and the counter slit, t is the thickness of the specimen and $2A$ is the breadth of the spot on which the incident beam falls. In this case, where the vertical diversion of the beam is neglected, both t and A are variable factors in the experiment. If the value of $\mu = 143$ cm^{-1}, estimated from the mass absorption coefficients of oxygen and silicon (Cullity, 1978) and the density of SiO_2, and the goniometer radius of $L = 175$ mm are entered into (13), $\Delta\theta$ is found to be less than $9 \times 10^{-3\circ}$ for $2\theta > 90°$. On the other hand, the analytical process of a personal computer is effective to six figures and its precision of calculation is better than $0.001°$. The difference between $2\theta_a$ and $2\theta_{th}$ is at most $0.02°$ because the goniometer has a precision of $2\theta = 0.01°$ and is scanned with a step width of $0.01°$ in 2θ. All errors involved in the analysis can therefore be reduced through the mechanical accuracy of the goniometer. Consequently, it is definitely possible by adopting this analytical method to obtain a higher analytical accuracy when the accuracy of the goniometer is improved and the step width is reduced.

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On the Structure and Symmetry of Incommensurate Phases. A Practical Formulation

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Abstract

The structural description, symmetry and diffraction properties of incommensurate modulated phases are revised using a real-space framework. The superspace formalism usually employed is reformulated using a practical description where no multidimensional geometrical constructions are needed. The incommensurate structural distortion is described in terms of 'atomic modulation functions' where the internal space is only considered as a continuous label for the cells of the non-distorted structure. Hence, no atomic positions or thermal tensors in a multidimensional space are defined. By this means and with the introduction of the concept of 'atomic modulation factors' a general expression for the structure factor is proposed which constitutes a direct generalization of the standard expression for a commensurate structure. The concept of superspace symmetry is reduced in this approach to a simple relation between the defined atomic modulation functions, which can be directly translated by means of the structure-factor expression into the symmetry and extinction rules of the diffraction diagram. The advantages of superspace formalism in the analysis of commensurate modulated phases are also discussed. The use of superspace groups for describing the symmetry of superstructures, contrary to some recent claims, does not formally reduce the number of structural parameters but may often allow some of them to be neglected.

1. Introduction

In the last few years, the structural analysis of incommensurate (IC) modulated phases has greatly progressed through the introduction of the superspace symmetry concept (de Wolff, 1974, 1977; Janner & Janssen, 1977, 1979, 1980; Yamamoto, 1982b). The number of IC structures which are determined using superspace formalism is increasing constantly (van Aalst, den Hollander, Peterse & de Wolff, 1976;

Yamamoto, 1982a, c, 1985; Yamada & Ikeda, 1984; Yamada, 1985; Baudour & Sanquer, 1983; Steurer & Adlhart, 1983; Kucharczyk & Paciorek, 1985; van Smaalen, Bronsema & Mahy, 1986; Madariaga, Zuniga, Perez-Mato & Tello, 1987). This formalism includes, in the form presently used, the definition of a 'supercrystal' in a $(3+d)$-dimensional space (superspace), where d is the number of independent modulation wave vectors. The structure factor and symmetry properties are then referred to this multi-dimensional construction, which includes $(3+d)$-dimensional atomic position vectors and $(3+d) \times (3+d)$ thermal tensors (Yamamoto, 1982b). This approach is specially useful for determining and classifying all possible symmetries (superspace groups) of an IC structure (de Wolff, Janssen & Janner, 1981; Janner, Janssen & de Wolff, 1983a, b, c).

Recently, a practical description of an IC structure, its diffraction pattern and its symmetry, equivalent to the usual superspace description but avoiding the 'supercrystal' concept, was suggested (Perez-Mato, Madariaga & Tello, 1986). In the present work this alternative approach is further developed. The concept of 'atomic modulation functions' is introduced for describing an IC modulated structure, and the superspace symmetry and structure factor are expressed in terms of them. The essential difference between the superspace formalism usually considered and its present formulation is that the 'internal space' is interpreted here as a parametric space on a different level from the real space, as proposed originally by de Wolff (1977) in the early stages of the theory. Consequently no multidimensional geometrical constructions are used. This approach introduces a working basis where all relevant expressions are easily interpretable as they refer to real-space physical magnitudes and their modulations. In this manner, some basic points are clarified.

In order to simplify the formulation, the case of an IC displacive structure with a one-dimensional modulation (one independent wave vector) is the one considered in detail. However, the formalism can easily be generalized and for further reference the expressions for a general IC structure with a d-dimensional modulation of mixed displacive and positional disorder character are given in the Appendix. It should be stressed that the following discussion only refers to modulated structures.

2. Structure description

In general, a displacive IC structure can be described by a non-distorted (commensurate) configuration, usually called basic structure and normally associated with a higher-temperature phase, and a displacement field $u(\mu, T)$. The position for each atom μ ($\mu = 1, \ldots, s$) in each basic primitive cell T is then given by

$$r(\mu, T) = r_b^\mu + T + u(\mu, T).$$ (1)

We denote by r_b^μ the basic structure position of atom μ with respect to the cell origin. The displacement field $u(\mu, T)$ therefore defines the distortion between the basic structure and the modulated one. In the case of a one-dimensional IC modulation this displacement field can be expressed in the form of a discrete Fourier series (de Wolff, 1977; Yamamoto, 1982a, b, c, d):

$$u(\mu, T) = \sum_n u_n^\mu \exp(i2\pi n k . T) \qquad n = 0, \pm 1, \ldots .$$ (2)

Thus, only one independent wave vector k exists in the modulation, which is incommensurate with the basic lattice in the sense that the identity

$$G_p + p k = 0,$$ (3)

where p is any integer and G_p any basic reciprocal-lattice vector, is only fulfilled if $G_p = 0$, $p = 0$. In (2), u_n^μ are complex vectorial amplitudes satisfying $u_{-n}^\mu = u_n^{\mu *}$.

