are coupled with 1*. In groups $\mathbf{Q}(\mathbf{H})\{\mathbf{H}\}$, the elements of $\mathbf{Q}$ not contained in $\mathbf{H}$ are coupled with $1'^*$. In groups $\mathbf{Q}(\mathbf{H})\{\mathbf{K}\}$, with $\mathbf{H} \neq \mathbf{K}$, there are elements of $\mathbf{Q}$ coupled with $1'$, coupled with 1* and coupled with $1'^*$. Those elements of $\mathbf{Q}$ not coupled with any of these constitute a subgroup $\mathbf{R}$ which is a subgroup of index 2 of both $\mathbf{H}$ and $\mathbf{K}$, and a subgroup of index 4 of $\mathbf{Q}$. Elements of $\mathbf{K}$ that are not in $\mathbf{R}$ are coupled with $1'$ and consequently double antisymmetry point groups of this type can be denoted by $\mathbf{Q}(\mathbf{H})\{\mathbf{K}(\mathbf{R})\}$. The mathematical equivalence of the magnetic twin laws given in equation (4) with the double antisymmetry groups listed in equation (A1) can now be easily seen: One can interchange the corresponding types of magnetic twin laws and double antisymmetry groups by interchanging the square brackets [] with the curly brackets {}. In the third column of symbols in Table 1, we give the double antisymmetry group symbol, equation (A1), of each of the listed magnetic twin laws.

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On the Use of Crenel Functions for Occupationally Modulated Structures

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Abstract

The use of a crenel function, *i.e.* a difference between two Heaviside functions of amplitude 1, for strong occupation modulation waves and its influence on the refinement of accompanying displacive modulation waves is discussed. The basic set of harmonic functions that is usually employed for the modelling of the displacive modulation wave is no longer orthogonal on the interval where the crenel function takes the value 1. This causes severe correlations between different displacive modulation amplitudes during refinement. The best solution to prevent these correlations is to select functions for inclusion in the refinement according to the criterion that their generalized cosine to the subspace of already selected functions has to be smaller than a certain threshold value. A quality-of-selection parameter is used to estimate the completeness of the selected functions. Finally, the selected functions are orthogonalized. One artificial illustration and one real example are given to demonstrate the use and application of the proposed methods.

Introduction

The theory of $(3 + d)$ superspace groups, introduced by de Wolff (1974, 1977), Janner & Janssen (1977) and de

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Wolff, Janssen & Janner (1981), is widely used to describe the symmetry of commensurate and incommensurate modulated structures. Modulations of the fractional coordinates, site occupancy factors and temperature parameters of the atoms in the basic structure are usually considered. The functions that describe these displacive, occupation and temperature-factor modulation waves, respectively, are expressed as periodic functions of the actual position in the crystal ($d = 1$):

$$f_{\eta}^{\nu} = f^{\nu}[\mathbf{q} \cdot (\mathbf{r}_0^{\nu} + \mathbf{n}) + t] = f^{\nu}(x_4), \qquad (1)$$

where $\mathbf{q}$ is the modulation wave vector, $\mathbf{r}_0^{\nu}$ the average position of the νth atom, $\mathbf{n}$ the actual basic unit cell, t a phase factor and x_4 the fourth (internal) coordinate. The periodic function $f^{\nu}(x_4) = f^{\nu}(x_4 + 1)$ is usually expanded in a Fourier series:

$$f^{\nu} = A_0^{\nu} + \sum_{n=1}^{\infty} A_{s,n}^{\nu} \sin[2\pi n x_4] + \sum_{n=1}^{\infty} A_{c,n}^{\nu} \cos[2\pi n x_4]. \quad (2)$$

