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On the Structure Factor for Commensurate Modulated Structures

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Abstract

A superstructure may be looked upon as a commensurate modulated structure and be described through the superspace formalism. It can be studied using low- or high-symmetry superspace groups. The possibility of adopting a high-symmetry description is related to the existence of at least two independent three-dimensional sections in the supercrystal with the same space-group symmetry. The usual structure-factor formula for commensurate structures [Yamamoto (1982). *Acta Cryst.* A**38**, 87–92] includes just one of these sections, thus allowing for a low-symmetry description only. A very simple generalization of this in the superspace formalism is presented, which allows for the use of either low- or high-symmetry superspace groups in the structural analysis. The reasons for a seemingly successful refinement found in the literature, making use of the high-symmetry description, are discussed.

1. Introduction

The superspace formalism (de Wolff, 1974; Janner & Janssen, 1977, 1980) has been shown to be a powerful tool for the description of modulated incommensurate phases. This formalism includes the definition of a supercrystal in a $(3 + d)$-dimensional space, where d is the number of independent modulation wave vectors. The multidimensional construction includes $(3 + d)$-dimensional atomic positions and $(3 + d) \times (3 + d)$ thermal tensors (Yamamoto, 1982*a*). The structure-factor formula and the symmetry operators are referred to this multidimensional space. The symmetry groups of this space are often called superspace groups (SSGs).

The superspace formalism has also been employed in the structural analysis of commensurate phases by Yamamoto & Nakazawa (1982), Yamamoto (1983), Hogervorst & Helmholdt (1988) and Sciau & Grebille (1989), among others. Their principle

motivation was that the superspace group may have more symmetry than that contained in the three-dimensional (3D) space group of the superstructure, with the consequent lowering of the number of structural parameters needed for the description, although this statement was shown not to be strictly valid (Perez-Mato, Madariaga, Zuñiga & Garcia-Arribas, 1987).

The choice of a superspace group for the description of a commensurate modulated structure is, in general, not unique (Perez-Mato *et al.*, 1987). For example, for a crystal that undergoes the normal–incommensurate–commensurate phase sequence as the temperature is lowered, the choice of the 3D part of the SSG for the latter phase can be either the actual 3D space group of the superstructure (low-symmetry SSG), or the space group of the normal phase (high-symmetry SSG), if the former is a subgroup of the latter.

The advantage of choosing a high-symmetry SSG for the structural analysis of a commensurate phase has been extensively discussed (Perez-Mato *et al.*, 1987; van Smaalen, 1988; Perez-Mato, 1991). However, the usual structure-factor formula for commensurate modulated structures (Yamamoto, 1982*a*) does not allow for structural analysis using a high-symmetry description. A proof of this is given by the fact that the latter yields different values of the structure factors when calculated using two alternative but otherwise equivalent indexings for the same reflection (as is shown in the example of § 4).

The aim of this paper is to give a generalized expression for the structure-factor formula for a commensurate structure in the superspace formalism, which will be valid irrespective of the description adopted. In § 2, the superspace formalism is briefly described and some general features in a high-symmetry description are analyzed. In § 3, a structure-factor formula consistent with this description is found. Finally, in § 4, we analyze an example in the literature of a structural analysis of a commensurate phase making use of a high-symmetry description and we show that the particular conditions occurring explain the unexpected success of the refinement.

2. Superspace formalism

In the superspace formalism, a d-dimensionally modulated structure is described through the definition of a $(3+d)$-dimensional space. In order to simplify the formulation, we consider in detail the case of a commensurate displacive structure with a one-dimensional modulation.

