Structure factor of modulated crystal structures

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

App. 1.

The formula (10) is simply derived from the usual formula for the crystal form factor. We consider the usual three-dimensional space in the following. In the displacive modulation, the i-th (i=1, 2, 3) component of the positional vector of the \( \nu \)-th atom in the \( \nu \)-th unit cell, which is written as \( x_{\nu}^{\mu} \) for convenience, is given by

\[
x_{1}^{\mu\nu} = x_{1}^{\nu} + u_{1}^{\mu}
\]  
(A1)

\[
u_{i}^{\mu} = \frac{2\pi}{L} \exp\left(2\pi i \sum_{j=1}^{n} m_{j} t_{j}^{\mu} \right) + \text{c.c.}
\]  
(A2)

\[
t_{j}^{\mu\nu} = x_{j}^{\nu} / \lambda
\]  
(A3)

where \( x_{1}^{\mu\nu} = x_{1}^{\nu} + x_{1}^{\mu} \), \( x_{1}^{\nu} \) is the i-th component (i=1, 2, 3) of the positional vector \( x_{1}^{\mu\nu} \) in the fundamental cell: \( x_{1}^{\mu} = x_{1}^{\mu} + x_{2}^{\mu} + x_{3}^{\mu} \), \( x_{1}^{\nu} \) is that of a lattice vector and \( u_{1}^{\mu} \) represents the displacement from the position in the fundamental structure. Since the displacement is a periodic function of \( t_{j}^{\mu\nu} \), this is written as (A2) in terms of the Fourier series, where \( u_{1}^{\mu} \) is the complex amplitude of a plane wave \( \exp\left[2\pi i \sum_{j=1}^{n} m_{j} t_{j}^{\mu} \right] \). To show that \( u_{1}^{\mu} \) is a function of \( t_{j}^{\mu\nu} \) (j=1, ..., n), we write \( u_{1}^{\mu} \) as \( u_{1}^{\mu}(t_{1}^{\mu\nu}, ..., t_{n}^{\mu\nu}) \). Similarly the temperature factor tensor \( B_{ij}^{\mu} \) and the occupation probability \( p^{\mu} \) are written as \( B_{ij}^{\mu}(t_{1}^{\mu\nu}, ..., t_{n}^{\mu\nu}) \) and \( p^{\mu}(t_{1}^{\mu\nu}, ..., t_{n}^{\mu\nu}) \). Then the right hand side of (A2) is obtained from (6) by replacing \( x_{1}^{\mu} \) with \( t_{j}^{\mu\nu} \) (j=1, ..., n). Similarly, \( B_{ij}^{\mu}(t_{1}^{\mu\nu}, ..., t_{n}^{\mu\nu}) \) and \( p^{\mu}(t_{1}^{\mu\nu}, ..., t_{n}^{\mu\nu}) \) are obtained from (7) and (9) by the same replacement. In the following calculations, their explicit expressions are
\[ x_{n}^L_{h_4, \ldots, h_{3+n}} \exp(-h \cdot B(t_{1}^U, \ldots, t_{n}^U) \cdot h + 2\pi i h \cdot u(t_{1}^U, \ldots, t_{n}^U)) \]

\[ + 2\pi i (h - \sum_{j} h_{3+j} \cdot k_{j}^U) \cdot \sum_{\nu} + 2\pi i \sum_{j} h_{3+j} \cdot t_{j}^U) g(h - \sum_{j} h_{3+j} \cdot k_{j}^U) \]

(A7)

where \( g(h - \sum_{j} h_{3+j} k_{j}^U) \) is the square root of the Laue function:

\[ g(h - \sum_{j} h_{3+j} k_{j}^U) = \sum_{\nu} \exp\{2\pi i (h - \sum_{j} h_{3+j} k_{j}^U) \cdot \bar{x}^\nu \} \]

