

## Combined Standard Uncertainties for Interatomic Distances in One-Dimensionally Modulated Crystals

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### Abstract

A method is proposed that allows a variance estimation for interatomic distances in the case of a one-dimensional incommensurate (or commensurate) displacively modulated structure to be derived. This method takes into account the covariance terms in the variance-covariance matrix  $\Sigma$  of the atomic pair, resulting from true linear relations between some positional parameters. These linear relations, arising in the case of symmetry-related atoms or in the case of special positions in crystals of high symmetry (trigonal, tetragonal or hexagonal systems), are carefully scrutinized. The results of these linear relations on the  $\Sigma$  matrix are specified for any order of the Fourier expansion of the modulated displacements and some examples of matrices are given. A general formula written in matrix form is then derived for the bond-length variance. This method is then exemplified by different typical examples, showing the usefulness of such a calculation for the comparison of different results or for the discussion of the significance of some interatomic distance variations.

### 1. Introduction

The determination of uncertainty for physical parameters refined from least-squares methods is important as it gives a range of significance for the corresponding results in relation to the actual values, which cannot be measured directly but are derived from the analysis of a set of measured data. For interatomic distances, the final result is obtained from a refinement process using refined structural parameters from experimental data through a functional relationship. The square root of the attached variance term characterizing the accuracy of this structural secondary parameter is defined as the combined standard uncertainty (c.s.u.), previously called estimated standard deviation (e.s.d.) (Schwarzenbach, Abrahams, Flack, Prince & Wilson, 1995). A structural study will be reliable if one can state that the actual values of the derived structural parameters lie in an interval centred at the refined value and with a width proportional to the c.s.u. However, the c.s.u. values that can be calculated from the previous analysis suppose that the model is adequate and that the chosen parameters on the whole can accurately describe the real structure. It

is well known, for example, that the calculated c.s.u. for the cell parameters of a single crystal determined from a four-circle goniometer measurement or for the thermal-motion parameters refined from a global profile analysis of a powder diffraction pattern are often underestimated; two independent measurements or two refinements using different profile or background models can give incompatible results within the range of their c.s.u.

Nevertheless, for structural studies, it is important to validate a refinement procedure with a critical examination of the derived parameters (*e.g.* thermal-motion or site-occupancy parameters) or of the secondary parameters (*e.g.* interatomic distances or bond lengths) that can be compared and should be compatible with known standard values within the range of their c.s.u.s. For a crystal that exhibits a displacive modulation, a variance estimation of interatomic distances is particularly interesting. In fact, because of the modulation and in particular in the case of an incommensurate modulation, the structural model involves a variation of the interatomic distances throughout the crystal. If large variations are observed, it is most important to know if the results are consistent with the type of chemical bond or with the chemical coordination of the species. On the contrary, if only small variations are observed, one has to decide about the real significance of these variations. Interatomic distances are not always tabulated as a function of the internal phase variable, even if it is important to check the potential validity of structural results from the values for interatomic distances in any cell of the modulated crystal.

To perform these statistical tests, the c.s.u. of the interatomic distances are required. A method has been suggested by D. E. Sands (1966) to compute bond-length and bond-angle variances in non-modulated crystals. It takes into account the possible linear relations occurring between the coordinates of symmetry-related atoms or of atoms on special Wyckoff positions through covariance terms. This type of calculation has not always been used in the available computer programs for interatomic distance calculation, so, for example, symmetry-equivalent interatomic distances are not always calculated with the same c.s.u.

This method may also be used in the case of displacively modulated crystals. Then, two types of parameter have to be considered: the average atomic coordinates and the Fourier terms describing the periodic displacements from the average position. In the general case of a  $d$ -dimensional modulation, these displacements are a function of  $d$  variables, the so-called internal parameters (de Wolff, Janssen & Janner, 1981). If the modulation is one dimensional, the number of Fourier terms per atom is six for a given harmonic of order  $n$ . As a result, the rank of the variance-covariance matrix  $\Sigma$  related to a given atomic pair is larger than in the usual case [ $2(3 + 6m)$  against  $2 \times 3$ , where  $m$  is the number of harmonics introduced in the model]. For a crystal of high symmetry (in trigonal, tetragonal or hexagonal systems for a one-dimensional modulation), linear relations may be involved both between average coordinates and between Fourier terms. Two cases are to be considered: one of the atoms of the pair either is generated from another one in a general position by a symmetry operator or lies in a special position in the average structure. The resulting linear links then induce covariance terms in the  $\Sigma$  matrix. The expression of the covariance terms related to the average coordinates is easy to write. As expected, the main difficulty is to find a general formula describing the possible linear relations between the Fourier terms with the aim of deriving the corresponding covariance terms for the generalized  $\Sigma$  matrix. Such relations have already been established for monoincommensurate modulated structures (Petricek & Coppens, 1988). In the present paper, the consequences on the variance-covariance matrices are considered in relation to the symmetry conditions of a given atomic pair and a method of calculating the interatomic distance c.s.u. is proposed.

## 2. Main assumptions and methodological considerations

Before defining how the bond-length variances can be derived from the variances of the refined parameters, let us first recall some results concerning general statistical properties and the description of modulated crystals.

### 2.1. Statistical properties

If we consider a non-linear function  $f(p_1, p_2, \dots, p_i, \dots)$  of several random variables  $p_i$ , it is possible to give an estimation of the variance of  $f$ ,  $\text{var}(f) = \sigma_f^2$ , by using the first two terms of the Taylor expansion of  $f$  about the mean values  $\langle p_i \rangle$  (Schwarzenbach *et al.*, 1995):

$$\sigma_f^2 \simeq \sum_i (\partial f / \partial p_i)^2 \text{var}(p_i) + \sum_{i \neq j} [(\partial f / \partial p_i)(\partial f / \partial p_j)] \text{cov}(p_i, p_j). \quad (1)$$

This relation can be expressed in matrix form as

$$\sigma_f^2 \simeq \langle G | \Sigma | G \rangle, \quad (2)$$

where  $\Sigma$  is the variance-covariance matrix associated with the parameters  $p_i$ ,  $\langle G | = (\partial f / \partial p_1, \partial f / \partial p_2, \dots, \partial f / \partial p_i, \dots)$  and  $|G \rangle$  is the transpose of  $\langle G |$ . The derived expression for  $\sigma_f^2$  is valid assuming a small dispersion of the random variables,  $p_i$ , around their mean values. Another possible method involves expressing  $f$  only as a function of rigorously independent parameters chosen among the parameters  $p_i$ . Consequently, (1) is much simpler, without covariance terms and the new  $\Sigma'$  matrix is smaller and diagonal. The similarity between the two methods is shown in Appendix A. This last method is perhaps easier in particular cases but requires simple relations between dependent parameters, which are not always easy to derive.

### 2.2. Modulated crystals

In a one-dimensionally modulated crystal, the displacive modulation of the  $i$ th atom is described with a periodic vector field  $\mathbf{U}^i$ , a function of the internal parameter  $x_\alpha^i = \mathbf{q}^* \cdot (\mathbf{r}_0^i + \mathbf{p})$ , where  $\mathbf{q}^*$  is the modulation vector,  $\mathbf{r}_0^i$  is the average position of the  $i$ th atom in the origin unit cell and  $\mathbf{p}$  is a direct-lattice vector (Janssen, Janner, Looijenga-Vos & de Wolff, 1992).  $\mathbf{q}^*$  may include a rational part  $\mathbf{q}_r$ , so that  $\mathbf{q}^* = \mathbf{q}_r + \mathbf{q}_i$ . The components  $U_\alpha^i$  of  $\mathbf{U}^i$  are expanded in Fourier series up to the  $m$ th order, which is usually the maximum order observed for the satellite reflections in the experimental diffraction pattern.

$$U_\alpha^i(t) = \sum_{n=1}^m \{ A_{\alpha,n}^i \cos[2\pi n(t_0^i + t)] + B_{\alpha,n}^i \sin[2\pi n(t_0^i + t)] \}, \quad (3)$$

where  $\alpha = 1, 2, 3$ ;  $t_0^i = \mathbf{q}^* \cdot \mathbf{r}_0^i = q_\alpha^* \bar{x}_\alpha^i$  (summation with Einstein's convention) and  $\bar{x}_\alpha^i$  is the  $\alpha$  component of the average position  $\mathbf{r}_0^i$ ; and  $t = \mathbf{q}^* \cdot \mathbf{p}$  is (modulo 1) a dense set of real numbers on the  $[0, 1]$  interval in the incommensurate case. The actual position of the  $i$ th atom in the  $\mathbf{p}$  unit cell is then given by

$$x_\alpha^i = \bar{x}_\alpha^i + p_\alpha + U_\alpha^i(t). \quad (4)$$

If the atomic pair of interest is denoted as  $i, j$ , the square of the corresponding interatomic distance can be expressed by

$$d^2 = \langle X | g | X \rangle, \quad (5)$$

where  $g$  is the metric tensor ( $g_{kl} = \mathbf{a}_k \cdot \mathbf{a}_l$ ,  $\{\mathbf{a}_k\}$  the unit-cell basic vectors) and  $\langle X | = (X_1, X_2, X_3)$  with  $X_\alpha = x_\alpha^i - x_\alpha^j$ .