A modulated structure is, in general, the result of a distortion of a basic structure. For a displacive modulation, the positions of the atoms in the unit cell of the supercrystal are given by the four coordinates

$$\mathbf{x}^\nu = (\mathbf{r}^\nu, \mathbf{x}_4^\nu) = (\mathbf{r}_0^\nu + \mathbf{u}^\nu, \bar{x}_4^\nu + u_4^\nu), \tag{1}$$

where $\mathbf{r}_0^\nu$ is the position of the atom labeled ν in the basic unit cell and $\mathbf{u}$ defines the distortion between the basic stucture and the modulated one, expressed in terms of Fourier series as

$$\mathbf{u}_\nu(\bar{x}_4^\nu) = \sum_n [\mathbf{a}_n^\nu \cos(2\pi n \bar{x}_4^\nu) + \mathbf{b}_n^\nu \sin(2\pi n \bar{x}_4^\nu)] \tag{2}$$

$$\bar{x}_4^\nu = \mathbf{q}\mathbf{r}_0^\nu + t, \quad \mathbf{u}_4^\nu = \mathbf{q}\mathbf{u}^\nu(\bar{x}_4^\nu), \tag{3}$$

where $\mathbf{q}$ is the modulation wave vector and t is the initial phase affecting the modulation wave, which defines the 3D section of the supercrystal at which the atom ν lies.

For an incommensurate $\mathbf{q}$, the different sections t of the supercrystal are all equivalent and no restrictions are imposed on t. If $\mathbf{q}$ is commensurate with the basic cell, t takes only a discrete set of values, which are related to the 3D space group of the superstructure.

A full treatment of the symmetry of one-dimensionally modulated structures has been given by de Wolff, Janssen & Janner (1981). A symmetry element of the SSG can be written as $(R_E R_I|\mathbf{v}_E\tau_4)$; $(R_E|\mathbf{v}_E)$ is a 3D operator that acts on the 3D real space and $(R_I|\tau_4)$ $(R_I = \pm 1)$ acts on the fourth coordinate. In what follows, we consider R_I to be refined as $R_I\mathbf{q} = R_E\mathbf{q}$, irrespective of the character of $\mathbf{q}$. This definition is equivalent, in direct space, to

$$R_I\mathbf{q}\mathbf{r} = \mathbf{q}R_E\mathbf{r} \tag{4}$$

for any vector $\mathbf{r}$ in the 3D space. Two atoms ν and μ in the supercrystal are then related by a superspace-group element if

$$\mathbf{r}_0^\mu = R_E\mathbf{r}_0^\nu + \mathbf{v}_E \tag{5}$$

$$x_4^\mu = \mathbf{q}\mathbf{r}_0^\mu + t' = R_I x_4^\nu + \tau_4 \tag{6}$$

$$\mathbf{u}^\mu(\bar{x}_4^\mu) = R_E\mathbf{u}^\nu(\bar{x}_4^\nu). \tag{7}$$

For a commensurate modulation with a wave vector of the form

$$\mathbf{q} = (1/M)\sum_i m_i\mathbf{a}_i^* \tag{8}$$

(M and m_i being integers and $\mathbf{a}_i^*$ basic unit reciprocal-lattice vectors), a superspace group corresponds to an infinite collection of different 3D structures, which are obtained by varying the initial phase t of the modulation wave. The condition for the superspace operation $(R_E R_I|\mathbf{v}_E\tau_4)$ to be a 3D symmtry operation $(R_E|\mathbf{v}_E)$ is that the atoms μ and ν belong to the same translationally equivalent section of the supercrystal, *i.e.* the condition $t = t'$ must hold in (6). This brings us to the following relation

between t and τ_4:

$$\tau_4 - \mathbf{q}\mathbf{v}_E + (R_I t - t) = 0. \quad (9)$$

Equation (9) is the same as in Perez-Mato (1991), setting $\tau' = \tau_4 - \mathbf{q}\mathbf{v}_E$, τ' being the translation of the phase t corresponding to the symmetry element $(R_E|\mathbf{v}_E)$.

The operators with $R_I = 1$ have a τ_4 value independent of the choice of origin along the fourth dimension; they will or will not be elements of the 3D space group independently of the chosen section t.