This shows that reflections are observed at \( h = h_{0} + \sum_{j} h_{3+j} k_{j}^U \), where \( h_{0} \) is the reciprocal lattice vector of the fundamental structure which is written as \( h_{1}^{a} + h_{2}^{b} + h_{3}^{c} \) with integers \( h_{1}, h_{2}, h_{3} \). In the incommensurate structure, this reflection \( h \) is uniquely assigned by integers \( h_{1}, \ldots, h_{3+n} \) as in (2). Therefore we have the structure factor for these reflections

\[ F_{h} = \sum_{\mu} \int_{0}^{1} dt_{1}^U \ldots \int_{0}^{1} dt_{n}^U f^{U}(h) \ p^{U}(t_{1}^U, \ldots, t_{n}^U) \]

\[ \times \exp(-h \cdot B(t_{1}^U, \ldots, t_{n}^U) \cdot h + 2\pi i h \cdot u(t_{1}^U, \ldots, t_{n}^U)) \]

\[ + 2\pi i (h_{0} \cdot \bar{x}^U + \sum_{j} h_{3+j} t_{j}^U) \]

(A8)

This is easily expressed as (10) if we use the multi-dimensional coordinate: the first, second and third components of vector \( x_{3}^U \) in \( R_{3+n} \) are the same as in \( R_{3} \) and \( \bar{x}_{3+j}^U \) and \( x_{3+j}^U \) are defined by

\[ \bar{x}_{3+j}^U = t_{j}^U \]

(A9)

\[ x_{3+j}^U = \bar{x}_{3+j}^U + k_{j}^U \cdot u^U \]

(A10)
not necessary, but only the properties of a periodic function is
necessitated.

A structure factor is calculated from a usual formula: the
crystal form factor \( F_h \) at any vector \( h \) in the reciprocal space of
\( R_3 \) is given by

\[
F_h = \frac{1}{N} \sum_{\nu} f^\nu(h) p^\nu(t^{\nu}_1, \ldots, t^{\nu}_N) \exp(-h \cdot B^\nu(t^{\nu}_1, \ldots, t^{\nu}_N) \cdot h)
+ 2\pi i h \cdot u^\nu(t^{\nu}_1, \ldots, t^{\nu}_N) + 2\pi i h \cdot \overline{x}^{\nu}
\]  
\tag{A4}

where \( N \) is the number of cells in a crystal. The index \( \nu \) runs over
all atoms in the fundamental cell and \( \nu \) is over all cells. Since
\( p^\nu(t^{\nu}_1, \ldots, t^{\nu}_N) \), \( B^\nu(t^{\nu}_1, \ldots, t^{\nu}_N) \) and \( u^\nu(t^{\nu}_1, \ldots, t^{\nu}_N) \) are periodic func-
tions of \( t^{\nu}_1, \ldots, t^{\nu}_N \), (A4) is rewritten as

\[
F_h = \frac{1}{N} \int_0^1 \cdots \int_0^1 \delta(t^{\nu}_1 - t^{\nu}_1) \cdots \delta(t^{\nu}_N - t^{\nu}_N)
\times \exp(-h \cdot B^\nu(t^{\nu}_1, \ldots, t^{\nu}_N) \cdot h + 2\pi i h \cdot u^\nu(t^{\nu}_1, \ldots, t^{\nu}_N) + 2\pi i h \cdot \overline{x}^{\nu})
\]  
\tag{A5}

by using the \( \delta \) function which is expressed by

\[
\delta(t^{\nu}_j - t^{\nu}_j) = \sum_{h_{3+j}} \exp(2\pi i h_{3+j} \cdot (t^{\nu}_j - t^{\nu}_j))
\]  
\tag{A6}

where \( h_{3+j} \) runs over all integers. Substituting this into (A5) and
summing over \( \nu \), we have

\[
F_h = \frac{1}{N} \int_0^1 \cdots \int_0^1 \int_0^1 f^\nu(h) p^\nu(t^{\nu}_1, \ldots, t^{\nu}_N)
\]  
\tag{A4}
Using these and the relation on the \( ij \) components of the temperature-factor tensor mentioned in the text, \( h \cdot B^u + h \cdot u^u + h_0 e^u \cdot \Xi^u \), \( \Sigma_{ij} h_{3} h_{ij} e^u \) in (A8) are rewritten as \( \Sigma_{ij} h_{1} h_{ij} e^u \) and \( \Sigma_{i=1}^{3+n} h_{i} x_{i}^{u} \). Thus we have (10).

App. 2.