To obtain a convenient form for the variance-covariance matrix  $\Sigma$  of the parameters related to the considered atomic pair, the following order is chosen for the different variables:

$$\overline{x_1^i}, \overline{x_2^i}, \overline{x_3^i}, A_{1,1}^i, A_{2,1}^i, A_{3,1}^i, B_{1,1}^i, B_{2,1}^i, B_{3,1}^i, \dots, \\ A_{1,m}^i, A_{2,m}^i, A_{3,m}^i, B_{1,m}^i, B_{2,m}^i, B_{3,m}^i,$$

$$\overline{x_1^j}, \overline{x_2^j}, \overline{x_3^j}, A_{1,1}^j, A_{2,1}^j, A_{3,1}^j, B_{1,1}^j, B_{2,1}^j, B_{3,1}^j, \dots, \\ A_{1,m}^j, A_{2,m}^j, A_{3,m}^j, B_{1,m}^j, B_{2,m}^j, B_{3,m}^j.$$

From (2), a variance estimation of the interatomic distance can be derived if the correct variance and covariance terms are introduced in the  $\Sigma$  matrix, remembering that the components of  $\langle G \rangle$  are the derivatives of  $d$  with respect to the previous variables.

### 2.3. Simplifying hypotheses and approximations

The determination of the c.s.u. for bond lengths or interatomic distances proposed in this paper is restricted to the case where the displacive modulation is one dimensional. Our aim is to describe a variance analysis as a function of the linear relations between positional parameters. Preliminary approximations can be carried out.

As is well known, on refining the independent parameters by least squares, unbiased estimates are obtained for the elements of the variance-covariance matrix  $V$  (Hamilton, 1964), providing the model is good. The covariance terms resulting from correlations between the so-called 'independent' parameters should be considered in the analysis of the bond-length variances. However, relatively small values can usually be expected for the correlation coefficients  $\rho_{k,l}$ , particularly for positional parameters, assuming that the crystal does not display any pseudosymmetrical character. Moreover, it is likely that a balanced proportion of positive and negative values occurs for the  $\rho_{k,l}$  coefficients, thereby minimizing their influence in the calculation of variances. Hence, in the following discussion, these covariance terms that do not correspond to true linear relations between positional parameters are neglected. If necessary, they could also be introduced.

The cell parameters and components of the modulation vector  $\mathbf{q}^*$  are usually accurately known. The corresponding variance terms are supposed to be negligible in the present study. We can, therefore, limit our analysis to the refined positional parameters.

### 3. Determination of the $\Sigma$ matrix

In the most favourable case of two independent atoms in general positions, the  $\Sigma$  matrix has a diagonal form composed of the different variance terms of mutually independent variables. However, it is often necessary

to consider more complex but not untypical cases that involve linear relations between the previous variables. Consequently, it becomes necessary to modify the simple diagonal form by adding covariance terms. Different cases can be distinguished:

(a) The atoms  $i$  and  $j$  are not symmetry related:  $\Sigma$  is then composed of diagonal blocks of matrices  $M^i, S_1^i, \dots, S_n^i, \dots, S_m^i, M^j, S_1^j, \dots, S_n^j, \dots, S_m^j$ , where  $M^i$  ( $3 \times 3$ ) and  $S_n^i$  ( $6 \times 6$ ) are variance-covariance matrices related to the average coordinates and to the Fourier terms of the  $n$ th harmonic, respectively. Covariance terms may be involved only in the  $M$  and  $S_n$  matrix of each of these atoms for crystals of high symmetry (HSC); in this case, the principal rotation axis will be supposed to be parallel to the  $x_3$  direction. Three subcases occur:

(a1) one atom of the pair (or both) is (are) on a special position in the average structure;

(a2) one of the atoms does not belong to the list, noted ( $L$ ), of the 'independent atoms' of the structure refinement. It is, therefore, generated from an atom  $\mu$  in a general position by a given symmetry operator, denoted ( $R, \mathbf{s}$ ), belonging to the symmetry space group associated with the average structure;

(a3) the third case is a combination of the first two: the atom  $i$ , on a special position in the average structure, is generated from another atom  $\mu$  of the list ( $L$ ).

(b) The atoms  $i$  and  $j$  are symmetry related: additional covariance terms have to be included in the  $\Sigma^{i,j}$  part of the  $\Sigma$  matrix ( $\Sigma^{i,j} = \Sigma^{j,i}$ ). The  $\Sigma^{i,j}$  part is then composed of diagonal blocks of matrices  $N, P_1, \dots, P_n, \dots, P_m$ .

#### 3.1. The $M$ matrix

3.1.1. *Case (a1)*. Some special positions only impose a constant rational value for some components of the average position of the considered atoms. The corresponding positional parameter simply disappears but, in HSC, linear relations between the  $x_\alpha^i$  coordinates may be involved. It is easy to see that they can be written in a general form  $x_\beta^j = \varphi x_\alpha^i$ , where  $\varphi$  is a rational number; then, the  $M^i$  matrix can easily be written using the relations

$$\text{var}\left(\overline{x_\beta^j}\right) = \varphi^2 \text{var}\left(\overline{x_\alpha^i}\right); \quad \text{cov}\left(\overline{x_\alpha^i}, \overline{x_\beta^j}\right) = \varphi \text{var}\left(\overline{x_\alpha^i}\right). \quad (6)$$

3.1.2. *Case (a2)*. The expression for  $M^i$  does not depend on the possible glide vector,  $\mathbf{s}$ , associated with  $R$ .  $M^i$  is deduced from  $M^\mu$ , which is then a diagonal matrix, by the classical formula:

$$M^i = RM^\mu \tilde{R}, \quad (7)$$

where  $\tilde{R}$  is the transpose of  $R$ . The terms of  $M^i$  are given by a single expression:

$$\text{cov}(\overline{x_\alpha^i}, \overline{x_\beta^i}) = R_{\alpha\gamma} R_{\beta\gamma} \text{var}(\overline{x_\gamma^i})$$

(Einstein's convention). (8)

The variance terms are of course obtained for  $\alpha = \beta$ .

3.1.3. *Case (a3)*. This case is a generalization of (7), with  $M^\mu$  not diagonal, but with the form (6):

$$\text{var}(\overline{x_\alpha^\mu}) = (R_{\alpha 1} + \varphi R_{\alpha 2})^2 \text{var}(\overline{x_1^\mu})$$

for  $\alpha = 1$  and  $2$

$$\text{var}(\overline{x_3^\mu}) = \text{var}(\overline{x_3^\mu}) \quad (9)$$

$$\text{cov}(\overline{x_1^\mu}, \overline{x_2^\mu}) = [R_{11}R_{21} + \varphi(R_{11}R_{22} + R_{12}R_{21}) + \varphi^2 R_{12}R_{22}] \text{var}(\overline{x_1^\mu}).$$

3.1.4. *Typical examples*. Let us give some typical examples illustrating the calculus of  $\sigma_d^2$  from (2). For simplicity, consider an unmodulated hexagonal crystal (space group  $P6mm$ ) with two equivalent atomic pairs  $i, \mu$  and  $i, j$ ; the atom  $i$  is at the origin of the coordinates and the atom  $j$  is generated from the atom  $\mu$  belonging to  $L$  by a rotation  $R$  of  $2\pi/6$  about  $c$ . Let us look at the following cases:

(i) the atom  $\mu$  is in a general position in the  $\mathbf{a}, \mathbf{b}$  plane ( $z^\mu = 0$ );

(ii) the atom  $\mu$  is in the special position  $2x^\mu, x^\mu, 0$ .

The  $\Sigma$  matrix related to the pair  $i, \mu$  can be reduced to the  $M^\mu$  matrix.

