

Structure Factor of Modulated Crystal Structures*

BY AKIJI YAMAMOTO

National Institute for Research in Inorganic Materials, Namiki, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

(Received 15 November 1980; accepted 13 July 1981)

Abstract

A general structure-factor formula for n -dimensionally modulated structures ($n = 1, 2, \dots$) has been derived to have both density (or substitutional) and displacive modulations. This structure-factor formula covers any modulated structure described by a $(3 + n)$ -dimensional space group. Future papers show the applications of this formula to one- and three-dimensional modulations.

1. Introduction

Modulated structures have periodic distortions of the atomic position and/or the occupation probability of atoms from some fundamental (basic) structure. These distortions are called the displacive and density (or substitutional) modulations. These structures show a variety of satellite reflections. The simplest case is of one-dimensional modulation. Then the diffraction vector \mathbf{h} of each spot can be written with the unit vectors \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* in the reciprocal lattice of the fundamental structure and a wave vector \mathbf{k} of the modulation wave as

$$\mathbf{h} = h_1 \mathbf{a}^* + h_2 \mathbf{b}^* + h_3 \mathbf{c}^* + h_4 \mathbf{k}, \quad (1)$$

where h_1 to h_4 are integers. The wave vector \mathbf{k} is written as $k_1 \mathbf{a}^* + k_2 \mathbf{b}^* + k_3 \mathbf{c}^*$. In some cases, the position of satellite reflections continuously changes with temperature and/or with the composition of a material. A characteristic feature of these so-called incommensurate structures is that \mathbf{k} is incommensurate with the reciprocal lattice of the fundamental structure: at least one of k_i ($i = 1, 2, 3$) is irrational. In other cases, the dimension of modulation is higher than one. In an n -dimensional modulation ($n = 1, 2, \dots$), the modulation wave has n vectors: all reflections are assigned by $3 + n$ integers h_1, h_2, \dots, h_{3+n} as

$$\mathbf{h} = h_1 \mathbf{a}^* + h_2 \mathbf{b}^* + h_3 \mathbf{c}^* + \sum_{i=1}^n h_{3+i} \mathbf{k}^i, \quad (2)$$

* A preliminary report has been published at the International Conference on Modulated Structures, Kailua Kona, Hawaii (Yamamoto, Nakazawa & Tokonami, 1979).

where $\mathbf{k}^1, \dots, \mathbf{k}^n$ are the wave vectors of which none are described by the integral linear combination of the others.

The theory of symmetry of such incommensurate structures progressed recently (de Wolff, 1974; Janner & Janssen, 1977). One-dimensionally modulated incommensurate structure is described by a fictitious four-dimensional lattice and its symmetry is described by a four-dimensional space group and, in general, an n -dimensionally modulated structure is described by a space group of $(3 + n)$ -dimensional space, considering a $(3 + n)$ -dimensional lattice, that is, the symmetry of the $(3 + n)$ -dimensional lattice is generally higher than that of the usual three-dimensional lattice.

Even in modulated structures with all wave vectors \mathbf{k}^i being commensurate, that is, the commensurate (super-) structure [many superstructures can be regarded as the modulated structure (Cowley, Cohen, Salamon & Wuensch, 1979)], their multi-dimensional symmetry is higher than or equal to their three-dimensional symmetry. If the multi-dimensional symmetry is higher than the three-dimensional one, the number of parameters is expected to reduce in comparison with those in the usual analysis. Furthermore, in some cases, the phenomena closely related to the symmetry of the crystal, for example the symmetry of cell constants, ferro-electricity, *etc.*, are correctly understood only by considering multi-dimensional symmetry. In such cases, the superstructure can conveniently be analyzed on the basis of a multi-dimensional description and multi-dimensional symmetry as will be shown in a following paper (Yamamoto, 1982a).

However, almost all modulated structures (including superstructures) have been analyzed on the basis of the three-dimensional symmetry until now. In these analyses, the superstructure is analyzed with the usual structure-factor formula while the incommensurate structure is analyzed with the formula derived for that structure because of the absence of a general structure-factor formula, or is analyzed based on the superstructure model. In this paper, a general structure-factor formula for modulated structures is derived. This gives a unified method of the analysis of incommensurate structures or superstructures mentioned above.