The IC modulation is therefore described by a superposition of plane-wave distortions whose wavelengths are successive harmonics of the one associated with the IC wave vector k. We have included in (2) a homogeneous term u_0^μ. Thus, the 'average' structure resulting from averaging the modulation in the whole crystal is then given by the basic lattice and the atomic positions,

$$r_{av}^\mu = r_b^\mu + u_0^\mu.$$ (4)

The concepts of basic and average structure have sometimes been confused (Fjaer, 1985). The choice of basic structure is not unique, the most convenient one usually being a high-temperature normal phase which can be independently determined. On the other hand, the average structure is in principle uniquely determined by the IC structure, but does not exist as a real structure. It is not completely known until the IC structure has been fully determined (see § 4). For practical reasons, the basic structure should have a space-group symmetry equal to or higher than the average structure.

A distorted structure as described by (1) and (2) has a diffraction pattern characterized by diffraction vectors of the form

$$H = (h_1, h_2, h_3, m) = G + m k,$$ (5)

where G is any basic reciprocal-lattice vector and m any integer. This is the four-integer indexation scheme characteristic of a one-dimensionally IC modulated structure (de Wolff, 1974). Owing to the small magnitude of the distortion, the reflections with $m = 0$ (main reflections) are typically much stronger than those with $m \neq 0$ (satellites) (de Wolff, 1974, 1977).

It should be noted that the description above is also valid for commensurate distorted structures (with a commensurate wave vector k_c). The only difference

is that in this case the number of terms in (2) is finite, as there is only a finite number of integers $\{n'\}$ which give rise to non-equivalent wave vectors $n'k_c$. In contrast, for an incommensurate wave vector the number of terms allowed in (2) is in principle infinite, as the n vectors are all non-equivalent. It is this situation that makes the indexation of reflexions according to (5) meaningful and unique. If we consider the commensurate case, (5) can always be reduced with the aid of (3) to a normal indexation in terms of a new three-dimensional reciprocal lattice.

We are making a very formal difference between commensurate and incommensurate wave vectors. Obviously such a sharp border between these two concepts does not exist from an empirical point of view. The continuous change of the wave vector with temperature or other variables has been taken as one of the few definite signs of the IC character of a structure, but even if the wave vector stays constant, the assignment of an IC character should not always be disregarded (see § 7).

In order to complete the preceding static description of an IC structure, the effect on its diffraction properties of the thermal vibrations must be included through the consideration of a thermal tensor $B(\mu, T)$ for each atom. The values of this symmetric tensor are necessarily distributed according to a modulation analogous to that for the atomic displacements:

$$B(\mu, T) = \sum_n B_n^\mu \exp(i2\pi nk \cdot T) \qquad n = 0, \pm 1, \ldots . \tag{6}$$

The sum is again extended to any integer n and B_n^μ are complex tensorial amplitudes (each component has its own independent phase) satisfying $B_{-n}^\mu = B_n^{\mu *}$.

Consequently a complete investigation of an IC structure should include the determination of the basic structure, the wave vector k and the Fourier amplitudes u_n^μ, B_n^μ ($n = 0, \pm 1, \ldots ; \mu = 1, \ldots, s$). The infinite number of parameters which in principle should be considered is no surprise, if we take into account that the number of different atomic displacements $u(\mu, T)$ present in the structure is also infinite. It could be argued that in a physical situation the number of non-zero terms in (2) will be quite low. This is not always true, as can be seen for instance for the predicted soliton regime (McMillan, 1976; Dvorak, 1980) in the vicinity of a lock-in phase, where the modulation wave vector takes a commensurate value. However, in this case also, the number of parameters to describe the distortion can be small if the atomic modulation functions introduced in the next section are used.

It should be stressed at this point that the amplitudes u_n^μ have in general independent phases (one for each component), which need to be determined in the structural analysis. Therefore, contrary to what has often been assumed (Blinc, 1981; Blinc, Lozar,

Milia & Kind, 1984), it is erroneous to consider that close atoms (in comparison with the wavelength of the modulation) 'are displaced in phase'. This approximation would be valid only if the modulation corresponds to an acoustic mode close to the Brillouin-zone centre. In fact, as will be discussed in § 5, in general only modulations of atoms related by superspace symmetry operations in the IC structure have non-independent initial phases.