For the operators with $R_I = -1$, the value of τ_4 can be chosen arbitrarily; for a given value of τ_4 the symmetry operation will be a space-group element only for the particular sections t fulfilling condition (9). It is easy to see that if t_0 is a section with the desired symmetry, the nontranslationally equivalent section $t' = t_0 + (1/2M)$ has the same symmetry. The set of symmetry operators that leaves invariant these sections forms the low-symmetry SSG ($\{G_L\}$). The possibility of choosing a high-symmetry SSG ($\{G_H\}$) is related to the existence of these two invariant sections in the supercrystal when there are symmetry operators $(R'|\tau') = (R'_E R'_I|\mathbf{v}'_E \tau'_4)$ that satisfy the following conditions:

(i) their 3D part $(R'_E|\mathbf{v}'_E)$ relates atoms in the basic structure;

(ii) $(R'|\tau')$ transforms atoms from section t_0 to section $t' = t_0 + (1/2M)$ (and *vice versa*) in order to keep the 3D symmetry of these sections.

The last condition leads to

$$\tau'_4 - \mathbf{q}\mathbf{v}'_E + (R'_I t_0 - t_0) = 1/2M. \quad (10)$$

Equation (10) has to be fulfilled by the non-3D operators $(R'|\tau')$ under the hypothesis that the low-symmetry SSG contains at least one element with $R_I = -1$. When no such elements exist, all the sections of the supercrystal have the same symmetry and no extra conditions are imposed over τ'_4.

For example, with $t_0 = 0$, (9) becomes

$$\tau_4 = \mathbf{q}\mathbf{v}_E \quad (11)$$

(Yamamoto & Nakazawa, 1982), as the one to be fulfilled by the operators belonging to $\{G_L\}$, and, if the latter contains some element with $R_I = -1$, (10) becomes $\tau'_4 - \mathbf{q}\mathbf{v}'_E = (1/2M)$ for the operators not belonging to $\{G_L\}$.

In this way, the real structure is built up from the independent ($t = 0$) atoms by the application of the symmetry operators belonging to $\{G_L\}$ and from the independent ($t = 1/2M$) atoms by the application of the symmetry operators $(R'|\tau')$ belonging to $\{G_H\}$. In the usual structure-factor formula for a commensurate structure (Yamamoto, 1982*a*), all the symmetry operators act on sections with $t = 0$ mod$(1/M)$; then, the possibility of a high-symmetry SSG description is not contemplated. As we see in the next section, the above features appear when an all-inclusive derivation of the structure-factor formula for a commensurate modulated structure is carried out.

3. Structure factor

In this section, an expression for the structure-factor formula that will allow for the structural analysis in a low- or a high-symmetry SSG is derived.

The diffraction pattern of a modulated structure with a one-dimensional modulation is given by a set of discrete Bragg peaks with diffraction vectors of the form

$$\mathbf{H} = \mathbf{h} + h_4\mathbf{q} = \sum_{i=1}^{3} h_i \mathbf{a}_i^* + h_4\mathbf{q}, \quad (12)$$

where h_i are integers for $i = 1,...,4$). For the commensurate vector (8), $\mathbf{g} = M\mathbf{q}$ is a vector in the basic reciprocal lattice. Hence, in contrast with the incommensurate case, the indexing of (12) with four indices is not unique and unambiguous and we have a set of equivalent expressions

$$\mathbf{H} = \mathbf{h} + h_4\mathbf{q} = (\mathbf{h} + n\mathbf{g}) + (h_4 - nM)\mathbf{q}, \quad (13)$$

where n is an integer. The structure factor at each diffraction vector $\mathbf{H}$ for such a commensurate modulated structure is given by the general expression (Perez-Mato, 1991)

$$F(\mathbf{H}) = \sum_n F(\mathbf{h} + n\mathbf{g}, h_4 - nM) \exp[-2\pi i(h_4 - nM)t_0], \quad (14)$$

where t_0 is the initial phase of the modulation wave and $F(\mathbf{h},h_4)$ is the structure-factor formula for an incommensurate structure, defined as (Yamamoto, 1982*a*)

$$F(\mathbf{h},h_4) = \sum_\nu \sum_{(R|\tau)} \int_0^1 \mathrm{d}\bar{x}_4^\nu \, p^\nu f^\nu(\mathbf{H}) \times \exp\left\{ -\sum_{ij} h_i [R\mathbf{B}^\nu(\bar{x}_4^\nu)R^T]_{ij} h_j + 2\pi i \sum_{i=1}^{4} (h_i [R\mathbf{x}^\nu(\bar{x}_4^\nu)]_i + h_i v_i) \right\}, \quad (15)$$

where p^ν is the multiplicity of the νth nonequivalent atom in the basic cell, $v_i = (\mathbf{v}_E)_i$ for $i = 1, 2, 3$, $v_4 = \tau_4$ and $(R|\tau)$ runs over only those symmetry operators that are representatives of the translationally equivalent classes of the SSG.