In the first case,  $M^\mu$  is diagonal since  $x^\mu$  and  $y^\mu$  are independent variables; (2) leads to

$$\begin{aligned} \sigma_{d_{i,\mu}}^2 &= (\partial d / \partial x^\mu)^2 \sigma_{x^\mu}^2 + (\partial d / \partial y^\mu)^2 \sigma_{y^\mu}^2 \\ &= (a^4 / 4d^2) [(2x^\mu - y^\mu)^2 \sigma_{x^\mu}^2 + (2y^\mu - x^\mu)^2 \sigma_{y^\mu}^2]. \end{aligned} \quad (10)$$

The  $\Sigma$  matrix related to the pair  $i, j$  can also be reduced to the  $M^j = RM^\mu R$  matrix. Then,

$$\begin{aligned} \sigma_{d_{i,j}}^2 &= (\partial d / \partial x^j)^2 (\sigma_{x^\mu}^2 + \sigma_{y^\mu}^2) + 2(\partial d / \partial x^j)(\partial d / \partial y^j) \sigma_{x^\mu}^2 \\ &\quad + (\partial d / \partial y^j)^2 \sigma_{y^\mu}^2 \\ &= (a^4 / 4d^2) \{ (x^\mu - 2y^\mu)^2 + 2(x^\mu - 2y^\mu)(x^\mu + y^\mu) \\ &\quad + (x^\mu + y^\mu)^2 \} \sigma_{x^\mu}^2 + (x^\mu - 2y^\mu)^2 \sigma_{y^\mu}^2. \end{aligned} \quad (11)$$

This variance is equal to  $\sigma_{d_{i,\mu}}^2$ , as expected.

In the second case, since  $M_{11}^\mu = 4\sigma_{x^\mu}^2$ ,  $M_{22}^\mu = \sigma_{x^\mu}^2$  and  $M_{12}^\mu = 2\sigma_{x^\mu}^2$ :

$$\sigma_{d_{i,\mu}}^2 = \left( \frac{\partial d}{\partial X^\mu} \right)^2 4\sigma_{x^\mu}^2 + 2 \frac{\partial d}{\partial X^\mu} \frac{\partial d}{\partial Y^\mu} 2\sigma_{x^\mu}^2 + \left( \frac{\partial d}{\partial Y^\mu} \right)^2 \sigma_{x^\mu}^2 \quad (12)$$

with  $X^\mu = 2x^\mu$  and  $Y^\mu = x^\mu$ ; the very simple expression

$$\sigma_{d_{i,\mu}}^2 = 3a^2 \sigma_{x^\mu}^2 \quad (13)$$

is then obtained, which can of course be derived directly by writing  $d_{i,\mu}$  as a function of  $x^\mu$ .

It is easy to find from (7) that  $M_{11}^j = \sigma_{x^\mu}^2$ ,  $M_{22}^j = 4\sigma_{x^\mu}^2$  and  $M_{12}^j = 2\sigma_{x^\mu}^2$ . From (2), the variance of  $d_{i,j}$

$$\sigma_{d_{i,j}}^2 = \left( \frac{\partial d}{\partial X^j} \right)^2 \sigma_{x^\mu}^2 + 2 \frac{\partial d}{\partial X^j} \frac{\partial d}{\partial Y^j} 2\sigma_{x^\mu}^2 + \left( \frac{\partial d}{\partial Y^j} \right)^2 4\sigma_{x^\mu}^2 \quad (14)$$

with  $X^j = x^\mu$  and  $Y^j = 2x^\mu$  is equal to  $\sigma_{d_{i,\mu}}^2$ , as expected.

### 3.2. The $S_n$ matrix

In a one-dimensional modulated crystal, the displacive modulation functions  $\mathbf{U}^\mu$  and  $\mathbf{U}^\nu$  associated with two atoms  $\mu$  and  $\nu$ , symmetry related by the operator  $(R, \mathbf{s})$  in the average structure, are interdependent according to the relation

$$\begin{aligned} \mathbf{U}^\nu(\overline{x_4^\nu}) &= R\mathbf{U}^\mu(\overline{x_4^\mu}) \\ &= R\mathbf{U}^\mu \left[ \varepsilon(\overline{x_4^\nu} - \tau + \mathbf{m}^* \cdot \mathbf{r}_0^i - \mathbf{q}_r^* \cdot \mathbf{s}) \right], \end{aligned} \quad (15)$$

where  $\varepsilon = \pm 1$  satisfies the condition  $R\mathbf{q}_{ir}^* - \varepsilon\mathbf{q}_{ir}^* = \mathbf{0}$ ;  $\tau$  is a phase shift in the internal space associated with the symmetry operator;  $\mathbf{m}^* = \varepsilon\mathbf{q}_r^* - R^{-1}\mathbf{q}_r^* = \varepsilon\mathbf{q}^* - R^{-1}\mathbf{q}^*$ . The rational part  $\mathbf{q}_r^*$  of  $\mathbf{q}^*$  involves a centring of the four-dimensional unit cell in  $R^4$ . It is always possible to do an appropriate basis transformation that leads to a zero value for  $\mathbf{q}_r^*$ . Then, the previous relation can be written in the simpler form

$$\mathbf{U}_\alpha^\nu(\overline{x_4^\nu}) = R_{\alpha\beta} U_\beta^\mu \left[ \varepsilon(\overline{x_4^\nu} - \tau) \right] \quad (16)$$

with  $\overline{x_4^\nu} = t_0^\nu + t$ . This relation associated with (3) leads to

$$\begin{aligned} U_\alpha^\nu(t) &= R_{\alpha\beta} \sum_n \{ (c_n A_{\beta,n}^\mu - \varepsilon s_n B_{\beta,n}^\mu) \cos[2\pi n(t_0^\nu + t)] \\ &\quad + (s_n A_{\beta,n}^\mu + \varepsilon c_n B_{\beta,n}^\mu) \sin[2\pi n(t_0^\nu + t)] \} \end{aligned} \quad (17)$$

with  $c_n = \cos(2\pi n\tau)$  and  $s_n = \sin(2\pi n\tau)$ , allowing  $A_{\alpha,n}^\nu$  and  $B_{\alpha,n}^\nu$  to be given as a function of  $A_{\beta,n}^\mu$  and  $B_{\beta,n}^\mu$ :

$$\begin{aligned} A_{\alpha,n}^\nu &= c_n (R_{\alpha\beta} A_{\beta,n}^\mu) - \varepsilon s_n (R_{\alpha\beta} B_{\beta,n}^\mu) \\ B_{\alpha,n}^\nu &= s_n (R_{\alpha\beta} A_{\beta,n}^\mu) + \varepsilon c_n (R_{\alpha\beta} B_{\beta,n}^\mu). \end{aligned} \quad (18)$$

These relations (18) can be written in matrix form:

$$|Y_n^\nu\rangle = |T_n| Y_n^\mu \quad (19)$$

$$\text{with } T_n = \begin{pmatrix} c_n R & -\varepsilon s_n R \\ s_n R & \varepsilon c_n R \end{pmatrix} \text{ and } \langle Y_n | = (A_{1,n}, A_{2,n}, A_{3,n}, B_{1,n}, B_{2,n}, B_{3,n}).$$

Then, in a similar way to (7), the  $S_n^\nu$  matrix can be related to that of  $S_n^\mu$ :

$$S_n^\nu = T_n S_n^\mu \tilde{T}_n. \quad (20)$$

The different previously defined cases are also considered now.

In case (a2),  $S_n^i$  is easily determined from (20) with  $\nu = i$  because the variance terms of  $S_n^\mu$  are directly found in the  $V$  matrix. In the other cases (with  $i = \mu$  or  $i \neq \mu$ ),  $S_n^\mu$  has to be derived taking into account the possible linear relations between the Fourier terms.