3. Atomic modulation functions

A very practical description of IC structures can be obtained by introducing the 'atomic modulation functions' (AMF's):

$$u^\mu(v) \equiv \sum_n u_n^\mu \exp(i2\pi nv) \qquad n = \pm 1, \ldots \tag{7a}$$

$$B^\mu(v) \equiv \sum_n B_n^\mu \exp(i2\pi nv) \qquad n = \pm 1, \ldots . \tag{7b}$$

Thus, the AMF's are periodic functions (of period 1) along a continuous 'internal' variable v, and they are defined as Fourier series with the same amplitudes as those corresponding to the discrete displacement and thermal tensor fields $u(\mu, T)$ and $B(\mu, T)$ in (2) and (6) respectively, except for the homogeneous terms u_0^μ and B_0^μ. Accordingly,

$$u(\mu, T) = u_0^\mu + u^\mu(v = k \cdot T) \tag{8a}$$

$$B(\mu, T) = B_0^\mu + B^\mu(v = k \cdot T). \tag{8b}$$

Owing to the periodicity of the AMF's, the value of $k \cdot T$ in (8) can be reduced to an equivalent one in the interval $(0, 1)$. On the other hand, the IC character of k ensures that these values form a dense set in the interval mentioned. The AMF's $u^\mu(v)$, $B^\mu(v)$, together with the homogeneous terms u_0^μ and B_0^μ and the wave vector k, contain therefore in a compact form complete information about the structural distortion. Only the additional knowledge of the basic structure is needed to reproduce by means of (8) the whole IC structure. This description does not imply a continuous approximation of the basic cell coordinate and is only based on the IC character of the modulation wave vector. It is obviously completely equivalent to the description of the distorted structure by means of the Fourier amplitudes u_n^μ and B_n^μ in (2) and (6). However, it can be much more effective to describe for instance symmetry properties, atomic displacement correlations and distortions whose AMF's are rather simple despite having as a Fourier series a slow convergence. Moreover, by use of the AMF's the structure factor of an IC structure can be expressed (see next section) in a compact and simple form.

In the usual superspace description (de Wolff, 1974, 1977; Janner & Janssen, 1977, 1979, 1980) the parameter v is put on the same level as the three-dimensional

coordinates, and a four-dimensional space (super-space) is constructed where the AMF's configure a four-dimensional structure (supercrystal). The symmetry operations and the structure factor are then referred to this supercrystal. Although this construction introduces complex geometrical relations and concepts like four-dimensional atomic thermal tensors, it was considered the simplest form for obtaining a simple expression for the structure factor, as well as describing and applying the symmetry properties of the structure. However, the AMF's can be introduced as above, without reference to a 'super-crystal'. The parameter v is then reduced to its strict meaning of a quasi-continuous label for the basic cells, while the magnitudes that the AMF's describe are kept three-dimensional. As will be shown in the next section, this approach does not imply any cost to the simplicity of describing the diffraction properties and symmetry relations. On the contrary, these latter can be reduced to clarifying and practical expressions.

It should be pointed out that according to (8) the AMF's can be globally translated along the internal coordinate v by an arbitrary amount without changing the structure that is being described. All the values represented by the AMF's are still realized in the structure following the same relative sequence in the basic cells. This corresponds to the well known phase-translation freedom of the modulation in IC systems (Cowley, 1980).

The long-range order expected in an IC structure is not obvious from the above description. In fact, as the form of the AMF's is in principle arbitrary it includes cases which will practically correspond to a disordered structure. As stressed by de Wolff (1984), an implicit qualitative property of the diffraction diagram of IC systems has to be considered to distinguish between the two cases: the fact that the index m [see (5)] of the observed satellites has rather low values. If this were not so, as any point of reciprocal space can be indexed according to (5), the corresponding diffraction pattern would approximate the diffuse diagram typical for a disordered system. This restriction on the number of observed reflexions has been assumed to imply in general that the AMF's are 'smooth' (de Wolff, 1984). This smoothness should, however, be interpreted in a broad sense. If the AMF's are for instance step functions with a small number of steps per period, the diffraction pattern is still typical of an IC structure (Perez-Mato & Madariaga, 1986). In any case, the number of parameters necessary for describing the AMF's must be small compared with the number of cells whose structural distortion they describe.

4. Structure factor

It was shown by Perez-Mato, Madariaga & Tello (1986) that the structure factor of an IC structure can

be expressed by means of the AMF's in a simple and clarifying form. To this end the so-called 'atomic modulation factors' were introduced to allow a discrete sum for all cells T to be reduced to an integral in the internal parameter v. We extend here these results when thermal parameters or more precisely their corresponding AMF's are considered. In this case, following the same arguments, the structure factor for an allowed reflexion H of the form (5) can be written as

$$F(\mathbf{H}) = \sum_{\mu=1}^{s} f^{\mu}(H)g^{\mu}(\mathbf{H})$$
$$\times \exp\left(-\tilde{\mathbf{H}}.\mathbf{B}_0^{\mu}.\mathbf{H}\right) \exp\left(i2\pi\mathbf{H}.\mathbf{r}_{av}^{\mu}\right), \quad (9)$$

where $f^{\mu}(H)$ denotes the atomic scattering factor and the 'atomic modulation factors' $g^{\mu}(\mathbf{H})$ are defined as

$$g^{\mu}(\mathbf{H}) = \int_0^1 dv \exp\left[-\tilde{\mathbf{H}}.\mathbf{B}^{\mu}(v).\mathbf{H}\right]$$
$$\times \exp\{i2\pi[\mathbf{H}.\mathbf{u}^{\mu}(v)+mv]\}. \quad (10)$$

Equation (9) is a simple extension of the usual form for commensurate structures. It can be interpreted as the 'normal' structure factor of the average structure corrected by means of the modulation factors $g^{\mu}(\mathbf{H})$. These latter contain in a compact form the effect caused by the modulation of the atomic positions and the thermal tensors. According to (9), this effect can be obviously assimilated to a correction through the factor $g^{\mu}(\mathbf{H})$ of the scattering power of each atom in the primitive cell of the average structure. However, it should not be disregarded that, in contrast to the normal structure-factor expression, (9) is also valid for diffraction vectors of the form (5) with $m \neq 0$.