With neglect, for simplicity, of the temperature factors and use of (3), (4) and (15), (14) leads to

$$F(\mathbf{H}) = \sum_\nu \sum_{(R|\tau)} \int_0^1 \mathrm{d}t \, p^\nu f^\nu(\mathbf{H}) \times \exp\{2\pi i[\mathbf{H}R_E(\mathbf{r}_0^\nu + \mathbf{u}^\nu(t))$$

$$+ h_4(R_I t - t_0 + \tau_4) + \mathbf{h}\mathbf{v}_E]\}$$
$$\times \sum_n \exp[-\pi 2inM(R_I t - t_0 + \tau_4 - \mathbf{q}\mathbf{v}_E)], \quad (16)$$

which in turn can be written as

$$F(\mathbf{H}) = \int_0^1 \mathrm{d}t f(t) \sum_n \exp[-2\pi inM(R_I t - t_0 + \tau_4 - \mathbf{q}\mathbf{v}_E)], \quad (17)$$

where $f(t+n) = f(t)$ (n integer). Using the fact that

$$\sum_n \exp[-2\pi inM(R_I t - t_0 + \tau_4 - \mathbf{q}\mathbf{v}_E)]$$
$$= (1/M) \sum_n \delta[R_I t - t_0 + \tau_4 - \mathbf{q}\mathbf{v}_E + (n/M)] \quad (18)$$

and the periodicity of the function $f(t)$, we find

$$F(\mathbf{H}) = \sum_\nu \sum_{(R|\tau)} \int_0^1 \mathrm{d}t\, p^\nu f^\nu(\mathbf{H})$$
$$\times \exp\{2\pi i[\mathbf{H}R_E(\mathbf{r}_0^\nu + \mathbf{u}^\nu(t))$$
$$+ h_4(R_I t - t_0 + \tau_4) + \mathbf{h}\mathbf{v}_E]\}$$
$$\times (1/M) \sum_{s=0}^{M-1} \delta[R_I t - t_0 + \tau_4 - qv_E + (s/M)]. \quad (19)$$

The delta function in (19) determines the (discrete) sections of the supercrystal from which an atom is brought, by each symmetry operator $(R|\tau)$, to the main 3D section. For the identity operator, the allowed values of t derived from (19) are $t = t_0 \bmod(1/M)$. This set must be common to all the superspace operators that are also 3D symmetry operators. Therefore, such elements must fulfil condition (9).

The operators $(R'|\tau')$, which do not fulfil condition (9), yield nonzero contributions to the structure factors only when they act on atoms placed on sections $t' = R_I'(t_0 + \mathbf{q}\mathbf{v}_E' - \tau_4') \bmod(1/M)$. With the fact that these sections should have the same symmetry as those with $t = t_0$ taken into account, condition (10) is recovered when $\{G_L\}$ contains some operator with $R_I = -1$. The result of the reduction of the independent atoms in the structure when a high-symmetry SSG is adopted is then compensated for by an increase in the number of values of $\bar{x}_4^\nu$ in (3) at which the modulation function (2) must be evaluated, a fact already noted by Perez-Mato *et al.* (1987).

In a return to the superspace formalism and after performance of the integral in (19), the structure-factor formula for a modulated commensurate structure with one-dimensional modulation is written as

$$F(\mathbf{H}) = F(\mathbf{h}, h_4)$$
$$= (1/M) \sum_{s=0}^{M-1} \sum_\nu \sum_{(R\tau)} p^\nu f^\nu(\mathbf{H})$$
$$\times \exp\left\{-\sum_{i,j}^4 h_i[R\mathbf{B}^\nu(\bar{x}_{4,s}^\nu(R))R^T]_{ij} h_j \right.$$
$$\left. + 2\pi i \sum_{i=1}^4 h_i[R\mathbf{x}^\nu(\bar{x}_{4,s}^\nu(R))]_i + h_i v_i\right\} \quad (20)$$

with

$$\bar{x}_{4,s}^\nu(R) = \mathbf{q}\mathbf{r}_0^\nu + R_I[t_0 - \tau_4 + \mathbf{q}\mathbf{v}_E + (s/M)]. \quad (21)$$