Since a structure-factor formula for incommensurate structures was first derived by Dehlinger (1927), many people have derived the formulas for several cases (Preston, 1938; Kochendorfer, 1939; Daniel & Lipson, 1943, 1944; Hargreaves, 1951). Recently, Korekawa (1967), Böhm (1975), Pynn, Axe & Thomas (1976) and Toman & Frueh (1976) have derived more general formulas. Korekawa derived a structure-factor formula for one-dimensional modulation in which the density modulation is accompanied by the displacive modulation provided that the modulation wave is harmonic. This is extended for the case of an anharmonic modulation wave by Toman *et al.* Böhm derived a simple formula for a displacive modulation with an anharmonic wave. On the other hand, Pynn *et al.* derived a formula for two-dimensional displacive modulations with a harmonic wave. The extension of these formulas for more general cases is easy. However, these expressions are not convenient to analyze a modulated structure on the basis of a multi-dimensional description because these do not take into account the multi-dimensional lattice and multi-dimensional symmetry.

de Wolff (1974) first derived a structure-factor formula based on the consideration of a multi-dimensional lattice describing a modulated structure. This formula has, however, some limitations: the modulation must be either one-dimensional displacive or one-dimensional substitutional. To obtain a more general and convenient formula, a structure-factor formula is derived for general cases of n -dimensional modulations with some wave vectors commensurable with \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* and others, incommensurable, including the cases with all wave vectors commensurable or incommensurable as special cases. The formula explicitly includes the symmetry operators in the multi-dimensional space group as in the usual structure-factor formula of the three-dimensional space. This makes it possible to derive easily the extinction rules in the modulated structure and makes the structure analysis based on the multi-dimensional description easy. This formula is successfully applied to the one-dimensional modulation of CuAu and the three-dimensional modulation of wüstite as shown in two following papers (Yamamoto, 1982a,b).

2. Structure-factor formula

In the multi-dimensional description of a modulated structure, the reflection (2) is made to correspond to the lattice point in the reciprocal lattice of $(3+n)$ -dimensional space R_{3+n} (see Janner & Janssen, 1977). The reciprocal lattice is spanned by $\mathbf{b}_1 = \mathbf{a}^*$, $\mathbf{b}_2 = \mathbf{b}^*$, $\mathbf{b}_3 = \mathbf{c}^*$ and $\mathbf{b}_{3+i} = \mathbf{k}^i + \mathbf{d}_i$ ($i = 1, 2, \dots, n$), where \mathbf{d}_i are the unit vectors perpendicular to the usual three-

dimensional space R_3 . It is easy to show that the lattice point

$$\mathbf{h}' = \sum_{i=1}^{3+n} h_i \mathbf{b}_i \quad (3)$$

in R_{3+n} is projected onto (2). The unit vectors of the direct space are given by $\mathbf{a}_1 = \mathbf{a} - \sum_{i=1}^n k_1^i \mathbf{d}_i$, $\mathbf{a}_2 = \mathbf{b} - \sum_{i=1}^n k_2^i \mathbf{d}_i$, $\mathbf{a}_3 = \mathbf{c} - \sum_{i=1}^n k_3^i \mathbf{d}_i$ and $\mathbf{a}_{3+i} = \mathbf{d}_i$ ($i = 1, 2, \dots, n$), where k_1^i, k_2^i, k_3^i are the \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* components of \mathbf{k}^i and $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are the unit vectors reciprocal to $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$. From the definition of these vectors, a vector $\mathbf{x} = x_1 \mathbf{a} + x_2 \mathbf{b} + x_3 \mathbf{c}$ in the usual three-dimensional space R_3 is expressed by $\mathbf{x} = \sum_{i=1}^{3+n} x_i \mathbf{a}_i$ with $x_{3+i} = k_1^i x_1 + k_2^i x_2 + k_3^i x_3$. (It should be noted that x_{3+i} is the scalar product of the wave vector \mathbf{k}^i and a vector \mathbf{x} in R_3 .) Therefore, the $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ components are the same as those referring to $\mathbf{a}, \mathbf{b}, \mathbf{c}$. Similarly, the components of the temperature-factor tensor B in R_3 are expressed by the components referring to \mathbf{a}_i ($i = 1, \dots, 3+n$). Then B_{ij} for $i, j \leq 3$ are the same as those referring to $\mathbf{a}, \mathbf{b}, \mathbf{c}$ while $B_{i,3+j}$ and $B_{3+j,i}$ for $i \leq 3$ are equal to $\sum_{m=1}^3 B_{im} k_m^j$ and $B_{3+i,3+j}$ are equal to $\sum_{m=1}^3 k_m^i B_{mn} k_n^j$.