The Fourier coefficients A_0^{ν}, $A_{s,n}^{\nu}$ and $A_{c,n}^{\nu}$ define the set of parameters of the $(3 + 1)$ dimensional structure. The main advantage of using Fourier series is that, according to Fejérov's lemma, the set of harmonic functions is complete. This makes it possible to express very general functions even when the infinite summation in (2) is truncated. Moreover, the functions of the set are mutually orthogonal in the sense of the scalar product defined by the integral

$$(g_i \cdot g_j) = \int_0^1 g_i(x) g_j(x)\, \mathrm{d}x = \delta_{ij}, \qquad (3)$$

where δ_{ij} is the Kronecker delta. The orthogonality condition is necessary to prevent correlations between the Fourier coefficients A_0^{ν}, $A_{s,n}^{\nu}$ and $A_{c,n}^{\nu}$ in the refinement process. With the expansion (2), it is also possible to find an analytical expression for the structure factor as a convolution of partial Fourier transforms of separable parts corresponding to the occupational, positional and temperature parameters, respectively (Pérez-Mato, Madariaga & Tello, 1986; Petříček & Coppens, 1988).

Usually, it suffices to take only a very limited number of harmonics to model the proper shape of the periodic functions defined in (1). However, in cases that require a large number of harmonics, special functions like sawtooth functions for a displacive modulation wave (Petříček, Gao, Lee & Coppens, 1990) or crenel (single-block) functions for an occupation modulation wave (van der Lee, Evain, Monconduit, Brec, Rouxel & Petříček, 1994) can be used with less parameters than would be necessary with a Fourier expansion (2).

It can be questioned whether discontinuous functions or functions whose derivatives are discontinuous might be used to model modulation waves in real crystals. Indeed, various faults disturb and smooth the ideal situation that sawtooth or crenel functions are supposed to model. However, discontinuous functions do describe in a first approximation the modulations in structures with, for example, discommensurations. It is therefore worthwhile to consider the use of these functions in the refinement of particular structures. Normally, these special functions are applied together with modulation functions of the form (2). However, the use of these special functions, in particular the crenel function for occupationally modulated structures, *i.e.* structures in which the scattering density of one or more sites is modulated, may create problems for the refinement of the accompanying displacive modulation parameters. For instance, if the crenel function takes either the values 1 or 0, the displacive modulation functions are no longer defined for all x_4 and the orthogonality condition (3) is no longer warranted, causing severe correlations between the displacive or the temperature Fourier coefficients.

The main purpose of this paper is to present some solutions of such problems for both incommensurate and commensurate modulated structures with strong occupational waves. One artificial example will be used to clarify the theoretical part and one real structure, *viz* the modulated structure of $TaSi_{0.410}Te_2$ (Evain, van der Lee, Monconduit & Petříček, 1994), will illustrate the application of the proposed methods.

Theory

The crenel function that describes the occupational modulation in a fully ordered structure is defined as

$$\begin{aligned} p(x_4) &= 1 \quad x_4 \in \langle x_4^0 - \Delta/2, x_4^0 + \Delta/2 \rangle \\ p(x_4) &= 0 \quad x_4 \notin \langle x_4^0 - \Delta/2, x_4^0 + \Delta/2 \rangle. \end{aligned} \qquad (4)$$

The crenel function can be formally defined as the difference between two Heaviside functions of amplitude 1. Straightforward application of Fourier analysis gives the Fourier amplitudes:

$$\begin{aligned} P_0 &= \Delta \\ P_{s,n} &= (2 \sin \pi n \Delta / \pi n) \sin 2\pi n x_4^0 \\ P_{c,n} &= (2 \sin \pi n \Delta / \pi n) \cos 2\pi n x_4^0. \end{aligned} \qquad (5)$$

The coefficients converge to zero only as $1/n$. Therefore, a rather large number of these Fourier coefficients is needed to reasonably approximate the shape of the block or crenel. It is noted that the intensities of nth-order satellites converge as $1/n^2$ in the case of a pure occupational modulated structure with only one independent atom. Thus, even when high-order satellites are not observed, crenel functions might be useful. This is easily checked for, for example, the modulated structure $Ni_{3-x}Te_2$ (Schutte & de Boer, 1993) where no satellite reflections higher than second order were observed. The refined occupancy wave of Ni(2) by two harmonic functions, as published by Schutte & de Boer (1993), was close to a crenel function. A new refinement of this structure by using the crenel function showed indeed that

the calculated intensity ratio of main reflections to first, second, third and fourth-order satellites was 1000:20:4:0.07:0.04, respectively. The refinement, with only one occupational parameter, resulted in an R factor only slightly higher than the one that was published before, with three occupational parameters and the use of a penalty function.