This expression differs from Yamamoto's in the set of values $\bar{x}_4^\nu$ for which each term is evaluated. In taking into account (21), we are including the possibility of transforming atoms from sections other than the $t = t_0 \bmod(1/m)$ one; this allows a high-symmetry description of the structure. If a low-symmetry SSG description is adopted, the structure-factor formula given by Yamamoto (1982*a*) is recovered.

Although the case of a modulated commensurate structure with one-dimensional modulation was the one considered in detail here, the extension to more dimensions is straightforward. For a d-dimensional modulated structure with wave vectors $\mathbf{q}^j = (1/M_j)\sum_i m_{ji}\mathbf{a}_i^*$ (M_j and m_{ji} integers for $j = 1, ..., d$), the structure-factor formula will depend on the d internal coordinates x_{3+j}. These coordinates transform under the action of a $(3+d) \times (3+d)$ symmetry operator $(R_E R_I | \mathbf{v}_E \mathbf{v}_I)$ as

$$x_{3+j}^\mu = \sum_{i=1}^d (R_I)_{ji} x_{3+i}^\nu + (\mathbf{v}_I)_j. \quad (22)$$

Requiring that $\bar{x}_{3+j}^\mu = \mathbf{q}^j \mathbf{r}_0^\mu + t_{0j} \bmod(1/M_j)$ (which ensures that the transformed atom belongs to the 3D real-space section of the supercrystal defined by t_{0j}, $j = 1, ..., d$), we obtain

$$\bar{x}_{3+j,s}^\nu(R) = \mathbf{q}^j \mathbf{r}_0^\nu + \sum_{i=1}^d (R_I^{-1})_{ji}[\mathbf{q}^i \mathbf{v}_E + t_{0i}$$
$$- (\mathbf{v}_I)_i + (s_i/M_i)], \quad (23)$$

where s_i are integers, as the points at which the structure-factor formula ought to be evaluated in order to make the high-symmetry description of the commensurate modulated structure feasible.

4. Example

In the light of the above-proposed modifications to the structure-factor formula, it is worth dealing with the only example the author could trace in the literature of a structural analysis in a high-symmetry SSG, using the refinement program *REMOS* (Yamamoto, 1982*b*), which was applied to the structure of the low-temperature phase of $KFeF_4$. The crystal structure of this phase had been previously solved in the *Pmcn* space group (Lapasset, Sciau, Moret & Gros, 1986) and was later described as a modulated structure with $\mathbf{q} = \frac{1}{2}\mathbf{b}^*$ and SSG $\{G_H\} = P_{1Ts}^{Amma}$ (Sciau & Grebille, 1989).

The low-symmetry SSG for this structure is $\{G_L\} = P^{Pmcn}_{1\Gamma_S}$. The elements of this group are given in Table 1.

The high-symmetry SSG can be expressed in terms of $\{G_L\}$ as

$$\{G_H\} = \{(E\,1|0,0,0,0);(E\,1|0,\tfrac{1}{2},\tfrac{1}{2},0)\} \otimes \{G_L\}. \quad (24)$$

The space group symmetry of the different sections t of the supercrystal can be obtained from (9). In Table 2, the space group of each section is given for two values of τ_4. Then, for $\tau_4 = \frac{1}{4}$, the $t = 0$ and $t = \frac{1}{4}$ sections have the desired symmetry. It is easy to see that the centering translation [and therefore all the operators generated from it through (24)] fulfil (10) for the $t = 0$ and $t = \frac{1}{4}$ sections.