Let us consider the action of symmetry constraints on the Fourier terms of the atom  $\mu$ , assumed to be located on a special position in the average structure. Denoting the point-group symmetry of this site by PS, the constraints are then found by writing the invariance of  $U^\mu$  under the action of the generator operations  $(R, \varepsilon|\tau)$  acting in  $R^4$ , associated with the generator operation  $R$  of PS (de Wolff *et al.*, 1981). For each generator operation, the relation

$$U^\mu(\overline{x_4^\mu}) = R U^\mu \left[ \varepsilon (\overline{x_4^\mu} - \tau) \right]$$

has to be satisfied; it turns out that the Fourier terms of the  $n$ th harmonic are found by solving

$$\langle T_n | Y_n^\mu \rangle = | Y_n^\mu \rangle. \quad (21)$$

From our choice of axis,  $U_1$  and  $U_2$  do not depend on  $U_3$ , and the condition (21) can be expressed from the two equations

$$\langle T_n' - I' | y_n^\mu \rangle = |0\rangle \quad (22)$$

$$\langle T_n'' - I'' | z_n^\mu \rangle = |0\rangle \quad (23)$$

with

$$T_n' = \begin{pmatrix} c_n R' & -\varepsilon s_n R' \\ s_n R' & \varepsilon c_n R' \end{pmatrix}, \quad R' = \begin{pmatrix} R_{11} & R_{12} \\ R_{21} & R_{22} \end{pmatrix},$$

$$T_n'' = R_{33} \begin{pmatrix} c_n & -\varepsilon s_n \\ s_n & \varepsilon c_n \end{pmatrix},$$

$$\langle y_n^\mu | = (A_{1,n}^\mu, A_{2,n}^\mu, B_{1,n}^\mu, B_{2,n}^\mu),$$

$$\langle z_n^\mu | = (A_{3,n}^\mu, B_{3,n}^\mu)$$

and  $I'$ ,  $I''$  are the unit matrices ( $4 \times 4$ ) and ( $2 \times 2$ ), respectively.

If the determinant  $\Delta |T_n' - I'| \neq 0$ , then  $U_1^\mu = U_2^\mu = 0$ .

If  $\Delta |T_n'' - I''| \neq 0$ , then  $U_3^\mu = 0$ .

Some trivial cases may occur when both  $s_n = 0$  and  $c_n R' - I' = 0$  (or  $R_{33} c_n - I'' = 0$ ). This leads to zero values for all the elements of the matrix  $T_n' - I'$  or  $T_n'' - I''$ . Such cases do not impose any constraint on the Fourier terms and are not of interest here.

If  $\Delta = 0$ , then, within a given harmonic, the symmetry constraints bring about the cancellation of some Fourier terms or linear relations between them (for HSC).

Let us first consider the usual case where a single symmetry element is involved in PS. The possible linear relations are derived from (22) and (23).

For  $\varepsilon = +1$ , the linear relations between the Fourier terms can always be written in the following way:

$$A_{1,n}^\mu = \alpha_n A_{2,n}^\mu + \beta_n B_{2,n}^\mu \quad (24)$$

$$B_{1,n}^\mu = -\beta_n A_{2,n}^\mu + \alpha_n B_{2,n}^\mu, \quad (25)$$

where the coefficients  $\alpha_n$  and  $\beta_n$  are functions of  $s_n$ ,  $c_n$  and  $R$ .

In this case,  $A_{3,n}^\mu$  and  $B_{3,n}^\mu$  are always independent.

For  $\varepsilon = -1$ , several forms of linear relations may be involved:

(i)  $A_{1,n}^\mu = \alpha_n' A_{2,n}^\mu$  and  $B_{1,n}^\mu = \alpha_n'' B_{2,n}^\mu$  simultaneously with  $\alpha_n'' = -\alpha_n'$ ;

(ii)  $A_{1,n}^\mu = \alpha_n' A_{2,n}^\mu$ ;

(iii)  $B_{1,n}^\mu = \alpha_n'' B_{2,n}^\mu$ ;

(iv)  $A_{3,n}^\mu = \gamma_n B_{3,n}^\mu$ .

In the first three cases, no linear dependence is involved between  $A_{3,n}^\mu$  and  $B_{3,n}^\mu$ , whereas, in case (iv),  $A_{1,n}^\mu = A_{2,n}^\mu = B_{1,n}^\mu = B_{2,n}^\mu = 0$ . All these linear dependences are tabulated in Appendix B.

The various matrices  $S_n^\mu$  were derived taking into account the previous linear relations (Table 1). For  $\varepsilon = +1$ , the Fourier terms  $A_{2,n}^\mu$  and  $B_{2,n}^\mu$  are arbitrarily chosen as reference terms and, consequently, are considered as independent parameters in the refinement. A zero value is, therefore, attributed to  $\text{cov}(A_{2,n}^\mu, B_{2,n}^\mu)$ .

Let us now consider the case where several symmetry elements are simultaneously involved in PS. The symmetry point groups that lead to linear relations between some Fourier terms (HSC) can be found by considering the appropriate associated symmetry in internal space, *i.e.* by looking at the possible 4D superspace groups for a one-dimensional modulation (de Wolff *et al.*, 1981; Janssen *et al.*, 1992). The following point groups are involved: 622, 422, 32, 222,  $mm2$ ,  $mmm$  and  $2/m$ . Two cases occur depending on whether the linear dependence(s) related to one symmetry element is (are) maintained or reduced. The corresponding  $S_n^\mu$  matrix can easily be derived from the variance-covariance matrices written in Table 1.

### 3.3. The $\Sigma$ matrix

The next step is now to write the  $\Sigma$  matrix related to the atomic pair  $i, j$  in all the relevant cases.

3.3.1. Case (a). Some typical examples, involving 4D symmetry described by standard superspace groups, are given in Table 2. Only the  $\Sigma^{i,i}$  part of  $\Sigma$  is written, assuming a modulation described by a single harmonic.

Table 1.  $S_n$  matrices for atoms in special positions with only one symmetry operation in the point group of the atomic site

(a)  $\varepsilon = +1$

$A_{2,n}, B_{2,n}, A_{3,n}$  and  $B_{3,n}$  are independent parameters.  $A_{1,n} = \alpha_n A_{2,n} + \beta_n B_{2,n}$ ;  $B_{1,n} = -\beta_n A_{2,n} + \alpha_n B_{2,n}$ .

	$A_{1,n}$	$A_{2,n}$	$A_{3,n}$	$B_{1,n}$	$B_{2,n}$	$B_{3,n}$
$A_{1,n}$	$\alpha_n^2 \sigma_{A_{2,n}}^2 + \beta_n^2 \sigma_{B_{2,n}}^2$	$\alpha_n \sigma_{A_{2,n}}^2$	0	$\alpha_n \beta_n (\sigma_{B_{2,n}}^2 - \sigma_{A_{2,n}}^2)$	$\beta_n \sigma_{B_{2,n}}^2$	0
$A_{2,n}$		$\sigma_{A_{2,n}}^2$	0	$-\beta_n \sigma_{A_{2,n}}^2$	0	0
$A_{3,n}$			$\sigma_{A_{3,n}}^2$	0	0	0
$B_{1,n}$				$\beta_n^2 \sigma_{A_{2,n}}^2 + \alpha_n^2 \sigma_{B_{2,n}}^2$	$\alpha_n \sigma_{B_{2,n}}^2$	0
$B_{2,n}$					$\sigma_{B_{2,n}}^2$	0
$B_{3,n}$						$\sigma_{B_{3,n}}^2$

The  $\alpha_n$  and  $\beta_n$  coefficients can be easily derived from the knowledge of the symmetry operator ( $R, \varepsilon, \tau$ ) using equation (22).

(b)  $\varepsilon = -1$

(i) Hexagonal, trigonal or tetragonal systems: symmetry operation  $\begin{pmatrix} 2x, \pm x, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 0$  or  $\tau = 1/2$ .

$A_{2,n}, B_{2,n}, A_{3,n}$  and  $B_{3,n}$  are independent parameters.  $A_{1,n} = \pm A_{2,n}$  and  $B_{1,n} = \mp B_{2,n}$ .

	$A_{1,n}$	$A_{2,n}$	$A_{3,n}$	$B_{1,n}$	$B_{2,n}$	$B_{3,n}$
$A_{1,n}$	$\sigma_{A_{2,n}}^2$	$\pm \sigma_{A_{2,n}}^2$	0	0	0	0
$A_{2,n}$		$\sigma_{A_{2,n}}^2$	0	0	0	0
$A_{3,n}$			$\sigma_{A_{3,n}}^2$	0	0	0
$B_{1,n}$				$\sigma_{B_{2,n}}^2$	$\mp \sigma_{B_{2,n}}^2$	0
$B_{2,n}$					$\sigma_{B_{2,n}}^2$	0
$B_{3,n}$						$\sigma_{B_{3,n}}^2$

(ii) Hexagonal system: symmetry operations  $\begin{pmatrix} 2x, 0, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 1/2$ ;  $\begin{pmatrix} 20, y, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 1/2$ ;  $\begin{pmatrix} 22x, x, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 0$ ;  $\begin{pmatrix} 2x, 2x, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 0$ .