The use of one or two harmonic functions for a function that is close to a crenel function may lead to a significant overshoot or undershoot to non-physical occupation probabilities larger than one or smaller than zero, respectively. This problem is solved by the use of 'penalty' functions that restrict the occupation probability in the physical range $\langle 0, 1\rangle$ (Yamamoto, 1981; Schutte & de Boer, 1993) or by modelling the least-squares determined wave by a crenel function (van der Lee, van Smaalen, Wiegers & de Boer, 1991) or by applying the parameters of the crenel function (4), x_4^0 and Δ, in the least-squares procedure itself (van der Lee *et al.*, 1994).

In all these cases, there is a significant interval of x_4 where the displacive and temperature modulation functions are not or are ill defined, *viz* for those values of x_4 where the occupancy probability is zero or close to zero, respectively. For instance, in the case of the crenel function (5), the set of harmonic functions in (2) is no longer orthogonal, since the functions are only defined for $x_4 \in \langle x_4^0 - \Delta/2, x_4^0 + \Delta/2\rangle$. This problem can be, in principle, solved in several ways:

Limitation of the Fourier expansion

The first method restricts the Fourier expansion of the modulation function to the Δ interval. This fully solves the orthogonalization problem but a large number of harmonics is then necessary to approximate a general displacement for which the value at $x_4^0 - \Delta/2$ and $x_4^0 + \Delta/2$ need not be the same. Moreover, difficulties connected with the analytical calculation of structure factors in the case where Δ is not rational make the method inapplicable.

Selection of basic functions

The second method consists of a selection of a particular subset of the full set of basic harmonic functions in the expansion of (2) on the basis of their mutual scalar products. This does not ensure orthogonality, but can nevertheless be used to approach orthogonality. The selection is as follows. A symmetrical matrix **G** is defined from scalar products according to the relations

$$G_{ij} = (g_i \cdot g_j)/[(g_i \cdot g_i)(g_j \cdot g_j)]^{1/2} \tag{6}$$

and

$$(g_i \cdot g_j) = \int_{x_4^0-\Delta/2}^{x_4^0+\Delta/2} g_i(x) g_j(x)\, \mathrm{d}x. \tag{7}$$

The **G** matrix has, by definition, all diagonal elements equal to 1.00. The off-diagonal elements define cosines of the generalized angle between two elements of the set of functions. The larger the off-diagonal element, the larger the correlations in the refinement. Note that the **G** matrix for the orthonormalized set of functions is equal to the unit matrix.

The quality of the selection of the proper functions under the requirements that they should be close to mutual orthogonality and that they should define an almost complete set can be based on their scalar products G_{ij}. The simplest criterion is to take a function set that has all corresponding G_{ij} lower than a certain limit λ. However, such a criterion is expected to work only if the limit is small enough to ensure that the functions will not make a linearly dependent set. As an example, let us take three vectors in a three-dimensional Eulerian space. These vectors can still be co-planar when their mutual angles defined by the scalar products are equal to 120°. Therefore, a more complicated procedure has to be applied. The function $g_i(x)$ will only be accepted to enlarge the subset $M_n = \{g_1', \ldots, g_n'\}$ of already selected functions if the cosine, ε_i, of its angle to the linear subspace M_n is smaller than the chosen limit λ. To do so, the function $g_i(x)$ can be split into two components, one perpendicular to M_n and one that is a linear combination of the functions of M_n:

$$g_i(x) = g_\perp(x) + g_{M_n}(x) = g_\perp(x) + \sum_{i=1}^{n} \alpha_i g_i'(x). \tag{8}$$