In the high-symmetry description, the structure-factor formula (19) for a vector $\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$ can be written as

$$F(\mathbf{H}) = F_0(\mathbf{H}) + F_{1/4}(\mathbf{H}) \exp\{i\pi[k + l + (m/2)]\}, \quad (25)$$

where $F_0(\mathbf{H})$ and $F_{1/4}(\mathbf{H})$ are the 'structure factors' of the 'hemistructures' lying at the sections $t = 0$ and $t = \frac{1}{4}$, respectively. They only differ at the points at which the modulation functions $\mathbf{u}(\bar{x}_4)$ are evaluated: $\bar{x}_4^\nu = \mathbf{q}\mathbf{r}_0^\nu$ for the former and $\bar{x}_4^\nu = \mathbf{q}\mathbf{r}_0^\nu + \frac{1}{4}$ for the latter. Because all the atoms in the basic structure lie in special positions (see Sciau & Grebille, 1989), the modulation function (2) can be written as

$$\mathbf{u}(\bar{x}_4) = \mathbf{u}_0 + \mathbf{u}_1(\cos 2\pi\bar{x}_4 + \sin 2\pi\bar{x}_4) + \mathbf{u}_2(\cos 2\pi x_4 - \sin 2\pi\bar{x}_4) + \mathbf{u}_3 \cos 4\pi\bar{x}_4, \quad (26)$$

with the parameters $\mathbf{u}_i$ calculated from the results of the standard refinement performed by Lapasset *et al.* (1986), given in Table 3. From this table and (26), it can be seen that $\mathbf{u}(\bar{x}_4)$ and $\mathbf{u}(\bar{x}_4 + \frac{1}{4})$ only differ in their y component. Following (25), the appearance of the second-order satellite reflections (main $k + l =$ odd reflections) is related to this difference; when this set of reflections is unobserved or very weak (as it is in this case), one can make the approximation $\mathbf{u}(\bar{x}_4) = \mathbf{u}(\bar{x}_4 + \frac{1}{4})$ and neglect the parameters u_{2y} ands u_{3y} in (26) with a convenient reduction in the number of structural parameters (from 20 to 12).

Let us now analyze the description performed by Sciau & Grebille (1989). The use of the refinement program *REMOS* with the high-symmetry description yields for the calculated structure-factors

$$F(\mathbf{H}) = F_0(\mathbf{H})\{1 + \exp[i\pi(k + l)]\}. \quad (27)$$

This expression has the following characteristics:

(i) the non-symmetry-imposed condition $\mathbf{u}(\bar{x}_4) = \mathbf{u}(\bar{x}_4 + \frac{1}{4})$ is introduced *ab initio*, thus removing any possibility of accounting for second-order satellite reflections;

Table 1. *Symmetry elements of the SSG* $P^{Pmcn}_{1\Gamma_S}$

$(E\,1\|0,0,0,0)$	$(I\,\bar{1}\|0,\frac{1}{2},\frac{1}{2},\frac{1}{2}+\tau_4)$
$(m_x\,1\|\frac{1}{2},0,0,0)$	$(C_{2x}\,\bar{1}\|\frac{1}{2},\frac{1}{2},\frac{1}{2},\tau_4)$
$(C_{2y}\,1\|0,0,0,\frac{1}{2})$	$(m_y\,\bar{1}\|0,\frac{1}{2},\frac{1}{2},\tau_4)$
$(m_z\,1\|\frac{1}{2},0,0,\frac{1}{2})$	$(C_{2z}\,\bar{1}\|\frac{1}{2},\frac{1}{2},\frac{1}{2},\tau_4)$

Table 2. *Space-group symmetry of the different sections of the supercrystal for* $\tau_4 = 0$ *and* $\tau_4 = \frac{1}{4}$

t	$\tau_4 = 0$	$\tau_4 = \frac{1}{4}$
$0 \bmod(\frac{1}{4})$	*Pmmn*	*Pmcn*
$t = \frac{1}{8} \bmod(\frac{1}{4})$	*Pmcn*	*Pmmn*
Other values	$Pm2_1n$	$Pm2_1n$

Table 3. $\mathbf{u}_i$ *parameters* ($\times 10^4$) *for the modulation functions* (24) *calculated from the independent parameters given by Lapasset et al.* (1986)

Dashes imply parameters fixed to zero by symmetry.