The advantage of expressions (9) and (10) over previous ones (de Wolff, 1974; Yamamoto, 1982a, b, c, d), apart from their simple interpretation given above, is that the magnitudes which appear in the formulas are all defined in the real three-dimensional space. Note that even the practical expression for the structure factor given in de Wolff (1974) after developing the four-dimensional structure factor is not directly analogous to (9) and (10). In our notation, the expression in de Wolff (1974) includes instead of $\mathbf{H}.\mathbf{r}_{av}^{\mu}$ the product $(\mathbf{H}-m\mathbf{k}).\mathbf{r}_{av}^{\mu}$, preventing the simple interpretation discussed above. A few further manipulations using the characteristics of the super-structure defined in the four-dimensional formalism are required to transform the expression into a form equivalent to (9) and (10).

It is important that (9) includes as a particular case that of a commensurate structure. Thus, if the AMF's are identically zero, the modulation factors (10) reduce to zero and unity for the satellites and the main reflexions respectively. Equation (9) then becomes the structure factor of a commensurate structure.

The effect of the temperature-factor modulation on the diffraction diagram as given in (9) and (10) can be compared (Garcia, Perez-Mato, Madariaga & Zuniga, 1987) with other approaches where particular models for the dynamics of the IC structure have been considered (Overhauser, 1971; Axe, 1980).

The average structure as defined in (4) is usually assumed to coincide with that resulting from considering only the main reflections ($m = 0$) in the diffraction pattern of the IC structure. According to (9), this assumption is valid if the factor $g^\mu(\mathbf{H})$ can be assimilated into an additional fictitious temperature factor. In fact, this happens approximately in the sinusoidal regime, when the AMF's for the atomic positions have only one harmonic. However, in a general case it is not even certain that the atomic modulation factors have real values (Perez-Mato & Madariaga, 1986).

5. Superspace symmetry

Equations (9), (10) and (8) can be taken as the starting point for a structural analysis of an IC phase based on its experimental X-ray diffraction pattern. However, as in the case of commensurate structures, symmetry arguments should be used to reduce to a minimum the number of structural parameters to be determined. Usually the AMF's of symmetry-related atoms in the basic structure are not all independent. There exist relations among them which cause the rotational symmetry and systematic extinctions of the diffraction pattern. From this perspective, the theory of superspace symmetry is a systematic method to describe and apply these relations and their consequences.

Superspace symmetry theory is normally introduced referring to the four-dimensional 'supercrystal' mentioned before. However, it has been shown in the preceding section that this construction can be avoided in obtaining a practical expression for the structure factor. Something similar happens with superspace symmetry and the resultant diffraction regularities.

Let us consider first what happens when we apply an operation $\{R|t\}$ of the basic structure space group $\mathcal{G}_b$ to the IC structure. In general, we obtain a new IC structure, whose basic structure coincides with the old one, but the atomic displacements have been interchanged and rotated according to the applied operation. Let us consider for instance two atoms, μ and ν, which are symmetry related by $\{R|t\}$ in the basic structure:

$$R\mathbf{r}_b^\mu + \mathbf{t} = \mathbf{r}_b^\nu + \mathbf{T}^\mu. \tag{11}$$

After the operation is applied, the new values, $\mathbf{u}_{tr}(\nu, \mathbf{T}^\mu)$ and $B_{tr}(\nu, \mathbf{T}^\mu)$, of the displacement and thermal tensor of atom $(\nu, \mathbf{T}^\mu)$ are then given, in terms

of the non-transformed values for atom $(\mu, \mathbf{0})$, by

$$\mathbf{u}_{tr}(\nu, \mathbf{T}^\mu) = R\mathbf{u}(\mu, \mathbf{0}), \tag{12a}$$

$$B_{tr}(\nu, \mathbf{T}^\mu) = RB(\mu, \mathbf{0})R^{-1}. \tag{12b}$$

In this manner, a new structural distortion is obtained, which is described in general by a new average structure, a new wave vector and new AMF's. Let us assume now that for this operation the average structure and the wave vector of the transformed structure coincide with those of the original one, while the new AMF's are the initial ones but translated by a common 'internal translation' $-\tau$:

$$\mathbf{u}_{tr}^\mu(v) = \mathbf{u}^\mu(v + \tau), \tag{13a}$$

$$B_{tr}^\mu(v) = B^\mu(v + \tau). \tag{13b}$$

The original structure can therefore be recovered if an opposite shift of τ along the internal coordinate is performed after the action of $\{R|t\}$. We say then that $\{R|t, \tau\}$ is a superspace symmetry element of the IC structure. The set of all possible elements of this type constitute the superspace group of the structure. In general, not all symmetry operations of the basic structure space group $\mathcal{G}_b$ satisfy the above conditions and therefore the real space parts $\{R|t\}$ of all superspace-group operations form a subgroup of $\mathcal{G}_b$ which is contained in the space group of the average structure and, except for accidental cases, will coincide with it.