The coefficients α_i $(i = 1, \ldots, n)$ follow from the matrix equation

$$\alpha = \mathbf{F}^{-1}\beta, \tag{9}$$

where $\beta_i = (g \cdot g_i')/[(g \cdot g)(g_i' \cdot g_i')]^{1/2}$ and the matrix **F** is composed from the subset M_n in the same way as the matrix **G** in (6). The length of $g_{M_n}(x)$ divided by the length of g_i represents the cosine of the angle

$$\varepsilon_i = [\beta^T \mathbf{F}^{-1} \beta/(g_i \cdot g_i)]^{1/2}. \tag{10}$$

Thus, g_i is rejected if $\varepsilon_i > \lambda$. The disadvantage of this method is that some of the harmonic functions g_i are skipped and that, therefore, the set is not necessarily complete. This means that a part of the displacive modulation in the crystal is not completely described. The quality of the selection can be estimated from the perpendicular components of the non-selected harmonic functions. The larger the perpendicular component, the higher the chance that a serious error occurs in describing the displacive modulation. Thus, the sum of all such contributions, ξ, is a measure of completeness of the selected set of g_i' functions:

$$\xi = \sum_{i=1}^{n} (1 - \varepsilon_i^2)^{1/2}. \tag{11}$$

Orthogonalization of basic functions

The third method is based on the Schmidt orthogonalization procedure by which an orthogonal set over an arbitrary interval can be constructed from a non-orthogonal set of linearly independent functions. The nth orthogonalized function $\gamma_n(x)$ is built from a combination of the first n basic functions $g_1(x), \ldots, g_n(x)$:

$$\gamma_n(x) = \sum_{i=1}^{n} T_{ni} g_i(x), \qquad (12)$$

where i runs over the non-selected functions. This means that the matrix **T** is triangular. The procedure is unique if the condition of orthogonality is combined with the normalization of the new functions. The main advantage of this method is that the procedure transforms the complete set onto a new complete set. The zeroth-order term A_0 of the expansion (2) is again the average value of the relevant parameter in the interval $\langle x_4^0 - \Delta/2, x_4^0 + \Delta/2\rangle$. This is not generally valid for the basic harmonic functions where the zeroth-order term is the average value over the complete interval $\langle 0, 1\rangle$.

The major problem of the orthogonalization method is that the calculation of the structure factors might be troublesome when the initial subset of functions is almost linearly dependent. This is because even small displacements are described as combinations of large partial displacements. The combination of the selection of basic functions (second method) together with the orthogonalization procedure (third method) is finally the best solution.

This procedure can also be applied to the commensurate case. The only difference is that the number N of functions in (2) is finite and all integrals have to be substituted by a summation over the discrete set of values of x_4. It is noted that the number of displacive Fourier amplitudes to be selected has to be equal to the number of degrees of freedom in the actual supercell. This number is, for an occupational modulated structure with site occupancy factors of either 1 or 0, in general lower than N. The foregoing selection procedure will exactly pick up those Fourier amplitudes that minimize correlations and avoid false minima.

All aforementioned theoretical results have been incorporated into a new version of the computing system *JANA*94 (Petříček, 1994). A special interactive routine makes it possible to select the most convenient set of functions that can be orthogonalized in the refinement process.

An artificial test case

The parameters of Table 1 were used to generate structure factors for a hypothetical structure. Noise from a random-number generator was applied to the structure factors to ensure similar conditions to a real refinement

Table 1. *Basic data for the artificial test example*

Formula:	Ta
Basic unit cell:	$a = 3.018$, $b = 4.031$, $c = 3.815$ Å
	$\alpha = 80$, $\beta = 75$, $\gamma = 80°$
Modulation wave vector:	$\mathbf{q} = 0.3412\mathbf{a}^* + 0.4091\mathbf{b}^* + 0.2752\mathbf{c}^*$
Superspace group:	$P1(\alpha\beta\gamma)$
hklm range:	all main reflections and satellites up to fifth order ($\sin\Theta/\lambda \leq 1.0$ Å^{-1})