$B_{1,n}, A_{2,n}, B_{2,n}, A_{3,n}$  and  $B_{3,n}$  are independent parameters.  $A_{1,n} = \alpha'_n A_{2,n}$  with  $\alpha'_n = [(1 - c_n R_{\lambda\lambda}) / c_n R_{\lambda\mu}]^{(-1)^\lambda}$  and  $\lambda = (3 + c_n R_{11}) / 2$ ;  $\mu = 3 - \lambda$ .

	$A_{1,n}$	$A_{2,n}$	$A_{3,n}$	$B_{1,n}$	$B_{2,n}$	$B_{3,n}$
$A_{1,n}$	$\alpha_n'^2 \sigma_{A_{2,n}}^2$	$\alpha_n' \sigma_{A_{2,n}}^2$	0	0	0	0
$A_{2,n}$		$\sigma_{A_{2,n}}^2$	0	0	0	0
$A_{3,n}$			$\sigma_{A_{3,n}}^2$	0	0	0
$B_{1,n}$				$\sigma_{B_{1,n}}^2$	0	0
$B_{2,n}$					$\sigma_{B_{2,n}}^2$	0
$B_{3,n}$						$\sigma_{B_{3,n}}^2$

(iii) Hexagonal system: symmetry operations  $\begin{pmatrix} 2x, 0, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 0$ ;  $\begin{pmatrix} 20, y, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 0$ ;  $\begin{pmatrix} 22x, x, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 1/2$ ;  $\begin{pmatrix} 2x, 2x, 0 \\ 1 \end{pmatrix}$ ,  $\tau = 1/2$ .

$A_{1,n}, A_{2,n}, B_{2,n}, A_{3,n}$  and  $B_{3,n}$  are independent parameters.  $B_{1,n} = \alpha''_n B_{2,n}$  with  $\alpha''_n = -[(1 + c_n R_{\mu\mu}) / c_n R_{\mu\lambda}]^{(-1)^\mu}$  and  $\lambda = (3 + c_n R_{11}) / 2$ ;  $\mu = 3 - \lambda$ .

	$A_{1,n}$	$A_{2,n}$	$A_{3,n}$	$B_{1,n}$	$B_{2,n}$	$B_{3,n}$
$A_{1,n}$	$\sigma_{A_{1,n}}^2$	0	0	0	0	0
$A_{2,n}$		$\sigma_{A_{2,n}}^2$	0	0	0	0
$A_{3,n}$			$\sigma_{A_{3,n}}^2$	0	0	0
$B_{1,n}$				$\alpha_n''^2 \sigma_{B_{2,n}}^2$	$\alpha_n'' \sigma_{B_{2,n}}^2$	0
$B_{2,n}$					$\sigma_{B_{2,n}}^2$	0
$B_{3,n}$						$\sigma_{B_{3,n}}^2$

Table 1. (cont.)

(iv) Trigonal, tetragonal or hexagonal systems:  $\tau = \pm 1/3, \pm 1/4, \pm 1/6; s_n \neq 0$ .

$A_{1,n} = B_{1,n} = A_{2,n} = B_{2,n} = 0$ .  $B_{3,n}$  is an independent parameter.  $A_{3,n} = \gamma_n B_{3,n}$  with  $\gamma_n = (c_n - 1)/s_n$ .

	$A_{1,n}$	$A_{2,n}$	$A_{3,n}$	$B_{1,n}$	$B_{2,n}$	$B_{3,n}$
$A_{1,n}$	0	0	0	0	0	0
$A_{2,n}$		0	0	0	0	0
$A_{3,n}$			$\gamma_n^2 \sigma_{B_{3,n}}^2$	0	0	$\gamma_n \sigma_{B_{3,n}}^2$
$B_{1,n}$				0	0	0
$B_{2,n}$					0	0
$B_{3,n}$						$\sigma_{B_{3,n}}^2$

It is verified from equation (22) that the expressions proposed for the  $\alpha'_n$  and  $\alpha''_n$  coefficients fit all the relevant symmetry cases ( $\varepsilon = -1$ ) shown in this table.

$\Sigma^{j,j}$  is either diagonal if the atom  $j$  is in a general position or takes a form similar to  $\Sigma^{i,i}$  in the other cases.  $\Sigma^{i,j}$  is zero.

3.3.2. Case (b). In this case, the  $\Sigma^{i,j}$  part of  $\Sigma$  includes covariance terms owing to the dependence between the parameters of the two atoms and will be described by blocks  $N$  and  $P_n$  related to the average positions and to the Fourier terms of the  $n$ th harmonic, respectively.

The relation between the average positions of the atomic pair is expressed by

$$\bar{x}_\alpha^j = R_{\alpha\beta} \bar{x}_\beta^i \quad (26)$$

By application of the covariance definition, the relation

$$\text{cov}(\bar{x}_\beta^j, \bar{x}_\alpha^j) = R_{\alpha\eta} \text{cov}(\bar{x}_\beta^i, \bar{x}_\eta^i) \quad (27)$$

is derived. For  $\eta = \beta$ ,  $\text{cov}(\bar{x}_\beta^i, \bar{x}_\eta^i)$  coincides with  $\text{var}(\bar{x}_\beta^i)$ . This relation can be written in the matrix form

$$N = M^T \tilde{R}. \quad (28)$$

Similarly, the relation between the Fourier terms of the atomic pair is described by  $|Y_n^j\rangle = |T_n|Y_n^i\rangle$  for the  $n$ th harmonic; it turns out that

$$P_n = S_n^T \tilde{T}_n. \quad (29)$$

Two typical examples of  $\Sigma$  matrix are given in Table 3.

#### 4. The interatomic distance c.s.u.

Knowledge of the  $\Sigma$  matrix now makes it possible to calculate the variance  $\sigma_d^2$  for the interatomic distances  $d$ , which can be considered as the sum of different terms. From (2), the following relation is found:

$$\begin{aligned} \sigma_d^2 = & \langle G_0^i | M^i | G_0^i \rangle + \langle G_0^j | M^j | G_0^j \rangle \\ & + \langle G_0^i | N | G_0^j \rangle + \langle G_0^j | N | G_0^i \rangle \end{aligned}$$

$$\begin{aligned} & + \sum_{n=1}^m [\langle G_n^i | S_n^i | G_n^i \rangle + \langle G_n^j | S_n^j | G_n^j \rangle \\ & + \langle G_n^i | P_n | G_n^j \rangle + \langle G_n^j | P_n | G_n^i \rangle]. \quad (30) \end{aligned}$$

The first part originates from the errors on the average coordinates while the second part describes the errors on the Fourier terms of the  $m$  harmonics. The components of  $\langle G_0^i |$  and  $\langle G_0^j |$  are the derivatives of  $d$  with respect to  $x_\beta^i$  and  $x_\beta^j$ , respectively. According to (5) and (3), they are given by the relations

$$\begin{aligned} \partial d / \partial \bar{x}_\beta^i &= (1/d) \langle X | g | \left( \partial X / \partial \bar{x}_\beta^i \right) \rangle \\ \partial d / \partial \bar{x}_\beta^j &= (1/d) \langle X | g | \left( \partial X / \partial \bar{x}_\beta^j \right) \rangle \quad (31) \end{aligned}$$

with

$$\begin{aligned} \partial X_\alpha / \partial \bar{x}_\beta^i &= +\delta_{\alpha\beta} + 2\pi q_\beta^* \\ & \times \left\{ \sum_n n [B_{\alpha,n}^i c_n^i(t) - A_{\alpha,n}^i s_n^i(t)] \right\} \\ \partial X_\alpha / \partial \bar{x}_\beta^j &= -\delta_{\alpha\beta} - 2\pi q_\beta^* \\ & \times \left\{ \sum_n n [B_{\alpha,n}^j c_n^j(t) - A_{\alpha,n}^j s_n^j(t)] \right\}. \quad (32) \end{aligned}$$

$\delta_{\alpha\beta}$  is the Kronecker symbol,  $c_n^i(t) = \cos[2\pi n(t_0^i + t)]$  and  $s_n^i(t) = \sin[2\pi n(t_0^i + t)]$ .

The components of  $\langle G_n^i |$  and  $\langle G_n^j |$  are the derivatives of  $d$  with respect to  $A_{\alpha,n}^i, B_{\alpha,n}^i$  and  $A_{\alpha,n}^j, B_{\alpha,n}^j$  and are given by

$$\begin{aligned} \partial d / \partial A_{\alpha,n}^i &= [c_n^i(t)/d] \langle X | g |_\alpha \\ \partial d / \partial B_{\alpha,n}^i &= [s_n^i(t)/d] \langle X | g |_\alpha \\ \partial d / \partial A_{\alpha,n}^j &= -[c_n^j(t)/d] \langle X | g |_\alpha \\ \partial d / \partial B_{\alpha,n}^j &= -[s_n^j(t)/d] \langle X | g |_\alpha, \quad (33) \end{aligned}$$

$\langle X | g |_\alpha$  denoting the  $\alpha$  component of  $\langle X | g |$ .