From the analogy with the four-dimensional description of the one-dimensionally modulated structure, we consider the 'atom' continuously over the extra space which is spanned by $\mathbf{a}_{3+i} = \mathbf{d}_i$ ($i = 1, \dots, n$). In this description, the fundamental structure is described by the atom which has the same x_1, x_2, x_3 coordinates over the extra space: these are independent of x_{3+i} ($i = 1, \dots, n$). The deviation in the modulated structure from the fundamental structure occurs on a hyperplane parallel to R_3 . Therefore, the $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ components of the atomic position of the μ th atom in the unit cell of a multidimensional lattice, x_i^μ ($i = 1, 2, 3$), are written as

$$x_i^\mu = \bar{x}_i^\mu + u_i^\mu \quad (i = 1, 2, 3), \quad (4)$$

where $\bar{x}_1^\mu, \bar{x}_2^\mu, \bar{x}_3^\mu$ are the $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ components of the atomic position of the μ th atom in the fundamental structure in R_{3+n} (which are equal to the $\mathbf{a}, \mathbf{b}, \mathbf{c}$ components of the positional vector in the three-dimensional fundamental structure[†] and $u_1^\mu, u_2^\mu, u_3^\mu$ are the displacements from $\bar{x}_1^\mu, \bar{x}_2^\mu, \bar{x}_3^\mu$ along the $\mathbf{a}, \mathbf{b}, \mathbf{c}$ axes. Then the \mathbf{a}_i ($i \geq 4$) components of the positional vector are given by

$$x_{3+i}^\mu = \bar{x}_{3+i}^\mu + u_{3+i}^\mu \quad (i = 1, 2, \dots, n), \quad (5)$$

where \bar{x}_{3+i}^μ is the $(3+i)$ th coordinate in the fundamental structure which is a continuous parameter (independent of μ) and $u_{3+i}^\mu = \sum_{m=1}^3 k_m^i u_m^\mu$. (See Fig. 1.) In the modulated structure, the displacements $u_1^\mu, u_2^\mu, u_3^\mu$ are the periodic functions of \bar{x}_{3+i}^μ ($i = 1, 2, \dots, n$).

[†]In some modulated structures, the fundamental structure is incommensurate and the three-dimensional fundamental structure cannot be taken (Janner & Janssen, 1980). Such a case is not considered in this paper.

Therefore, these are expressed in terms of the Fourier series as

$$u_i^\mu = \frac{1}{2} \sum_{\{\mathbf{m}\}} u_{i\{\mathbf{m}\}}^\mu \exp \left\{ 2\pi i \sum_j m_j \bar{x}_{3+j}^\mu \right\} + \text{c.c.}, \quad (6)$$

where m_j means the order of harmonics for the j th wave, the wave vector of which is \mathbf{k}^j , $\{\mathbf{m}\}$ denotes one set of m_j , (m_1, m_2, \dots, m_n) , $\sum_{\{\mathbf{m}\}}$ stands for the sum over all sets, $u_{i\{\mathbf{m}\}}^\mu$ is the complex amplitude of the plane wave $\exp \{ 2\pi i \sum_j m_j \bar{x}_{3+j}^\mu \}$ and c.c. denotes the complex conjugate.

Similarly, the ij components of the temperature-factor tensor B_{ij} ($i, j = 1, 2, 3$) can be written as

$$B_{ij}^\mu = \frac{1}{2} \sum_{\{\mathbf{m}\}} B_{ij\{\mathbf{m}\}}^\mu \exp \left\{ 2\pi i \sum_{j=1}^n m_j \bar{x}_{3+j}^\mu \right\} + \text{c.c.}, \quad (7)$$

where $B_{ij\{\mathbf{m}\}}^\mu$ is the complex amplitude. Because the thermal motion occurs on a hyperplane parallel to R_3 , $B_{i,3+j}^\mu$ ($i \leq 3$) and $B_{3+i,3+j}^\mu$ ($i, j = 1, \dots, n$) are obtained from (7) by the relation mentioned before. For isotropic temperature factors, we have, instead of (7),

$$B^\mu = \frac{1}{2} \sum_{\{\mathbf{m}\}} B_{\{\mathbf{m}\}}^\mu \exp \left\{ 2\pi i \sum_{j=1}^n m_j \bar{x}_{3+j}^\mu \right\} + \text{c.c.} \quad (8)$$

The occupation probability in the density modulation is given by

$$P^\mu = \frac{1}{2} \sum_{\{\mathbf{m}\}} P_{\{\mathbf{m}\}}^\mu \exp \left\{ 2\pi i \sum_{j=1}^n m_j \bar{x}_{3+j}^\mu \right\} + \text{c.c.}, \quad (9)$$

where $P_{\{\mathbf{m}\}}^\mu$ is the complex amplitude.