Amplitudes of the displacive modulation function

n	$A_{x,s,n}$	$A_{y,s,n}$	$A_{z,s,n}$	$A_{x,c,n}$	$A_{y,c,n}$	$A_{z,c,n}$
0				0.0000	0.0000	0.0000
1	0.0500	−0.0500	0.0500	−0.0250	−0.0350	0.0350
2	0.0250	0.0100	−0.0150	0.0500	0.0500	−0.0250
3	0.0350	0.0150	0.0300	0.0250	0.0150	0.0000

Crenel function parameters $\Delta = 0.577807$ $x_4^0 = 0.833037$

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
0.0150	0.0150	0.0200	0.0050	−0.0050	0.0050

Table 2. *Selection parameters of the artificial test case*

The selection code in the table applies to the basic harmonics from set (13): 1 means that the corresponding function was selected, 0 means that it was not.

λ	Selection code	ξ	$\langle\lvert G_{ij}\rvert\rangle$ $i \neq j$	$\max\lvert G_{ij}\rvert$ $i \neq j$
0.4	10100110010011	1.859	0.088	0.365
0.5	10101010100110	1.773	0.123	0.402
0.6	10111010101000	0.198	0.186	0.506
0.7	11100110110000	0.132	0.167	0.678
0.8	11101011100000	0.147	0.200	0.678
0.9	11111001100000	0.167	0.189	0.678
1.0	11111110000000	0.000	0.237	0.678

based on experimental data. Seven different subsets of the following basic functions:

$$\{1, \sin(2\pi x_4), \cos(2\pi x_4), \ldots, \sin(14\pi x_4), \cos(14\pi x_4)\} \qquad (13)$$

were selected according to the afore-described criteria for λ from 0.4 to 1.0. The number of selected functions in each selected set was kept the same as the number of waves used for the generation of the model, *i.e.* seven (one absolute term, three sine and three cosine waves). The basic characteristics of these sets are summarized in Table 2.

This artificial case provides a very simple test of the completeness of the selected functions since the modulation wave is exactly known. Therefore, the summation of (11) runs over the rejected basic harmonics of the first seven functions of the set (13).

The selected sets were used to refine the structure without and with orthogonalization. The results are summarized in Table 3. It is obvious by the rather high values of reliability factors R and R_w that the first two selections ($\lambda = 0.4$ and 0.5) considerably violate the condition of completeness. The best selection, except the limiting case $\lambda = 1.0$, when all the first seven functions are accepted, is the case $\lambda = 0.7$. These facts correspond very well to the estimated criterion ξ from Table 2. The accordance of the refined modulations with the waves used to generate the artificial case is visualized for the

Table 3. *Refinement results of the artificial test case*

The second column of the table contains the final R values; Nc and Nc_{orth} refer to the number of correlations higher than 0.5 in the refinement without and with orthogonalization; Mc and Mc_{orth} refer to the largest correlation in the refinement without and with orthogonalization.

λ	R/R_w	Nc/Nc_{orth}	Mc/Mc_{orth}
0.4	17.9/23.5	6/7	0.617/0.623
0.5	19.2/26.4	16/3	0.657/0.625
0.6	7.1/8.5	24/3	0.810/0.620
0.7	6.8/8.1	19/4	0.762/0.615
0.8	7.1/8.5	34/4	0.900/0.615
0.9	7.1/8.5	42/1	0.977/0.545
1.0	6.5/7.6	33/1	0.996/0.601

worst ($\lambda = 0.5$) and the best ($\lambda = 0.7$) in Figs. 1(*a*) and (*b*), respectively. It can be seen that for $\lambda = 0.5$ significant parts of the modulation are not well described, which is caused by a lack of completeness of the set of functions used ($\xi = 1.773$, Table 2). The correspondence for $\lambda = 0.7$ is very good for all three coordinates: $\xi = 0.132$. Note that in both cases the correspondence outside the physically relevant interval is very bad.

The largest correlations and the number of correlations higher than 0.5 is different for each set and follow quite well the characteristics based on the off-diagonal term of the **G** matrix from Table 2. It is obvious that the selection method itself is not sufficient; important features of the real modulation function are easily lost. On the other hand, an orthogonalization alone might give numerical problems. Applied together with the selection procedure, it reduces the correlations in all cases. In the presented artificial example, the selection is not really necessary and the orthogonalization could be applied even in the limiting case when all functions are selected.