To show the structure-factor formula (11) is the extension of the formulas derived by Korekawa (1967) and Toman & Frueh (1976), we consider the case in which the modulation waves for the displacement and occupation probability of atoms are expressed by the Fourier series up to the second-order harmonics and the temperature factor is neglected. In this case, the displacement and the occupation probability is written as

\[
U^{u}_{1} = \sum_{m=1}^{2} U_{1m}^{u} \exp 2\pi i m x_{4} + c.c. \quad (A11)
\]

\[
P^{u}_{0} = \sum_{m=1}^{2} P_{m}^{u} \exp 2\pi i m x_{4} + c.c. \quad (A12)
\]

where \( U_{1m}^{u} \) and \( P_{m}^{u} \) are the complex amplitudes for the \( m \)-th-order harmonics \( (m=1,2) \) and \( P_{0}^{u} \) represents the average occupation probability of the \( u \)-th atom. Substituting these into (11) and using the formulas for the Bessel function

\[
J_{n}(x) \exp i n\theta = \frac{1}{2\pi} \int_{0}^{2\pi} \exp 2\pi i (\frac{1}{2} x e^{i\theta} + c.c.) + n\theta
\]

\[
e^{ix \sin \theta} = \sum_{n=-\infty}^{\infty} J_{n}(x) e^{in\theta}
\]

we can express \( P_{h}^{u} \) of (11) as the sum of the five terms:
\[ F_{h^t} = F_{h^t}^0 + F_{h^t}^1 + F_{h^t}^{-1} + F_{h^t}^2 + F_{h^t}^{-2} \]  

(A15)

In the right hand side, \( F_{h^t} \) \((t=0, \pm 1, \pm 2)\) represent

\[ F_{h^t} = \sum_\nu \exp\left(2\pi i \left( \sum_{j=1}^{3} h_j x_j^\nu \right) \right) R_{t}^{\nu} \]

\( x_{n_2}^{n_1} \sum_{n_2=0}^{\infty} J_{n_1}^{-} (a_{n_2}^{\nu}) J_{n_2} (a_{n_2}^{\nu}) \exp\left(2\pi i (n_1 x_1^{\nu} + n_2 x_2^{\nu})\right) \)

(A16)

where \( R_{0}^{\nu} = f_{0}^{\nu}(h) \), \( R_{\pm t}^{\nu} = f_{\pm t}^{\nu}(h)/2 \) \((t=1, 2, \text{ } p_{-t} \text{ means } p_t^*)\), \( n_1 = h_4 - 2n_2 \) and

\[ a_{m}^{\nu} = 2\pi \left| \sum_{j=1}^{4} h_j u_{m j}^{\nu} \right| \quad (m=1, 2) \]  

(A17)

\[ \chi_{m}^{\nu} = \arg\left( \sum_{j=1}^{4} h_j \bar{u}_{m j}^{\nu} \right) + \pi/2 \quad (m=1, 2) \]  

(A18)

In the case of harmonic modulation as considered by Korekawa, (A16) reduces to

\[ F_{h^t} = \sum_\nu \exp\left(2\pi i \left( \sum_{j=1}^{3} h_j x_j^\nu \right) \right) R_{t}^{\nu} J_{n_1}^{-} (a_{n_2}^{\nu}) \exp\left(2\pi i h_4 x_1^{\nu} \right) \]  

(A19)

for \( t=0, \pm 1 \) and \( F_{h^t} \neq 0 \) since \( J_{n} (0) \) is one for \( n=0 \) and zero otherwise.

Korekawa has been derived somewhat complicated expression:

\[ F_{h^t} = \sum_\nu \exp\left(2\pi i \left( \sum_{j=1}^{3} h_j x_j^\nu \right) \right) R_{t}^{\nu} J_{n_1}^{-} (b_{n_2}^{\nu}) J_{n_2} (b_{n_2}^{\nu}) \exp\left(2\pi i \left( n_1 \phi_1^{\nu} + (n_2 - n_1) \phi_2^{\nu} + (h_4 - n_2) \phi_3^{\nu} \right) \right) \]  