The structure-factor formula for the n -dimensional modulation is the direct extension of de Wolff's formula, which has the following form.

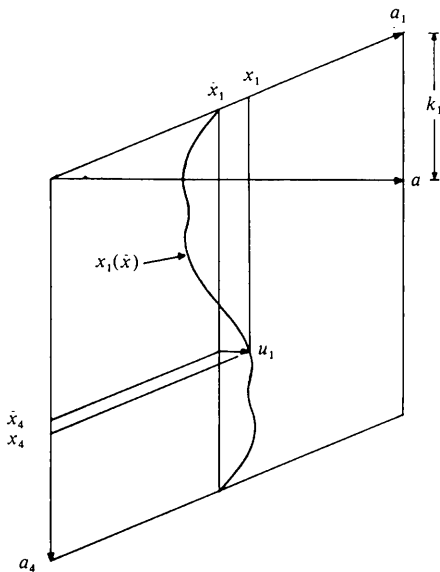


Fig. 1. The relationships between $\bar{x}_1, \bar{x}_4, x_1, x_4$ and u_1 in the case of one-dimensional modulation with $\mathbf{k} = k_1 \mathbf{a}^*$.

$$F_{\mathbf{h}'} = \sum_{\mu} \int_0^1 d\bar{x}_4^\mu \dots \int_0^1 d\bar{x}_{3+n}^\mu f^\mu(\mathbf{h}) P^\mu \times \exp \left\{ - \sum_{ij} h_i B_{ij}^\mu h_j + 2\pi i \sum_j h_j x_j^\mu \right\}, \quad (10)$$

where \mathbf{h}' is the reciprocal-lattice vector of (3) in R_{3+n} and \mathbf{h} is its projection onto R_3 which is represented by (2), $f^\mu(\mathbf{h})$ is the usual atomic scattering factor for the μ th atom at the point \mathbf{h} . The indices i and j run from one to $3+n$. The derivation of the formula is based on the consideration of a multi-dimensional description of the modulated structure and is quite intuitive. The other simple derivation from the usual formula in the three-dimensional space is given in Appendix 1.* In one-dimensional modulation, (10) reduces to

$$F_{\mathbf{h}'} = \sum_{\mu} \int_0^1 d\bar{x}_4^\mu f^\mu(\mathbf{h}) P^\mu \times \exp \left\{ - \sum_{ij} h_i B_{ij}^\mu h_j + 2\pi i \sum_j h_j x_j^\mu \right\}, \quad (11)$$

where $\mathbf{h}' = \sum_{i=1}^4 h_i \mathbf{b}_i$ and \mathbf{h} is its projection onto R_3 and i and j run from one to four. This is the extension of de Wolff's formula to the case which includes both the density and displacive modulations. This is also the extension of formulas derived by Korekawa and Toman *et al.* (see Appendix 2). Formula (10) has a convenient form to introduce explicitly the symmetry operation into the formula because this is expressed in terms of the multi-dimensional space.

The symmetry of an n -dimensionally modulated structure is specified by a space group in R_{3+n} (Janner & Janssen, 1977). Therefore, it is convenient to express the summation of μ over all atoms in the unit cell in (10) by using the summation over all non-equivalent atoms and all symmetry operators in R_{3+n} .

As mentioned previously, u_i^μ is a periodic function of $\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu$ and consequently x_i^μ is a function of them. Similarly, B_{ij}^μ, P^μ are periodic functions of them. To show this we write x_i^μ, B_{ij}^μ and P^μ as $x_i^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu), B_{ij}^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu), P^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)$ and call them modulation functions or modulation waves. Since \bar{x}_i^μ and x_i^μ are the \mathbf{a}_i components of vectors in R_{3+n} , the coordinates of the λ th atom equivalent to the μ th atom are obtained from $x^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)$ by the symmetry operation $(\mathbf{R}|\boldsymbol{\tau})$ in R_{3+n} :

$$x_i^\lambda(\bar{x}_4^\lambda, \dots, \bar{x}_{3+n}^\lambda) = [\mathbf{R}\mathbf{x}^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)]_i + \tau_i \\ = \sum_{ij} R_{ij} x_j^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu) + \tau_i, \quad (12)$$

