi_j^\mu)/2 \quad (5.6)$$

so only $\beta_{ij,2}^\mu$ terms are the refined quantities.

In all the corrections of the temperature factors known so far from the literature the appearance of $B_{ij,1}^\mu$ terms is not expected. There is, however, a refinement procedure proposed by Yamamoto where such terms (and also higher-order harmonics) are taken into account. This leads to a considerable increase of the number of parameters to be refined (twelve parameters per one harmonic in the general anisotropic case). A strict relationship between such a treatment of the temperature factors and that discussed above is not established yet and would require further investigation.

6. Comments

There are generally two trends among crystallographers when dealing with modulated structure

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analysis. The first is to apply the three-dimensional symmetry for basic or average structure and to develop a model SFF, usually simplified, based on extra periodic parameters, without definite solution of the symmetry problems [eventually reducing the problem to that of the superstructure, see *e.g.* Böhm (1975), Shiozaki (1971) and Schulz (1974)]. The second approach is based on the development of the $(3+d)$-dimensional space-group theory (Yamamoto, 1983). This makes it possible to refine the modulated structure in an analogous way to that of normal structure, but at the cost of a more complicated form of SFF, which requires numerical integration. In addition, one has to face ambiguity when dealing with the temperature factors. The present study shows that the $(3+1)$-dimensional symmetry approach to the structure refinement can be simplified in many cases important in practice.

The analytical form of the SFF has been presented for harmonic approximation with arbitrarily oriented amplitudes (*e.g.* elliptic waves), small displacive amplitudes, the corresponding mixed displacive and occupational modulations and for the temperature factors in a new form able to describe the thermal vibrations in the case of elliptic displacive harmonic waves. The temperature-factor corrections obtained are in keeping with corrections by Axe based on physical assumptions. We have shown that these corrections correspond to the zero- and second-order temperature-factor harmonics among those introduced by Yamamoto.

The results of this paper have been used to prepare a set of least-squares-refinement-type programs to refine the modulated structures. These programs have been successfully applied in the refinement of the modulated phase of $NaNO_2$.

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Refinement of the Incommensurate Crystal Structure of NaNO₂ in (3+1)-Dimensional Space Groups

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Abstract

Two basic models of the incommensurate (IC) structure of $NaNO_2$, one with purely occupational modulation and one with mixed modulation, have been tested using $(3+1)$-dimensional space groups. The refinements were performed in the two superspace groups $P^{I\frac{m}{1}\frac{m}{s}\frac{m}{1}}$ and $P^{I\frac{2}{s}\frac{m}{s}\frac{m}{1}}$. The main feature of this IC structure is the presence of the weak displacive waves superposed on the main modulating waves of the occupational type. The displacements of atoms take place only along the b axis. The amplitude of the displacive wave of the Na^+ ion was found to be almost twice as large $(0\cdot077\ \text{Å})$ as that of the NO_2^- molecule $(0\cdot042\ \text{Å})$ with the occupational amplitudes approximately the same. The best refinement yields an overall R factor of $0\cdot063$ in the $P^{I\frac{2}{s}\frac{m}{s}\frac{m}{1}}$ group, revealing a small phase shift between individual waves of the Na^+ ion and the NO_2^- molecule. There are, however, practically no phase shifts between the two kinds of modulation waves involved. All waves were found to be harmonic.

Introduction

The structure of the antiferroelectric (AF) phase of $NaNO_2$ was refined by Kucharczyk, Pietraszko &