(A20)

where \( R_{t}^{\nu} \) \((t=0, \pm 1)\) are the same as those defined above and
\[ b_i^\mu = 2\pi |(h_i + h_qk_i^\mu)| u_i^\mu | \] (i=1, 2, 3) \hspace{1cm} (A21)

\[ \phi_i = \text{arg}(h_i + h_qk_i^\mu) \] (i=1, 2, 3) \hspace{1cm} (A22)

The formula (A20) is rewritten as (A18) by using

\[ J_n(|x|) e^{i\theta} = \sum_{m=-\infty}^{\infty} J_m(|y|) J_{n-m}(|z|) e^{im\phi+i(n-m)\psi} \] \hspace{1cm} (A23)

where \( x, y, z \) are the complex numbers, \( x=y+z, \theta=\text{arg} \ x, \phi=\text{arg} \ y \) and \( \psi=\text{arg} \ z \). On the other hand, Toman et al. derived the formula for the anharmonic modulation including up to the second-order harmonics:

\[ P_{h', t} = \sum_R \exp\left(2\pi i \sum_{j=1}^{3} \frac{h_j^\mu}{j} \right) R_{t}^\mu \]

\[ x_{\ell}^{m} = \sum_{n_2=-\infty}^{\infty} \frac{\Gamma_{m-n_2}^{\infty}}{(m-n_2/2)!(m+n_2/2)!} J_{n_1}^1(a_{1}^\mu) \]

\[ \times \exp\{2\pi i[(n_1+t)x_1^\mu+2n_2(x_2^\mu-\frac{1}{4})]\} \] \hspace{1cm} (A24)

Changing the order of summation with respect to \( m \) and \( n_2 \) and introducing the new variable \( n=m-|n_2| \) instead of \( m \), we have:

\[ P_{h', t} = \sum_R \exp\left(2\pi i \sum_{j=1}^{3} \frac{h_j^\mu}{j} \right) R_{t}^\mu \]

\[ x_{\ell}^{n_2} = \sum_{n_2=-\infty}^{\infty} \frac{(ia_2/2)^{n_2+|n_2|}}{(n_2+n/2)!(n/2)!} J_{n_1}^1(a_{1}^\mu) \]

\[ \times \exp\{2\pi i[n_1x_1^\mu+2n_2(x_2^\mu-\frac{1}{4})]\} \] \hspace{1cm} (A25)

This is rewritten as (A16) by using
\[ i^{m+n}J_{m}(2x) = \sum_{n=0}^{\infty} \frac{(ix)^{m+n}}{(m+n/2)!(n/2)!} \]  

(A26)

\[ J_{-m}(x) = (-1)^{m}J_{m}(x) \]  

(A27)

Therefore the formulas derived by Korekawa (1967) and Toman & Frueh (1976) are included in (11) as special cases.

App. 3.

As shown by Janner & Janssen (1977), the extinction rule is derived by the following consideration. Since \( F_{h'} \) is the Fourier coefficient of the electron density in \( R_{3+n} \), a symmetry operator \( (R|I) \) in \( R_{3+n} \) transforms \( F_{h'} \) into itself. On the other hand, (15) shows that \( F_{h'} \) is transformed into \( F_{h''} \exp(2\pi i \sum_{j} h_{j} \tau_{j}) \), where \( h'' = Rh' = \sum_{j} \tilde{R}_{ij} h_{j} \). Therefore, if the reflection \( h' \) is invariant under \( (R|I) \), that is, \( \sum_{j} \tilde{R}_{ij} h_{j} = h_{i} \), this means that \( F_{h''} \) vanishes if \( \exp(2\pi i \sum_{j} h_{j} \tau_{j}) \neq 1 \). Consequently, the extinction rule

\[ \sum_{i=1}^{3+n} h_{i} \tau_{i} \neq 0 \pmod{1} \]  

(A28)

is obtained for the reflections which fulfills

\[ h_{i} = \sum_{j=1}^{3+n} \tilde{R}_{ij} h_{j} \quad (i=1, \ldots, 3+n) \]  

(A29)

This is the extinction rule for \( F_{h''} \). As stated in the text, the projected structure factor \( F_{h} \) has one-to-one correspondence to \( F_{h''} \) in the incommensurate structure. Therefore the extinction rule derived above is observed in this case. It should be noted however that in the commensurate structure, some extinction rules may dis-
appear because of the superposition of reflections on $R_3$. 