*Appendices 1, 2 and 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36225 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

where $\bar{x}_i^\lambda = (R\bar{x}^\mu)_i + \tau_i$, R_{ij} is the ij element of $(3+n) \times (3+n)$ rotation matrix R which is $(3+n)$ -reducible (Janner & Janssen, 1977) and τ_i is the a_i component of the translation vector τ in R_{3+n} . (Mathematically, the matrix R is an orthogonal matrix representation of one of the proper or improper rotations of the point group but is simply called the rotation matrix in this paper.) Similarly, the symmetric tensor of second rank, B_{ij}^μ ($\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu$), in R_{3+n} is transformed as

$$B_{ij}^\lambda(\bar{x}_4^\lambda, \dots, \bar{x}_{3+n}^\lambda) = [RB^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)\tilde{R}]_{ij} \\ = \sum_{lm} R_{il} B_{lm}^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu) \tilde{R}_{mj}, \quad (13)$$

where \tilde{R} is the transpose matrix of R . A scalar $P^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)$ in R_{3+n} is transformed as

$$P^\lambda(\bar{x}_4^\lambda, \dots, \bar{x}_{3+n}^\lambda) = P^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu). \quad (14)$$

The isotropic temperature factor, $B^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)$ has the same transformation property as the occupation probability $P^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)$.

Substituting (12)–(14) into (10), and using a property of periodic functions, we have a final form

$$F_{h'} = \sum_{\mu(R|\tau)} P^\mu \int_0^1 d\bar{x}_4^\mu \dots \int_0^1 d\bar{x}_{3+n}^\mu f^\mu(\mathbf{h}) P^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu) \\ \times \exp\left(-\sum_{ij} h_i [RB^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)\tilde{R}]_{ij} h_j \right. \\ \left. + 2\pi i \sum_j \{h_j [R\mathbf{x}^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)]_j + h_j \tau_j\}\right), \quad (15)$$

where P^μ is the multiplicity of the μ th non-equivalent atom in the fundamental cell, μ runs over all non-equivalent atoms and $(R|\tau)$ is over all symmetry operators in R_{3+n} which generate new atoms from the non-equivalent atoms.

3. Electron density and structure factor in R_3

The electron density in the $(3+n)$ -dimensional space is obtained from the usual formula:

$$\rho(x_1, \dots, x_{3+n}) = \frac{1}{V} \sum_{h_1, \dots, h_{3+n}} F_{h'} \exp\left\{2\pi i \sum_{j=1}^{3+n} h_j x_j\right\}, \quad (16)$$

where V is the volume of the fundamental cell in R_3 and h_1, \dots, h_{3+n} run over all integers. As stated before, a point in the usual three-dimensional space is expressed by $x_1, x_2, x_3, x_{3+i} = \sum_{j=1}^3 k_j^i x_j$ ($i = 1, \dots, n$). Therefore, the electron density in R_3 is given by

$$\rho(x_1, x_2, x_3) = \frac{1}{V} \sum_{h_1, \dots, h_{3+n}} F_{h'} \exp\left\{2\pi i \sum_{j=1}^3 \left(h_j \right. \right. \\ \left. \left. + \sum_{m=1}^n h_{3+m} k_j^m\right) x_j\right\}. \quad (17)$$

In the incommensurate structure, the reciprocal-lattice points \mathbf{h}' in R_{3+n} are projected onto \mathbf{h} in R_3 and the correspondence between \mathbf{h}' and \mathbf{h} is one-to-one. Therefore, the structure factor in R_3 , $F_{\mathbf{h}}$, is equal to $F_{\mathbf{h}'}$ (see Fig. 2a). Then the electron density in R_3 is given by

$$\rho(x_1, x_2, x_3) = \frac{1}{V} \sum_{\mathbf{h}} F_{\mathbf{h}} \exp\{2\pi i \mathbf{h} \cdot \mathbf{x}\}, \quad (18)$$