An experimental case: $TaSi_{0.414}Te_2$

The MA_xTe_2 (M = Nb, Ta; A = Si, Ge; $1/3 \leq x \leq 1/2$) phases have compositionally driven modulated structures with strong accompanying displacive waves (van der Lee *et al.*, 1994; Evain *et al.*, 1994). The basic unit cell contains four independent atoms: Ta(1), Ta(2), Si with average occupancies of $1 - x$, x and x, respectively, and Te, which is only displacively modulated. The (3 + 1)-D superspace group that describes the symmetry of most MA_xTe_2 commensurate and incommensurate modulated phases is $Pnma(00\gamma)s00$ with $\gamma = x$. In the case of $TaSi_{0.414}Te_2$, satellite reflections up to sixth order are observed. The occupational modulation waves of the cations are most easily described by crenel functions [equation (4)]. A refinement of the parameters of the accompanying displacive waves suffers from strong correlations between the different-order Fourier amplitudes if no selection and/or orthogonalization of the waves is applied.

We performed four different refinements to illustrate the methods described in the theory section. The first refinement used all harmonics without any selection and/or orthogonalization. A second refinement used orthogonalization without selection of proper harmonics. The

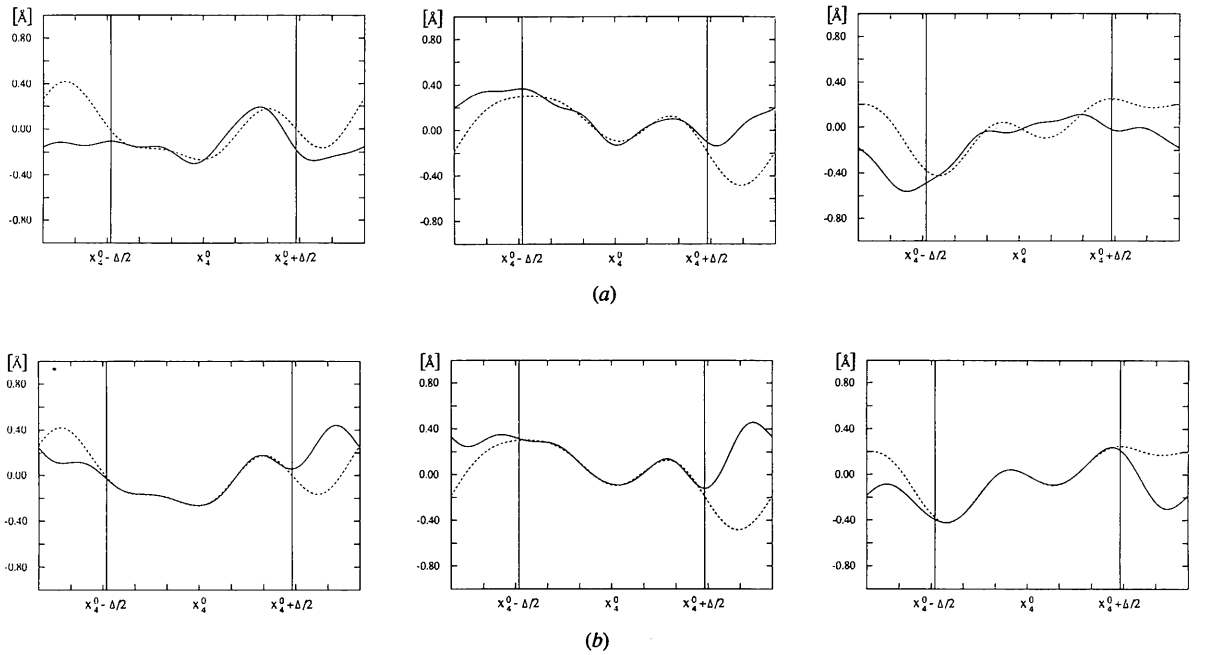

Fig. 1. Displacive modulation of Ta in the artificial test case as a function of x_4 for x (left), y (centre) and z (right) for (*a*) $\lambda = 0.5$ and (*b*) $\lambda = 0.7$. The modulation only has physical meaning in the interval $\langle x_4^0 - \Delta/2, x_4^0 + \Delta/2\rangle$. The dotted line represents the ideal case and the full line represents the results from the refinement.