From the definition of the AMF's, it can easily be seen that the operations $\{E|\mathbf{T}, -\mathbf{k}.\mathbf{T} + n\}$ ($n =$ integer), where $\{E|\mathbf{T}\}$ is any basic lattice translation, are always elements of the superspace group. They do not therefore cause any particular restriction on the structure and correspond to the four-dimensional Bravais lattice of the supercrystal in the superspace formalism. The existence of any other superspace symmetry operation $\{R|t, \tau\}$ implies, however, definite relations between the AMF's of those atoms which are symmetry related in the average structure by $\{R|t\}$. The relations can be expressed in a simpler form if the origins of the AMF's are shifted in the form

$$\mathbf{u}'^\mu(v) = \mathbf{u}^\mu(v - \mathbf{k}.\mathbf{r}_b^\mu) \tag{14}$$

and similarly for the thermal tensor functions $B'^\mu(v)$. These shifted AMF's exclude the phase differences between the atomic modulations owing to their different atomic positions in the basic cell. A necessary and sufficient condition for $\{R|t, \tau\}$ to be a superspace-group operation is then that for any two atoms μ, ν, related by $\{R|t\}$ in the basic and average structures [see (11)], their shifted AMF's are related in the form

$$\mathbf{u}'^\nu(R_l v + \tau_0) = R\mathbf{u}'^\mu(v) \tag{15a}$$

and analogously

$$B'^\nu(R_l v + \tau_0) = RB'^\mu(v)R^{-1} \tag{15b}$$

where $R_I = +1$ (-1) if $\mathbf{Rk} = +\mathbf{k}$ $(-\mathbf{k})$ and $\tau_0 = \tau + \mathbf{k} . \mathbf{t}$. The proof of the preceding statement is rather cumbersome but straightforward if (12) and (13) are used and the procedure indicated in Perez-Mato, Madariaga & Tello (1986) is followed. Note that in (15) the case of the superspace-group operations $\{\mathbf{E}|\mathbf{T}, -\mathbf{k} . \mathbf{T} + n\}$ is trivially included. The internal law of the group can also be obtained from (15):

$$\{\mathbf{R}_2|\mathbf{t}_2, \tau_2\}\{\mathbf{R}_1|\mathbf{t}_1, \tau_1\} = \{\mathbf{R}_2\mathbf{R}_1|\mathbf{R}_2\mathbf{t}_1 + \mathbf{t}_2,$$
$$R_I(\mathbf{R}_2)\tau_1 + \tau_2\}. \quad (16)$$

Relations (15) reduce the number of independent AMF's to an 'asymmetrical unit', in terms of which the structure factor [(9), (10)] can be expressed. For atoms in special positions, such that they are kept invariant in the average structure by the operation $\{\mathbf{R}|\mathbf{t}\}$, (15) can imply particular restrictions on the form of the AMF's, since in this case the labels μ and ν coincide.

Another approach to the description of the structure and symmetry of an IC modulated phase has been given in McConnell & Heine (1984). We consider that this approach, which differs considerably from the present formulation and the standard superspace formalism, is not the most appropriate way to describe IC structures from a crystallographic viewpoint. McConnell & Heine restrict the distortion to a sinusoidal modulation, where the real and imaginary parts of the amplitudes describe two separate 'component structures'. The symmetry conditions for these components are justified, in part, by using physical models such as the Landau theory. These conditions are equivalent to some, but not all, of the relations deducible from (15a), employing the group structure of the superspace group. Furthermore, the generalization of this approach to non-sinusoidal distortions becomes unpractical, because each new harmonic in the modulation requires two additional 'component structures' to be considered (in general with new symmetries). In addition, while superspace formulation includes those IC structures with more than one independent modulation wave vector (see Appendix), the approach in McConnell & Heine (1984) cannot be directly extended to this general case.

6. Diffraction symmetry

The concept of superspace symmetry of IC phases would not have any practical relevance if it did not give rise, as it does, to important regularities in the properties of the material. In the case of X-ray diffraction, the symmetry of the diffraction pattern including the extinction rules can be directly related to the superspace group of the structure described in the preceding section.

It is straightforward that the structure factor F_{tr} of any structure transformed according to an operation $\{\mathbf{R}|\mathbf{t}\}$ is related to that of the initial structure, F, in the form

$$F_{tr}(\mathbf{h}) = F(\tilde{\mathbf{R}}\mathbf{h}) \exp (i2\pi\mathbf{h} . \mathbf{t}), \quad (17)$$

where $\mathbf{h}$ is any reciprocal-space vector. On the other hand, according to (9) and (10), and considering (13), the structure factor of the transformed structure for any allowed diffraction vector $\mathbf{H}$ should differ from the initial one according to the relation

$$F_{tr}(\mathbf{H}) = F(\mathbf{H}) \exp (-i2\pi m\tau); \quad (18)$$

consequently

$$F(\tilde{\mathbf{R}}\mathbf{H}) = F(\mathbf{H}) \exp [-i2\pi(\mathbf{H} . \mathbf{t} + m\tau)]. \quad (19)$$

This last expression summarizes the symmetry properties of the diffraction pattern resulting from the existence of the superspace symmetry operation $\{\mathbf{R}|\mathbf{t}, \tau\}$ in the structure, and corresponds to the one obtained in the 'supercrystal' formulation for the four-dimensional structure factor (Janner & Janssen, 1980). It indicates that reflexions $\tilde{\mathbf{R}}\mathbf{H}$ and $\mathbf{H}$, for any $\mathbf{H}$, are equivalent. Furthermore (19) implies an extinction rule, given by the simultaneous conditions

$$\tilde{\mathbf{R}}\mathbf{H} = \mathbf{H} \quad (20a)$$

$$\exp[-i2\pi(\mathbf{H} . \mathbf{t} + m\tau)] \neq 1. \quad (20b)$$

It is interesting to see that, if we consider (20) for the case of the superspace-group lattice elements $\{\mathbf{E}|\mathbf{T}, -\mathbf{k} . \mathbf{T} + n\}$, the reflection condition (5) is again obtained in a self-consistent way.