		$\mathbf{u}_0$	$\mathbf{u}_1$	$\mathbf{u}_2$	$\mathbf{u}_3$
K	x	–	–	–	–
	y	–	–	9	−89
	z	7	−37	–	–
Fe	x	–	4	–	–
	y	–	–	–	−11
	z	–	10	–	–
F(1)	x	–	313	–	–
	y	–	–	–	17
	z	–	−46	–	–
F(2)	x	–	–	–	–
	y	–	–	−358	−224
	z	0	−14	–	–
F(3)	x	1	10	–	–
	y	–	–	−56	−40
	z	5	−15	–	–

(ii) equivalent h,k,l,m and $h,k-1,l,m+2$ reflections have different calculated structure factors.

The latter is a general consequence of misuse of the formalism as it stands and would prevent any attempt at an accurate structural analysis in a high-symmetry description. However, in the particular case we are analyzing, the extinction rule arising from (27) gives a natural way of indexing the diffraction pattern with no harmful consequences for the refinement procedure: the first-order satellite reflections can only be referred to main $k + l =$ even reflections and the second-order satellite reflections can only be indexed as main $k + l =$ odd ones.

Then, the apparent success of the refinement performed by Sciau & Grebille (1989) must be looked at as the conjunction of two particular conditions: the weakness of the second-order satellite reflections and an almost inescapable 'unambiguous' indexing of the diffraction pattern. However, for a fair comparison between the R factors obtained in both the superspace description and the standard 3D one, the same number and type of reflections ought to be taken into account for the R calculation. Neglect of the

subset of second-order satellites in the former might invalidate the apparent equivalence of both results.

Summarizing, we conclude that a less-favorable case could hardly be dealt with by the high-symmetry SSG description using the formalism as it stands in, for example, Yamamoto's *REMOS*. On the other hand, none of the above-stated problems appears when the correct structure-factor formula (20)–(21) for the high-symmetry SSG description is employed: no ambiguity appears in the indexing of the diffraction pattern, no reflections must be ignored and no non-symmetry-imposed conditions result for the modulation functions. Thus, the advantages of employing a high-symmetry SSG description will be fully exploited in the resolution of commensurate modulated structures only after the proposed modifications to the structure-factor formula are taken into account.

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A New Algorithm for Computation of X-ray Multiple Bragg Diffraction

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Abstract

A new method for computation of X-ray multiple Bragg diffraction in perfect crystals is presented. The method is based on the extended dynamical diffraction theory and implies the reduction of the diffraction equations to a generalized eigenvalue problem. The advantage of the proposed approach is the possibility of decreasing the scattering-matrix size and simplifying the solution when some X-ray beams are not grazing. The boundary conditions are also simplified by the analysis of Bloch-wave structure inside the crystal and the proper selection of their polarization states.

1. Introduction

In recent years, application of bright synchrotron radiation to a broad range of X-ray experiments has aroused interest in X-ray multiple Bragg diffraction, giving us a new opportunity to measure the fine structure of multiple Bragg peaks. These measurements can form the basis for new methods of studying crystals and their surfaces (see Golovin, Imamov & Kondrashkina, 1985; Kazimirov, Kovalchuk, Kohn, Ishikawa & Kikuta, 1991; Kazimirov, Kovalchuk, Kohn, Kharitonov, Samoilova, Ishikawa, Kikuta & Hirano, 1993; Kohn, 1988; Kohn & Samoilova, 1992; Kov'ev & Simonov, 1986; Stepanov, Kondrash kina & Novikov, 1991; Stepanov, Kondrashkina, Novikov & Imamov, 1994). However, they require a proper theoretical interpretation.

The theoretical analysis of X-ray multiple diffraction in perfect crystals can be based on the dynamical diffraction equations with respect to $2N$ wavefield amplitudes (the factor 2 is due to the vectorial nature of electromagnetic waves). As shown by Kohn (1976, 1979), these equations can be reduced to a simply soluble routine eigenvalue problem for a $2N \times 2N$ scattering matrix.

The problem becomes considerably more complicated if at least one X-ray beam grazes the crystal surface and consequently experiences specular reflection. These grazing cases are of special interest for crystal-surface studies. Also, accounting for specular reflection is often important in the rapidly developing optics of soft X-rays.