where $\sum_{\mathbf{h}}$ means the summation over all \mathbf{h} and \mathbf{x} is $x_1 \mathbf{a} + x_2 \mathbf{b} + x_3 \mathbf{c}$. On the other hand, in the commensurate case, an infinite number of lattice points are projected onto the same point in R_3 . For example, we consider the case in which \mathbf{k}^1 is commensurate with \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* : k_1^1, k_2^1, k_3^1 are expressed by fractional numbers with a common denominator M , that is, $k_1^1 = m_1/M$, $k_2^1 = m_2/M$, $k_3^1 = m_3/M$, where m_1, m_2, m_3 and M are integers. Then for any integer i , all lattice points in R_{3+n} specified by $h_1 + im_1, h_2 + im_2, h_3 + im_3, h_4 - im_4, h_5, \dots, h_{3+n}$ are projected onto the same point $\mathbf{h} = \mathbf{h}_0 + \sum_{j=1}^n h_{3+j} \mathbf{k}^j$, where $\mathbf{h}_0 = h_1 \mathbf{a}^* + h_2 \mathbf{b}^* + h_3 \mathbf{c}^*$ (see Fig. 2b). Therefore, the structure factor in R_3 , $F_{\mathbf{h}}$, is defined by the summation of $F_{h'}$ over all reflections which are projected onto \mathbf{h} and then the electron density is also given by (18).

This structure factor is given explicitly as follows.

$$F_{\mathbf{h}} = \frac{1}{M} \\ \times \sum_{\mu(R|\tau)} \sum_{v=1}^M P^\mu \int_0^1 d\bar{x}_3 \dots \int_0^1 d\bar{x}_{3+n} f^\mu(\mathbf{h}) P^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu) \\ \times \exp\left(-\sum_{ij} h_i [RB^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)\tilde{R}]_{ij} h_j \right. \\ \left. + 2\pi i \sum_j \{h_j [R\mathbf{x}^\mu(\bar{x}_4^\mu, \dots, \bar{x}_{3+n}^\mu)]_j + h_j \tau_j\}\right), \quad (19)$$

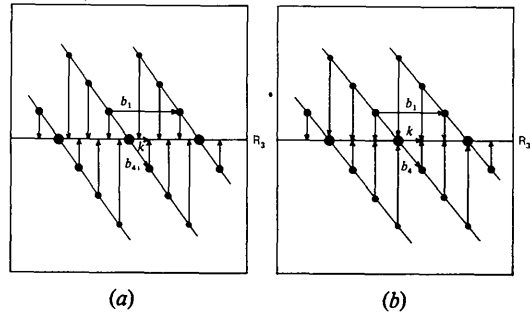


Fig. 2. The projection of four-dimensional lattice points in the reciprocal space in R_4 onto R_3 . In the incommensurate structure (a), the lattice points in R_4 and the reflections in R_3 have one-to-one correspondence while some lattice points in R_4 are superposed on R_3 in the commensurate structure (b).

where $\bar{x}_4^\mu = v/M + \sum_{i=1}^3 k_i^\dagger \bar{x}_i^\mu$. Similarly, if several wave vectors \mathbf{k}^i are commensurable with \mathbf{a}^* , \mathbf{b}^* , \mathbf{c}^* , the integrals with respect to \bar{x}_{3+i}^μ are replaced with the summations. Since the structure factor obtained from experiments is the absolute value of the structure factor in R_3 , this structure-factor formula must be used in the commensurate phase. However, if the reflections with high satellite indices (corresponding to the commensurable wave vectors) are weak enough so that the superposition of reflections in R_3 mentioned above can be neglected, the structure factor in R_3 is approximately equal to $F_{\mathbf{h}}$ of (15).

The structure-factor formula (15) or (19) is convenient to analyze modulated structures on the basis of a multi-dimensional symmetry. The extinction rules are easily derived from (15), as shown in Appendix 3, and a computer programming of the formula is easy because all atomic positions are given from the atomic position of non-equivalent atoms by the symmetry operators of a space group in R_{3+n} . This makes it possible to write a computer program available for the refinement of any modulated structures. The formula was successfully applied to a CuAu alloy and wüstite (Fe_{1-x}O) as shown in future papers (Yamamoto, 1982a,b). These have both the substitutional (or density) and displacive modulations. The dimensions of the modulations are one in CuAu and three in wüstite.