Table 2. Some typical examples of  $\Sigma_{i,i}$  parts of the  $\Sigma_{i,j}$  matrices related to first-order Fourier terms of the displacive modulation of the atom  $i$  of a pair  $i, j$

(a) Atom  $i$  on a site of symmetry  $\begin{pmatrix} 4 \\ q \end{pmatrix}$ :  $\tau = 1/4$ ; in SSG  $P4(00\gamma)q$ ;  $i$  belongs to  $(L)$

$\bar{x}_3^i, A_2^i$  and  $B_2^i$  are independent parameters.

	$\bar{x}_1^i$	$\bar{x}_2^i$	$\bar{x}_3^i$	$A_1^i$	$A_2^i$	$A_3^i$	$B_1^i$	$B_2^i$	$B_3^i$
$\bar{x}_1^i$	0	0	0	0	0	0	0	0	0
$\bar{x}_2^i$		0	0	0	0	0	0	0	0
$\bar{x}_3^i$			$\sigma_{\bar{x}_3^i}^2$	0	0	0	0	0	0
$A_1^i$				$\sigma_{B_2^i}^2$	0	0	0	$\sigma_{B_2^i}^2$	0
$A_2^i$					$\sigma_{A_2^i}^2$	0	$-\sigma_{A_2^i}^2$	0	0
$A_3^i$						0	0	0	0
$B_1^i$							$\sigma_{A_2^i}^2$	0	0
$B_2^i$								$\sigma_{B_2^i}^2$	0
$B_3^i$									0

(b) Atom  $i$  generated from atom  $\mu$  [belonging to  $(L)$ ] by the  $\begin{pmatrix} 4 \\ q \end{pmatrix}$  operator:  $\tau = 1/4$ ; in SSG  $P422(00\gamma)q00$

$\bar{x}_1^\mu, \bar{x}_2^\mu, \bar{x}_3^\mu, A_1^\mu, A_2^\mu, A_3^\mu, B_1^\mu, B_2^\mu$  and  $B_3^\mu$  are independent parameters.

	$\bar{x}_1^i$	$\bar{x}_2^i$	$\bar{x}_3^i$	$A_1^i$	$A_2^i$	$A_3^i$	$B_1^i$	$B_2^i$	$B_3^i$
$\bar{x}_1^i$	$\sigma_{\bar{x}_2^\mu}^2$	0	0	0	0	0	0	0	0
$\bar{x}_2^i$		$\sigma_{\bar{x}_1^\mu}^2$	0	0	0	0	0	0	0
$\bar{x}_3^i$			$\sigma_{\bar{x}_3^\mu}^2$	0	0	0	0	0	0
$A_1^i$				$\sigma_{B_2^\mu}^2$	0	0	0	0	0
$A_2^i$					$\sigma_{B_1^\mu}^2$	0	0	0	0
$A_3^i$						$\sigma_{B_3^\mu}^2$	0	0	0
$B_1^i$							$\sigma_{A_2^\mu}^2$	0	0
$B_2^i$								$\sigma_{A_1^\mu}^2$	0
$B_3^i$									$\sigma_{A_3^\mu}^2$

(c) Atom  $i$  generated from atom  $\mu$  [belonging to  $(L)$ ] in special position  $\begin{pmatrix} m \\ 1 \end{pmatrix}$ , by the  $\begin{pmatrix} 6 \\ s \end{pmatrix}$  operator:  $\tau = 1/2$ ; in SSG  $P6mm(00\gamma)s0s$

$\bar{x}_1^\mu, \bar{x}_3^\mu, A_2^\mu, A_3^\mu, B_2^\mu$  and  $B_3^\mu$  are independent parameters.

	$\bar{x}_1^i$	$\bar{x}_2^i$	$\bar{x}_3^i$	$A_1^i$	$A_2^i$	$A_3^i$	$B_1^i$	$B_2^i$	$B_3^i$
$\bar{x}_1^i$	$\sigma_{\bar{x}_1^\mu}^2$	$-\sigma_{\bar{x}_1^\mu}^2$	0	0	0	0	0	0	0
$\bar{x}_2^i$		$\sigma_{\bar{x}_1^\mu}^2$	0	0	0	0	0	0	0
$\bar{x}_3^i$			$\sigma_{\bar{x}_3^\mu}^2$	0	0	0	0	0	0
$A_1^i$				$\frac{1}{4}\sigma_{A_2^\mu}^2$	$-\frac{1}{4}\sigma_{A_2^\mu}^2$	0	0	0	0
$A_2^i$					$\frac{1}{4}\sigma_{A_2^\mu}^2$	0	0	0	0
$A_3^i$						$\sigma_{A_3^\mu}^2$	0	0	0
$B_1^i$							$\frac{1}{4}\sigma_{B_2^\mu}^2$	$-\frac{1}{4}\sigma_{B_2^\mu}^2$	0
$B_2^i$								$\frac{1}{4}\sigma_{B_2^\mu}^2$	0
$B_3^i$									$\sigma_{B_3^\mu}^2$





Table 3. (cont.)

(ii)  $\Sigma^{j,j}$  part of the  $\Sigma$  matrix.

	$\bar{x}_1^j$	$\bar{x}_2^j$	$\bar{x}_3^j$	$A_1^j$	$A_2^j$	$A_3^j$	$B_1^j$	$B_2^j$	$B_3^j$
$\bar{x}_1^j$	$\sigma_{\bar{x}_1}^2$	$-\sigma_{\bar{x}_1}^2$	0	0	0	0	0	0	0
$\bar{x}_2^j$		$\sigma_{\bar{x}_1}^2$	0	0	0	0	0	0	0
$\bar{x}_3^j$			$\sigma_{\bar{x}_3}^2$	0	0	0	0	0	0
$A_1^j$				$\sigma_{A_1}^2$	$\sigma_{A_2}^2$	0	0	0	0
$A_2^j$					$\sigma_{A_2}^2$	0	0	0	0
$A_3^j$						0	0	0	0
$B_1^j$							$\sigma_{B_1}^2$	$\sigma_{B_2}^2$	0
$B_2^j$								$\sigma_{B_2}^2$	0
$B_3^j$									0

(iii)  $\Sigma^{i,j}$  part of the  $\Sigma$  matrix.

	$\bar{x}_1^j$	$\bar{x}_2^j$	$\bar{x}_3^j$	$A_1^j$	$A_2^j$	$A_3^j$	$B_1^j$	$B_2^j$	$B_3^j$
$\bar{x}_1^i$	$-\sigma_{\bar{x}_1}^2$	$\sigma_{\bar{x}_1}^2$	0	0	0	0	0	0	0
$\bar{x}_2^i$	$-\sigma_{\bar{x}_1}^2$	$\sigma_{\bar{x}_1}^2$	0	0	0	0	0	0	0
$\bar{x}_3^i$	0	0	$\sigma_{\bar{x}_3}^2$	0	0	0	0	0	0
$A_1^i$	0	0	0	$-\sigma_{A_2}^2$	$-\sigma_{A_2}^2$	0	0	0	0
$A_2^i$	0	0	0	$\sigma_{A_2}^2$	$\sigma_{A_2}^2$	0	0	0	0
$A_3^i$	0	0	0	0	0	0	0	0	0
$B_1^i$	0	0	0	0	0	0	$-\sigma_{B_1}^2$	$-\sigma_{B_2}^2$	0
$B_2^i$	0	0	0	0	0	0	$\sigma_{B_1}^2$	$\sigma_{B_2}^2$	0
$B_3^i$	0	0	0	0	0	0	0	0	0

5. Illustrations

The previous method has been applied in some chosen cases where intrinsic non-zero covariance terms are implied. These examples do not necessarily concern only modulated structures. Consider, for example, a hypothetical structure in the hexagonal system with space group  $P6mm$  (with  $a = 8 \text{ \AA}$ ) with an atom  $i$  at the origin of the cell and an atom  $j$  in special position  $6(d)$  [ $x = y = 0.3500(5)$ ]. The distance  $AB$  is then calculated as  $2.8000 \text{ \AA}$  with a c.s.u. of  $0.0040 \text{ \AA}$ . Without taking into account the covariance terms resulting from the special position of the atom  $j$ , this c.s.u. would be calculated as  $0.0028 \text{ \AA}$ . Furthermore, the c.s.u. corresponding to the symmetry-related distance  $ij'$ , with  $j'$  at  $(x, 0, 0)$  would not be calculated with the same value.