7. Commensurate structures

Superspace formalism and symmetry have also been successfully employed in the analysis of commensurate modulated phases. It has been claimed that this approach reduces the number of independent structural parameters to be determined (Yamamoto, 1982a, b, c, d; van Smaalen, 1985) when compared with standard methods. Using the preceding framework, we look again in this section at the advantages of such a procedure and particularly the validity of the claim of reducing the number of free structural parameters.

Let us consider, to be specific, a commensurate modulated structure such that its primitive cell parameter along the c axis is p times that of the basic structure, $\mathbf{c}$. The distortion $\mathbf{u}(\mu, \mathbf{T})$ relating the two structures is then periodic,

$$\mathbf{u}(\mu, \mathbf{T} + p\mathbf{c}) = \mathbf{u}(\mu, \mathbf{T}), \quad (21)$$

and it can also be expressed in the form (2) with $\mathbf{k} = \mathbf{k}_c = (1/p)\mathbf{c}^*$. However, the sum in (2) is reduced to a finite number of terms, owing to the equivalence between the wave vectors $n\mathbf{k}_c$, the largest integer n being $p/2$ $[(p-1)/2]$ for p even [odd]. Thus, the

number, $3p$, of distinct atomic displacement components $u_i(\mu, T)$ (μ fixed) coincides with the number of free parameters determining the necessary complex amplitudes $\mathbf{u}_n^\mu$. In fact, the choice of the wave vector $\mathbf{k}_c$ in (2) is not unique and any vector of the form $(r/p)\mathbf{c}^*$ (r, p prime integers) would also be valid, as the vectors $n(r/p)\mathbf{c}^*$ are equivalent one-to-one to those used when $\mathbf{k}_c = (1/p)\mathbf{c}^*$. We shall later discuss the differences between these possible choices. The AMF's (7) can also be defined in this commensurate case, but from (8) only their values at a discrete set of p points ($v_l = l/p$, $l = 0, \ldots, p-1$) are relevant, each value corresponding to one of the basic subcells in the p-fold cell of the distorted structure.

Expression (9) for the structure factor was obtained under the assumption that the wave vector was incommensurate. Otherwise the index m in (5) is not unique, and the structure factor for a reflexion $\mathbf{H}$ is then given by (Yamamoto, 1982a, b, c, d; Perez-Mato, Madariaga & Tello, 1986)

$$F(\mathbf{H}) = \sum_{m'} F_{m'}(\mathbf{H}), \qquad (22)$$

where the sum extends to all possible equivalent choices for the satellite index m, and $F_{m'}(\mathbf{H})$ corresponds to (9) for a particular choice ($m = m'$).

Note that each different indexation influences in $F_{m'}(\mathbf{H})$ only the value of the atomic modulation factors $g^\mu(\mathbf{H})$. Therefore we can also say that (9) is still valid with the atomic modulation factors given by

$$g^\mu(\mathbf{H}) = \sum_{m'} g_{m'}^\mu(\mathbf{H}), \qquad (23)$$

where the meaning of the subindex m' and the sum are analogous to (22). Expression (22) is clarified if we consider the case when $\mathbf{k} = (1/p + \delta)\mathbf{c}^*$, δ being small and incommensurate. In this case, for each integer n the diffraction vector $(h_1, h_2, h_3 - n, m + np)$ corresponds to a different reflexion, separated from the reflexion (h_1, h_2, h_3, m) by $np\delta\mathbf{c}^*$. When δ becomes zero, all of them superpose coherently, and the structure factor of the unique reflection is now the sum of the structure factors of the reflections that are superposed, as given in (22).

The point gives a clue for deciding when to consider a phase from the experimental point of view as IC, even if the modulation wave vector does not depend on temperature or other thermodynamic variables. From (22) and (9), the incommensurability hypothesis implies the assumption for all reflexions that only one term in the sum (22) is non-negligible. As stressed in Perez-Mato, Madariaga & Tello (1986), the validity of this approximation depends not only on the value of the modulation wave vector (a high value of p) but also on the influence of higher harmonics on the AMF's describing the distortion.

Even in the case that the structure is clearly commensurate, it is always possible to use the above AMF description including expression (9) for the structure factor if, instead of (10), (23) is employed for the atomic modulation factor. This expression can be reduced to a form where only the values of the AMF's at the points $v_l = l/p$ are relevant, as one would expect from the fact that these are the only values of the AMF's which really describe the structure. From (23) we have

$$g^\mu(\mathbf{H}) = \sum_n \int_0^1 dv \exp[-\tilde{\mathbf{H}} \cdot \mathbf{B}^\mu(v) \cdot \mathbf{H}]$$
$$\times \exp\{i2\pi[\mathbf{H} \cdot \mathbf{u}^\mu(v) + (m + np)v]\}; \qquad (24)$$

but

$$\sum_n \exp(i2\pi npv) = (1/p) \sum_l \delta(v - l/p), \qquad (25)$$

and if (25), (24) and (9) are considered, we obtain

$$F(\mathbf{H}) = (1/p) \sum_{\mu=1}^s f^\mu(H)$$
$$\times \sum_{l=0}^{p-1} \exp\{-\tilde{\mathbf{H}} \cdot [\mathbf{B}_0^\mu + \mathbf{B}^\mu(v_l)] \cdot \mathbf{H}\}$$
$$\times \exp(i2\pi\{\mathbf{H} \cdot [\mathbf{r}_{av}^\mu + \mathbf{u}^\mu(v_l) + l\mathbf{c}]\}), \qquad (26)$$

where we have used the fact that $\exp(i2\pi\mathbf{H} \cdot l\mathbf{c}) = \exp[i2\pi(ml)/p]$. Thus, (22) reduces to the standard expression for the structure factor of the p-fold cell, with the atomic displacements at the basic cells $l\mathbf{c}$ ($l = 0, \ldots, p-1$) given by the values of the AMF's at $v_l = l/p$. All this reasoning indicates that the number of structural parameters to be determined does not decrease in the superspace approach and the number of independent parameters to be included in the AMF for one atom μ is equal to $3p$ (the number of different μ atomic-position components in the p-fold cell).