third one used only a selection procedure. Finally, the last one combined the othogonalization with the selection of harmonics. It is noted that the second refinement is basically the same as the one previously described (Evain *et al.*, 1994). Along with the refinements, a special 'overlap' procedure was applied, that is, the intensities of reflections that are so close in the diffraction pattern that they effectively overlap were taken into account as such.

A difficulty that did not arise for the artificial test case is that the shape of the modulation wave is not *a priori* known. The decision whether to use a new harmonic function was therefore taken on the basis of R factors and the presence or absence of a change of the modulation curves. Four displacive harmonic amplitudes, including the zeroth-order harmonic, were found to be sufficient for all cations. Nine amplitudes were used for Te. Table 4 compiles the characteristics of the selection procedure and Table 5 the results of the refinements.

It can be seen that the final reliability factors do not differ much, but that the number of important correlations is greatly reduced compared with the classical refinement, *i.e.* a refinement without any selection and/or orthogonalization procedure. However, the modulation waves for Ta(2) resulting from the classical refinement and the refinement of the orthogonalized reduced set of harmonics significantly differ, especially near the edges of the crenel [Figs. 2(*a*) and (*b*)]. It is now interesting to compare the distance between Ta(1) and Ta(2) calculated from the two different refinements. The minimum and maximum distances from the classical refinement are 2.62 and 2.93 Å, respectively. The second refinement yields 2.72 and 2.89 Å, respectively. The results of the second refinement are in better agreement with already published values of commensurate structures.

As shown in Fig. 2(*c*), the use of only the selection procedure already creates an almost complete set of functions. The curves for the heavier atoms Ta(1) and Ta(2) completely overlap. As in the artificial test case, an orthogonalization procedure without any selection would suffice to refine the structure without too severe correlations.

Table 4. *Selection procedure for* $TaSi_{0.414}Te_2$

	Δ	x_4^0	Selection code	ξ	$\langle\|G_{ij}\|\rangle$ $i \neq j$	$\max\|G_{ij}\|$ $i \neq j$
Ta(1)	0.58603	0.831291	1110010	0.351	0.247	0.671
Ta(2)	0.41397	0.331876	1010011	0.373	0.196	0.544
Si	0.41397	0.464117	1100110	0.150	0.255	0.322

Note: $\lambda = 0.7$.

Table 5. *Refinement results for* $TaSi_{0.414}Te_2$

Nc is the number of correlations larger than 0.5; *Mc* is the largest correlation. These numbers only apply to the displacive modulation waves of the cations.

Refinement	R/R_w	*Nc*	*Mc*
Classical	10.94/12.39	42	0.998
Selection alone	10.88/12.38	19	0.898
Orthogonalization alone	10.99/12.46	2	0.605
Selection plus orthogonalization	10.87/12.38	0	—

Concluding remarks

We have proposed some methods to reduce strong correlations between displacive Fourier amplitudes in the refinement of occupationally modulated structures. Although the use of these methods is not always a prerequisite to obtain the final structure model, it is expected to be indispensable for more complicated displacive modulation waves and also for commensurate modulated structures, where a selection of basic functions inevitably has to be made.

The following guidelines can be given. Once the approximate position and width of the crenel have been determined, a pure orthogonalization can be applied ($\lambda = 1.0$). If numerical problems occur, a set of λ values should be chosen and corresponding ξ values have to be calculated. Choose, then, a λ on the basis of a low ξ value and combine the selected functions in an orthogonalization procedure for refinement. For a commensurate case, a selection of functions suffices.