Now consider the similar case of a hypothetical incommensurate structure with space group  $P4mm(0, 0, \gamma)s0s$  ( $a = b = 3.5, c = 10 \text{ \AA}, \gamma = 0.213$ ) with an atom  $i$  at the origin of the cell and an atom  $j$  in special position  $4(d)$  [ $x = y = 0.3500(5), A_2^j = 0.050(2), B_2^j = 0.030(2)$ ]. Symmetry constraints impose  $A_1^j = -A_2^j$  and  $B_1^j = -B_2^j$  and  $A_3^j = B_3^j = 0$ . The corresponding  $\Sigma$  matrix is shown in Table 3(b) and the calculated bond length,  $d_{ij}$ , is represented as a function

of  $t$  in Fig. 1; the curves correspond to  $d_{ij} \pm 3\sigma$  and  $d_{ij} \pm 3\sigma^*$ , where  $\sigma$  is the rigorous calculation of the c.s.u. taking into account covariance terms and  $\sigma^*$  is an approximate value that does not take into account the covariance terms. The error in neglecting covariance terms in such a case is obvious.

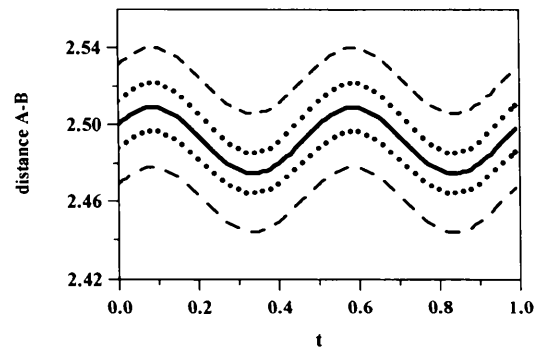


Fig. 1. Solid line: interatomic distance  $d_{ij}$  versus  $t$ , in superspace group  $P4mm(00\gamma)s0s$  with atom  $i$  at  $(0, 0, 0)$  and atom  $j$  at  $(0.3500(5), 0.3500(5), 0)$ . Dotted lines:  $d_{ij} \pm 3\sigma$ , taking into account covariance terms; dashed lines:  $d_{ij} \pm 3\sigma^*$ , taking into account no covariance term.

If we now look at three real examples of monoincommensurate structures, it is possible to decide about the real significance of variations in interatomic distances. When considering, for example, the small variations of the Te—Te distance in  $\text{NbTe}_4$  (van Smaalen & Bronsema, 1986) (Fig. 2) and the larger interatomic variations of the Zn—Cl and Cl—Cl distances in  $\text{Rb}_2\text{ZnCl}_4$  (Hédoux & Grebille, 1989) (Fig. 3), it can be seen that the former are significant because of the very small c.s.u. values of the refined parameters in this structure refine-

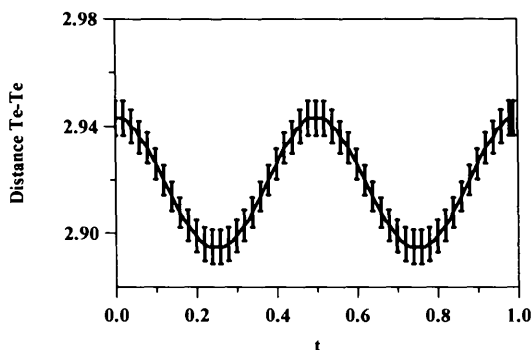


Fig. 2. Te—Te interatomic distances in  $\text{NbTe}_4$  (van Smaalen *et al.*, 1986). Error bars correspond to  $\pm 3\sigma$ .

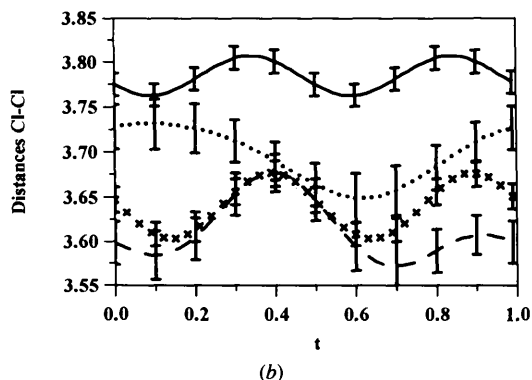
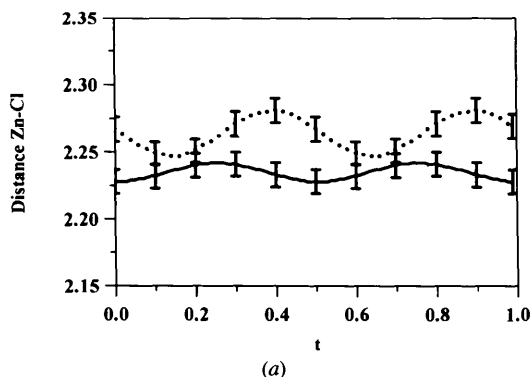


Fig. 3. Interatomic distances in  $\text{Rb}_2\text{ZnCl}_4$  (Hédoux & Grebille, 1989): (a) Zn—Cl(1) (solid line) and Zn—Cl(2) (dotted line); (b) Cl(1)—Cl(2) (solid line), Cl(1)—Cl(3) (dotted line), Cl(1)—Cl(4) (dashed line), Cl(3)—Cl(4) (crosses). Error bars correspond to  $\pm 3\sigma$ .

ment. In the second case, however, because of the larger uncertainty on the refined parameters, one can consider that the corresponding interatomic distances are constant within the experimental error. Thus, the global motion of the  $\text{ZnCl}_4$  tetrahedra is to a good approximation rigid-body motion. In the first case, calculations of the c.s.u. for Te—Te distances lead to an average value of 0.0020; without taking into account the covariance terms due to the symmetry relation between the two atoms, the c.s.u. would have been calculated as 0.0015.

A recent study of the modulated structure of the so-called  $\text{Bi2212}$  superconducting copper oxide (Grebille, Leligny, Ruyter, Labbé & Raveau, 1996) showed that disorder in the location of the Bi atom occurs. The distance between the two split Bi sites is shown in Fig. 4 as a function of the internal variable  $t$  and the corresponding c.s.u. is also given. In this particular case, the disorder is clearly significant for  $0.7 \leq t \leq 1.1$  (modulo 1); for the other values of  $t$ , however, one can consider that the deviation of the value of this distance from zero is not significant with regard to the corresponding c.s.u. Rigorously speaking, it should appear significant according to the usual  $3\sigma$  criterion as is represented in Fig. 4 but the proposed value of the c.s.u. in this study is probably underestimated. In fact it supposes that the structural model chosen for the refinement is reliable but only two orders could be introduced for the Fourier expansion of the displacement functions; this limitation is already an approximation.

## 6. Conclusions

In the structural study of incommensurate or commensurate modulated structures, particular attention should be paid to the derivation of interatomic distances and to the interpretation of their variations as a function of the phase variable of the modulation functions. A careful calculation of these values should also be accompanied by a realistic estimation of the related combined standard uncertainty. This is not always an easy task since it

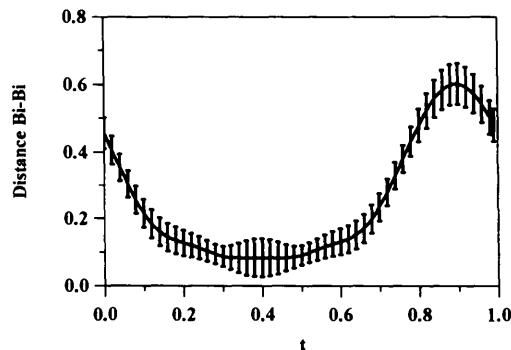


Fig. 4. Bi—Bi interatomic distances between the two disordered Bi sites in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (Grebille *et al.*, 1996). Error bars correspond to  $\pm 3\sigma$ .

assumes that all the variance terms of the independent parameters involved in the definition of the periodic modulation functions have been taken into account. The present study gives a detailed description of a method of calculation of the c.s.u., which takes into account all the variance terms attached to the relative atomic modulated coordinates and all the possible covariance terms resulting from linear relations imposed by symmetry considerations. It neglects the variance on the values of the cell parameters and of the components of the modulation wave vector, which are supposed to be known to within very good accuracy. From all the possible symmetry constraints, general formulas are proposed for the corresponding linear relations, which allow a general matrix form for the c.s.u. to be derived.