The advantage of the use of AMF's to describe the structure and its diffraction pattern rests however on the fact that the new structural parameters (amplitudes of the harmonics in the AMF's) are well adapted to exhibit the physical origin of this type of structure. The number of effective structural parameters decreases when some of the relevant higher harmonics are considered negligible for physical reasons. In fact, in most cases the amplitudes strongly decrease with the order of the harmonic. The different possibilities for the value of $\mathbf{k}_c$ mentioned above correspond then to a different choice of what can be considered the first and most important harmonic in the distortion. As shown below, a different choice for $\mathbf{k}_c$ implies in general a different choice for the superspace group to be assigned to the structure.

This situation presented above does not vary qualitatively if the effect of rotational symmetry is included. As an example, let us consider a modulated commensurate structure with space group $P2_1cn$, having a fivefold cell along the c axis with respect to a

basic structure of symmetry *Pmcn*. In addition, let us suppose that the strongest 'satellite' reflexions are those for $H = G \pm (2/5)c^*$, and consequently we choose k_c as $(2/5)c^*$.

Consider an atom γ with a general position in the basic structure. In the unit (primitive) cell of this structure there are eight symmetry-related γ atoms (γi, $i = 1, \ldots, 8$), while the 40 γ atoms in the fivefold cell of the modulated structure form ten independent groups of four atoms which are symmetry related by the elements of $P2_1cn$. Therefore the number of independent atomic coordinates to be determined for this set of atoms in the modulated structure is 30.

In the superspace formalism, according to ($8a$) and with the fact that for this case $k = k_c = (2/5)c^*$, the displacements in the distorted structure of the five atoms associated with five consecutive basic cells, which are in the basic structure translationally equivalent to one of the eight atoms γi, are described by the values of the corresponding AMF at the points $v_l = l/5$ [$l = 0$(basic cell 0), $l = 1$ (basic cell 3), $l = 2$ (basic cell 1), $l = 3$ (basic cell 4), $l = 4$ (basic cell 2)]. If only these five points in the AMF's are physically relevant, only terms up to second order are necessary in (2) for describing the AMF's and the structure.

$$\mathbf{u}^{\gamma i}(v) = \sum_n \mathbf{u}_n^{\gamma i} \exp{(i2\pi nv)} \qquad n = 0, \pm 1, \pm 2. \quad (27)$$

Thus, considering in (27) the complex conjugate relation between the vectorial amplitudes of opposite index, the number of free parameters to describe an AMF is equal to 15, the number of parameters for describing the five independent atomic displacements for a given atom γi.

Each of the eight γi atoms, which are symmetry related in the basic structure cell, has therefore associated in the modulated structure a certain AMF which describes its displacements in five consecutive basic cells. However, assignment of a superspace group to the modulated structure implies in general that not all of them are independent. Let us assign first the superspace group $P(P2_1cn):(\bar{1}1\bar{1})$ (for notation see de Wolff, Janssen & Janner, 1981). The three non-trivial non-translationally equivalent elements of this group are $\{C_{2x}|1/2\,0\,0, 0\}$, $\{\sigma_y|0\,1/2\,1/2, -\alpha/2\}$ and $\{\sigma_z|1/2\,1/2\,1/2, -\alpha/2\}$, where $\alpha = |k|/|c^*|$. From the translation operations of the group, the product rule explained in § 5 and the fact that in our case $\alpha = 2/5$, it is easy to check that the superspace group considered also contains the operations $\{\sigma_y|0\,1/2\,5/2, 0\}$ and $\{\sigma_z|1/2\,1/2\,5/2, 0\}$. According to § 5, the existence of these latter superspace operations, together with the first of the three above, implies that the modulated structure is invariant for the space-group operations $\{C_{2x}|1/2\,0\,0\}$, $\{\sigma_y|0\,1/2\,5/2\}$ and $\{\sigma_z|1/2\,1/2\,5/2\}$. This ensures that the structure has the desired space group $P2_1cn$. Note that, in contrast to the incommensurate case, here an appropriate

choice of origin in the internal space when describing the superspace symmetry operations is fundamental for reflecting the desired normal space-group symmetry.