4. Comment and discussion

In the final formula (15) for the incommensurate phase, $F_{\mathbf{h}}$ is invariant for the replacement of \bar{x}_{3+i}^μ with $\bar{x}_{3+i}^\mu + t$ in the integrand because P^μ , B_{ij}^μ and u_i^μ are the periodic functions of \bar{x}_{3+i}^μ , where t is an arbitrary number, and consequently the integral gives the same value except for the phase factor, that is, a uniform phase shift of the modulation functions for all atoms does not affect the intensity. This shows that the absolute phase of the modulation function is not determined in principle although the relative phase among the modulation waves of atoms can be determined. On the other hand, this can be determined in the commensurate phase because the integral is replaced by the summation. It should be noted that if the higher-order satellite reflections are so weak that superposition of satellite reflections in R_3 can be neglected as mentioned in the previous section, it is difficult to determine the precise phase regardless of the commensurability because $F_{\mathbf{h}}$ is almost independent of the phase.

Another phase problem occurs in the substitutional modulation without an accompanying displacive modulation. For simplicity, we consider one-dimensional modulation in the commensurate case. Then the structure-factor formula (19) reduces to

$$F_{\mathbf{h}} = \frac{1}{M} \sum_{\mu(R|\tau)} P^\mu f^\mu(\mathbf{h}) P^\mu(\bar{x}_4^\mu) \times \exp \left\{ 2\pi i \sum_j [h_j(R \bar{x}^\mu)_j + h_j \tau_j] \right\}, \quad (20)$$

where $\bar{x}_4^\mu = v/M + k_1 \bar{x}_1^\mu + k_2 \bar{x}_2^\mu + k_3 \bar{x}_3^\mu$ and the temperature factor is neglected for simplicity. From (9), $P^\mu(\bar{x}_4^\mu)$ is written as

$$P^\mu(\bar{x}_4^\mu) = \frac{1}{2} \sum_m P_m^\mu \exp \{ 2\pi i m \bar{x}_4^\mu \} + \text{c.c.} \quad (21)$$

The P_0^μ term in (21) contributes only to the fundamental (main) reflections $h_1 h_2 h_3 0$. Similarly, the P_m^μ term ($m = 1, 2, \dots$) and its complex conjugate contribute only to the m th-order satellite reflections, $h_1 h_2 h_3 \pm m$, and these satellites do not superpose on the other satellites with different m except for $m = M/2$ in an even- M case. Therefore, the intensity for $h_1 h_2 h_3 m$ is proportional to

$$\left| \sum_{\mu} P^\mu f^\mu(\mathbf{h}) \times \left(\sum_{(R|\tau)} P_{-m}^\mu \exp \left\{ 2\pi i \sum_{j=1}^3 [h_j(R \bar{x}^\mu)_j + h_j \tau_j] + 2\pi i m \tau_4 \right\} + \sum_{(R'|\tau')} P_m^\mu \exp \left\{ 2\pi i \sum_{j=1}^3 [h_j(R' \bar{x}^\mu)_j + h_j \tau_j] + 2\pi i m \tau'_4 \right\} \right) \right|^2, \quad (22)$$

where P_{-m}^μ is the complex conjugate of P_m^μ , $(R|\tau)$ runs over all symmetry operators transforming \mathbf{k} into \mathbf{k} and $(R'|\tau')$ over those transforming \mathbf{k} into $-\mathbf{k}$ if any. The phase of the modulation function of (21) is determined by the argument of the complex amplitude P_m^μ . Expression (22) shows that the uniform phase shift of P_m^μ for all the non-equivalent atoms gives the same intensity if the second term does not exist. Even if the second term exists, the ambiguity of the sign of P_m^μ remains. Therefore, in the case of pure substitutional modulation, the relative sign of different Fourier terms P_m^μ ($m = 1, 2, \dots$) cannot be determined in principle except for the case of $m = M/2$. This fact has been shown by Korekawa (1964) for a primitive lattice with only one atom in the unit cell. The above argument shows that this is true for a general one-dimensional modulation and a similar consideration concludes that this is also the case regardless of the commensurability and the dimension of modulation. If the density (or substitutional) modulation is not accompanied by the displacive modulation, the structure cannot generally be determined from diffraction experiments without the constraint from the physical point of view. The

constraint on the occupation probability plays an essential role in this case. For instance, in a completely ordered structure with vacancies, the occupation probability of each atomic site is one or zero. Such a condition makes it possible to determine the density modulation. In this respect, the extension of de Wolff's formula for the density (substitutional) modulation to the case including the displacive modulation is essential to the density modulation analysis. When the displacive modulation is weak, the modulation function synthesized by P_m^μ with correct absolute value but wrong sign (phase) may give a subminimum with a notably small R factor.