Consequently, a rigorous determination of the c.s.u. of interatomic distances as well as their possible variation as a function of the phase variable of the modulation can be given. It has allowed us to give justified interpretations of structural results in terms of rigid-body motion or of residual disorder. Nevertheless, one has to bear in mind that the present estimation can only give an underestimated value because it supposes that the structural model used to describe the crystal structure exactly is reliable and sufficient.

#### APPENDIX A

Two methods can be used to derive the variance of a function  $f(p_1, p_2, \dots, p_i, \dots)$ , where the  $p_i$  variables are not necessarily independent. Either, as in the present study,  $\sigma_f^2$  is calculated taking into account the variance and covariance terms associated with the  $p_i$  variables or  $f$  is expressed as a function of a reduced set of independent parameters and  $\sigma_f^2$  is estimated from their corresponding c.s.u. without any covariance term. The present Appendix shows that both methods are formally equivalent in the case where only linear relations are involved between the  $p_i$  parameters.

For instance, let us assume that the parameter  $p_k$  is related to the  $p_{k+1}$  and  $p_{k+2}$  parameters through the linear relation

$$p_k = \alpha p_{k+1} + \beta p_{k+2},$$

where  $p_{k+1}$  and  $p_{k+2}$  are independent parameters derived, for example, from a least-squares refinement.

Considering the other parameters as strictly independent, (1) leads to

$$\begin{aligned} \sigma_f^2 &\simeq (\partial f / \partial p_1)^2 \text{var}(p_1) + \dots + (\partial f / \partial p_k)^2 \text{var}(p_k) \\ &+ (\partial f / \partial p_{k+1})^2 \text{var}(p_{k+1}) \\ &+ (\partial f / \partial p_{k+2})^2 \text{var}(p_{k+2}) + \dots \\ &+ (\partial f / \partial p_n)^2 \text{var}(p_n) \end{aligned}$$

$$\begin{aligned} &+ 2[(\partial f / \partial p_k)(\partial f / \partial p_{k+1}) \text{cov}(p_k, p_{k+1}) \\ &+ (\partial f / \partial p_k)(\partial f / \partial p_{k+2}) \text{cov}(p_k, p_{k+2})] \\ &= \langle G | \Sigma | G \rangle, \end{aligned}$$

where  $\Sigma$  ( $n \times n$ ) includes covariance terms. From  $\text{var}(p_k) = \alpha^2 \text{var}(p_{k+1}) + \beta^2 \text{var}(p_{k+2})$  and  $\text{cov}(p_k, p_{k+1}) = \alpha \text{var}(p_{k+1})$ ,  $\text{cov}(p_k, p_{k+2}) = \beta \text{var}(p_{k+2})$ , it follows that

$$\begin{aligned} \sigma_f^2 &\simeq (\partial f / \partial p_1)^2 \text{var}(p_1) + \dots \\ &+ (\partial f / \partial p_{k+1} + \alpha \partial f / \partial p_k)^2 \text{var}(p_{k+1}) \\ &+ (\partial f / \partial p_{k+2} + \beta \partial f / \partial p_k)^2 \text{var}(p_{k+2}) + \dots \\ &+ (\partial f / \partial p_n)^2 \text{var}(p_n) \\ &= \langle G' | \Sigma' | G' \rangle, \end{aligned}$$

where  $\Sigma'$  [ $(n-1) \times (n-1)$ ] is a diagonal matrix and the components of  $\langle G' |$  [ $1 \times (n-1)$ ] are the derivatives of  $F = f(p_1, \dots, p_k(p_{k+1}, p_{k+2}), p_{k+1}, p_{k+2}, \dots, p_n)$  with respect to the independent parameters;  $(\partial f / \partial p_{k+1} + \alpha \partial f / \partial p_k)$  and  $(\partial f / \partial p_{k+2} + \beta \partial f / \partial p_k)$  stand for  $\partial F / \partial p_{k+1}$  and  $\partial F / \partial p_{k+2}$ , respectively. Consequently, if true linear relations are implied between some parameters, an estimation of  $\sigma_f^2$  can be given using either the  $\langle G | \Sigma | G \rangle$  or the  $\langle G' | \Sigma' | G' \rangle$  relation.

#### APPENDIX B

When an atom sits on a special position for a symmetry operation  $(R, \varepsilon, \tau)$ , the refinement parameters  $A_{\alpha, n}$  and  $B_{\alpha, n}$  of the cos and sin terms of the  $\alpha$  components of the  $n$ th-order Fourier term of the displacive modulation are constrained. In the present Appendix, all possible corresponding linear relations are given for  $\alpha = 1, 2$  (standard settings of the superspace groups). These linear relations depend on the values of  $\varepsilon$  and  $n\tau$ .

In all cases not tabulated in the present Appendix, no linear relation occurs either because the corresponding refinement parameters are constrained to be zero or because they are free and are independent parameters.

##### B1. Cases with $\varepsilon = +1$

When they exist, the linear relations can always be written as (24):

$$\begin{aligned} A_{1, n} &= \alpha_n A_{2, n} + \beta_n B_{2, n} \\ B_{1, n} &= -\beta_n A_{2, n} + \alpha_n B_{2, n}. \end{aligned}$$

$\alpha_n$  and  $\beta_n$  are expressed as a function of  $s_n = \sin(2\pi n\tau)$  and  $c_n = \cos(2\pi n\tau)$ .

In all these cases,  $\beta_n = s_n$ .

$n\tau$	System	Sym. op.	$\alpha_n$	$n\tau$	System	Sym. op.	Case	$\alpha'_n$	$\alpha''_n$	$\gamma_n$
0, 1/2	Trig., hex., tetr.	$m_{x,-x,z}$	$-c_n$	1/2	Trig., hex.	$2_{2x,x,0}$	(iii)			2
0, 1/2	Trig., hex., tetr.	$m_{x,x,z}$	$c_n$	0	Trig., hex.	$2_{x,0,0}$	(iii)			1/2
0	Trig., hex.	$m_{2x,x,z}$	2	1/2	Trig., hex.	$2_{x,0,0}$	(ii)	1/2		
1/2	Trig., hex.	$m_{0,y,z}$	2	0	Trig., hex.	$2_{x,2x,0}$	(ii)	1/2		
0	Trig., hex.	$m_{x,2x,z}$	1/2	1/2	Trig., hex.	$2_{x,2x,0}$	(iii)			1/2
1/2	Trig., hex.	$m_{x,0,z}$	1/2	1/4, 3/4	Tetr.	$4_{0,0,z}$	(iv)			$-s_n$
1/4, 3/4	Tetr.	$4_{0,0,z}$	0							
1/3, 2/3	Trig., hex.	$3_{0,0,z}$	$-c_n$							
1/6, 5/6	Trig., hex.	$6_{0,0,z}$	$c_n$							

### B2. Cases with $\epsilon = -1$

When they exist, the linear relations can always be expressed by one of the following forms:

(i)  $A_{1,n}^\mu = \alpha'_n A_{2,n}^\mu$  and  $B_{1,n}^\mu = \alpha''_n B_{2,n}^\mu$  simultaneously

with  $\alpha''_n = -\alpha'_n$ ;

(ii)  $A_{1,n}^\mu = \alpha'_n A_{2,n}^\mu$ , no linear relation for  $B_{1,n}^\mu$  and  $B_{2,n}^\mu$ ;

(iii)  $B_{1,n}^\mu = \alpha''_n B_{2,n}^\mu$ , no linear relation for  $A_{1,n}^\mu$  and  $A_{2,n}^\mu$ ;

(iv)  $A_{3,n}^\mu = \gamma_n B_{3,n}^\mu$ , no linear relation for  $A_{1,n}^\mu$ ,  $A_{2,n}^\mu$ ,  $B_{1,n}^\mu$  and  $B_{2,n}^\mu$ .

$n\tau$	System	Sym. op.	Case	$\alpha'_n$	$\alpha''_n$	$\gamma_n$
0, 1/2	Trig., hex., tetr.	$2_{x,x,0}$	(i)	$c_n$	$-c_n$	
0, 1/2	Trig., hex., tetr.	$2_{x,-x,0}$	(i)	$-c_n$	$c_n$	
0	Trig., hex.	$2_{0,y,0}$	(iii)		2	
1/2	Trig., hex.	$2_{0,y,0}$	(ii)	2		
0	Trig., hex.	$2_{2x,x,0}$	(ii)	2		

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