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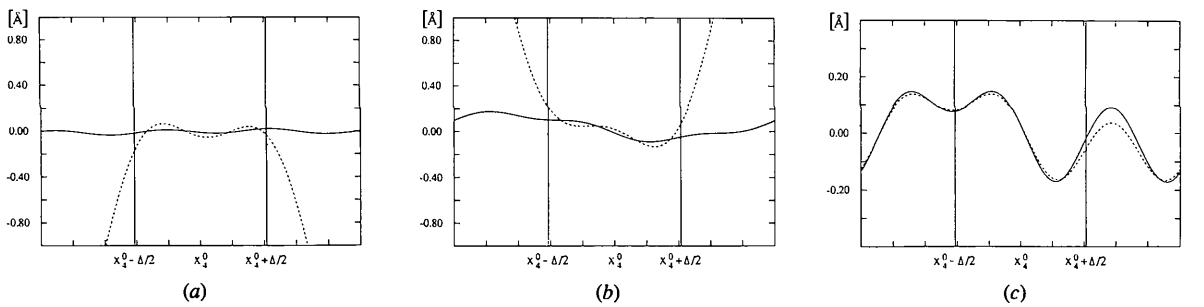

Fig. 2. Modulations in $TaSi_{0.414}Te_2$. (*a*) Displacive modulation of the x coordinate of Ta(2); (*b*) displacive modulation of the z coordinate of Ta(2); (*c*) displacive modulation of z coordinate of Si. In (*a*) and (*b*), the dotted line represents the modulation from a classical refinement, in (*c*) the modulation from a refinement with a selection of basic functions. The full lines represent the results from the refinement with a selection of basic functions together with orthogonalization.

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TDSIR Phasing: Direct Use of Phase-Invariant Distributions in Macromolecular Crystallography

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Abstract

A new strategy for employing three phase triples invariant estimates from Hauptman's single isomorphous replacement (SIR) and anomalous dispersion (SAS) joint probability distribution formulae is outlined which produces a single unique phase-invariant solution in the case where the positions of the heavy-atom scatterers is known. A similar but non-identical result is obtained for the phase invariants of a structure for which a molecular-replacement solution has been obtained. It is important to note that the values of the individual native/derivative phases can be determined directly from the probability distribution formulae without having to utilize the phase-invariant estimates in an active way. Elimination of the multisolution aspect of utilizing phase-invariant estimates should have important repercussions with regard to phasing macromolecular sets of derivatized data. Trial calculations based on experimentally measured 2.5 Å data for three derivatives of cytochrome c_{550} are encouraging. The average of the three SIR maps resolves a number of structural ambiguities seen in the published multiple isomorphous replacement (MIR) map obtained from eight derivatives.

Introduction

Probabilistic formulae to estimate the three phase triples invariants of macromolecular structures using SIR (Hauptman, 1982*a*) and SAS (Hauptman, 1982*b*) data were first derived by Hauptman more than ten years ago. Whereas a unique solution exists for the phase invariant within the interval 0 to 2π from the conditional probability distribution formula in the SAS case, only the sign of the cosine of the phase invariant, but not its modulus, was obtained from the analogous SIR distribution formula if the positions of the derivative heavy atoms were unknown. A more specific formula appropriate to the two-derivative MIR situation was developed (Fortier, Weeks & Hauptman, 1984) that improved the accuracy of the estimates. It was noted that, if the reciprocal-lattice vectors, rather than the atomic coordinates, were considered the primitive random variables in the derivation of the SIR distribution function, a slightly different result could be obtained (Giacovazzo, Cascarano & Zheng, 1988), but still only the mode of the phase invariant, 0 or π, could be determined without knowledge of the heavy-atom scatterers. A prior study had meanwhile indicated that both the sign and modulus of the cosine invariant within the full range of +1 to −1 was obtainable if the positions of the heavy-atom scatterers were known for the SIR case (Fortier, Moore & Fraser, 1985); improved phase-invariant estimates for the SAS case were also reported (Fortier, Fraser & Moore, 1986).

In this paper, we have reinvestigated Hauptman's original SIR work to discover that both the sine and cosine of the phase invariant can be obtained from the joint probability distribution function in a rather obvious way if the positions of the derivative heavy atoms are known. Moreover, unique values for the native and derivative phases can be directly obtained from the