Another important conclusion from (22) is that the structure factor of the m th-order satellite reflection depends linearly only on P_{+m}^μ . Therefore, the least-squares refinement taking $P_{\pm m}^\mu$ as the variable parameters [in which $\sum_{\mathbf{h}} (|F_{oh}| - |F_{ch}|)^2$ is minimized] will rapidly converge owing to this linear dependence, although the phase problem mentioned above remains. A similar situation exists in the displacive modulation with small displacement. We also consider a case of one-dimensional modulation with a commensurate wave vector. In this case the structure factor is approximated by

$$F_{\mathbf{h}} = \frac{1}{M} \sum_{\mu(\mathbf{R}|\tau)} p^\mu \sum_{\nu=1}^M f^\nu(\mathbf{h}) \left[1 + 2\pi i \sum_j h_j u_j^\nu(\bar{x}_4^\mu) \right] \times \exp \left\{ 2\pi i \left[\sum_j h_j (\mathbf{R}\bar{x}^\mu)_j + h_j \tau_j \right] \right\} \quad (23)$$

Therefore, the u_{im}^μ linearly contribute to the satellite reflections. This will also give smooth convergence. The above arguments conclude that, if the displacement from the fundamental structure is small, it is expected that the least-squares refinement taking u_{im}^μ , P_m^μ as parameters smoothly converges from the fundamental structure. This property is independent of the commensurability, so that the present method will give some advantages not only in the incommensurate structure analysis but in the superstructure analysis. In fact, the analyses based on (15) and (19) smoothly converged for the cases of CuAu (commensurate structure) and wüstite (incommensurate structure) which will be mentioned in the succeeding papers. In many

modulated structures, the displacement from the fundamental structure is small, so that the present method can be conveniently applied to the analyses of such structures.

The author greatly thanks Dr H. Nakazawa for instructive discussions and advice during the present work and also thanks Professor N. Morimoto, Dr M. Kitamura and Dr K. Koto for valuable discussions as well as critically reading an earlier version of this paper.

References

- COWLEY, J. M., COHEN, J. B., SALAMON, M. B. & WUENSCH, B. J. (1979). *Modulated Structures-1979, Kailua Kona, Hawaii. AIP Conf. Proc.* No. 53. New York: American Institute of Physics.
- BÖHM, H. (1975). *Acta Cryst.* A31, 622-628.
- DANIEL, V. & LIPSON, H. (1943). *Proc. R. Soc. London Ser. A*, 181, 368-378.
- DANIEL, V. & LIPSON, H. (1944). *Proc. R. Soc. London Ser. A*, 182, 378-387.
- DEHLINGER, U. Z. (1927). *Z. Kristallogr.* 65, 615-631.
- HARGREAVES, M. E. (1951). *Acta Cryst.* 4, 301-309.
- JANNER, A. & JANSSEN, T. (1977). *Phys. Rev. B*, 15, 643-658.
- JANNER, A. & JANSSEN, T. (1980). *Acta Cryst.* A36, 399-408, 408-415.
- KOCHENDORFER, A. (1939). *Z. Kristallogr.* 101, 149-155.
- KOREKAWA, M. (1964). *Nippon Kessho Gakkaishi*, 1, 2-16. (In Japanese.)
- KOREKAWA, M. (1967). *Theorie der Satellitenreflexe. Habilitationsschrift der Ludwig Maximilian-Univ. München.*
- PRESTON, G. D. (1938). *Proc. R. Soc. London Ser. A*, 167, 526-538.
- PYNN, R., AXE, J. D. & THOMAS, R. (1976). *Phys. Rev. B*, 13, 2965-2975.
- TOMAN, K. & FRUEH, A. J. (1976). *Acta Cryst.* B32, 521-525.
- WOLFF, P. M. DE (1974). *Acta Cryst.* A30, 777-785.
- YAMAMOTO, A., NAKAZAWA, H. & TOKONAMI, M. (1979). *Modulated Structures-1979, Kailua Kona, Hawaii*, edited by J. M. COWLEY, J. B. COHEN, M. B. SALAMON & B. J. WUENSCH, *AIP Conf. Proc.* No. 53, pp. 84-86. New York: American Institute of Physics.
- YAMAMOTO, A. (1982a). Submitted to *Acta Cryst.*
- YAMAMOTO, A. (1982b). Submitted to *Acta Cryst.*