The superspace-group operations in $P(P2_1cn)$: $(\bar{1}1\bar{1})$ have four different rotational parts. Consequently, from ($15a$) the eight AMF's describing the displacements of the atoms γi ($i = 1, \ldots, 8$) form two independent groups, each with four symmetry-related AMF's. As from (27) the number of free parameters per AMF is 15, the total number of free parameters to describe the whole set of AMF's for the γ atoms is 30, the same as in a standard treatment. However, what happens if we consider the superspace group $P(Pmcn):(s1\bar{1})$, instead of the previous one? This group contains $P(P2_1cn):(\bar{1}1\bar{1})$ as a subgroup. The space group $P2_1cn$ for the modulated structure is therefore still ensured. In fact, it can be checked that the additional superspace-group operations present in this larger group do not cause any new space-group symmetry operation in the structure. Nevertheless, these operations further reduce the number of independent AMF's of the γ atoms to a single one. The other seven are related to it according to ($15a$) through the operations of the assigned superspace group. Thus, the number of structural parameters for the γ atoms has apparently been reduced by this means from 30 to 15. This impression is, however, illusory. We consider for instance how the superspace-group operation $\{\sigma_x|1/2\,0\,0, 1/2\}$ relates two AMF's. Note that the 'real-space' part of this operation, although present in the basic structure, does not belong to the space group $P2_1cn$. From ($15a$) we have

$$u_x^{\gamma j}(v + 1/2) = -u_x^{\gamma i}(v), \qquad u_{y,z}^{\gamma j}(v + 1/2) = u_{y,z}^{\gamma i}(v), \quad (28)$$

where γj and γi are two γ atoms related in the basic structure by the symmetry operation $\{\sigma_x|1/2\,0\,0\}$. For simplicity r_b^γ has been taken in the ab plane, so that the shifted AMF's [see (14)] coincide with the original ones. An example of two AMF's related according to (28) is shown in Fig. 1. It can be seen in the figure that the function $\mathbf{u}^{\gamma j}(v)$ can certainly be obtained from the other one [$\mathbf{u}^{\gamma i}(v)$], but the physically relevant values (at $v_l = l/5$) of the former are related to the values of the function $\mathbf{u}^{\gamma i}(v)$ at the points $v_l' = (l/5) + (1/10)$. In other words, the values of the symmetry-related AMF which are physically realized in the structure are related one-to-one to values of the initial AMF at points in the internal parameter v different from those corresponding to the five inequivalent basic cells. Thus, the reduction to one half of the number of independent AMF's has been done at the cost of doubling the number of physically relevant points in the AMF's describing the actual atomic displacements in the structure. Consequently the reasoning leading to (27) is no longer valid and

the number of parameters describing an AMF should also be doubled with the introduction of higher harmonics. However, if we can neglect some of these higher harmonics for some physical or experimental reason, a definite correlation between the ten independent atomic positions is introduced, which is not present in the standard treatment or in the superspace formalism when the complete set of harmonics for the AMF's is considered.

If, instead of $(2/5)c^*$, $(1/5)c^*$ is taken as the main modulation wave vector of the fivefold structure, the reasoning is similar but the possible superspace groups to be assigned to the structure are different. The minimal superspace group containing the required space-group symmetry $P2_1cn$ is now $P(P2_1cn):(\bar{1}s\bar{1})$. As before, there exists a second possible choice of higher superspace symmetry, in this case the superspace group $P(Pmcn):(ss\bar{1})$.

Summarizing, we can conclude that, in the superspace description of commensurate modulated structures, the reduction in the number of independent AMF's using a high-symmetry superspace group is achieved at the cost of increasing the number of relevant discrete values of v necessary in each independent AMF for describing the structure. Therefore, the number of harmonics determining the AMF's of the asymmetric unit is in principle increased, and the fixed number of free parameters in the structure is again recovered. As indicated above, the number of structural parameters to be considered are only reduced if these additional higher harmonics are neglected for physical reasons (for instance, the weakness of higher-order satellites). This approximation introduces a correlation between

atomic positions not contained in a standard treatment. The correlation disappears when all harmonics allowed in the modulation are included. Therefore, we can conclude that in general the power of superspace formalism applied to commensurate structures is based on the fact that the magnitude of some of the structural parameters employed can be very small for physical reasons. This approach will be particulary useful when the commensurate phase is due to a sinusoidal distortion slightly modified by secondary modes of shorter wavelength.

If the commensurate structure originates in a phase transition where Landau theory is applicable, superspace formalism is the adequate form for separating in the description of the structural distortion the contributions of the order-parameter mode from those of other coupled secondary modes, whose magnitude strongly decreases with their coupling order (Perez-Mato, Madariaga & Tello, 1984; Perez-Mato, Gaztelua, Madariaga & Tello, 1986).

According to the preceding discussion, the assignment of a superspace group to a commensurately modulated structure is not unique. This fact is reflected by the structure factor (22) which loses the properties (19) resulting from superspace symmetry, even if they are valid for the terms $F_{m'}$ in the sum. However, the *approximate* symmetry and extinction rules of the diffraction pattern, explained in terms of equations (19) and (20), is still a sure guide for a choice of a superspace group appropriate for neglecting the highest harmonics in the modulation (the small deviations from the superspace symmetry diffraction considered should be due mainly to these higher harmonics).

APPENDIX

In this Appendix the expressions appearing in the previous text for an IC modulated structure with a one-dimensional displacive modulation are generalized, for futher reference, to a general IC modulated structure, with a d-dimensional displacive and occupational modulation.

In this general case, the structure is described by a basic structure, a displacement field $u(\mu, \alpha, T)$ and an occupation probability field $p(\mu, \alpha, T)$, where α $(\alpha = 1, \ldots, m_\mu)$ now labels the different positions associated with a unique atom μ. This occupation probability field will satisfy

$$\sum_{\alpha=1}^{m_\mu} p(\mu, \alpha, T) = 1. \qquad (A1)$$

The basic structure is given by the atomic positions $r_b^{\mu,\alpha}$ and an occupation probability for each of them, $p_b^{\mu,\alpha}$, also fulfilling $\sum_\alpha p_b^{\mu,\alpha} = 1$. In the case of a pure
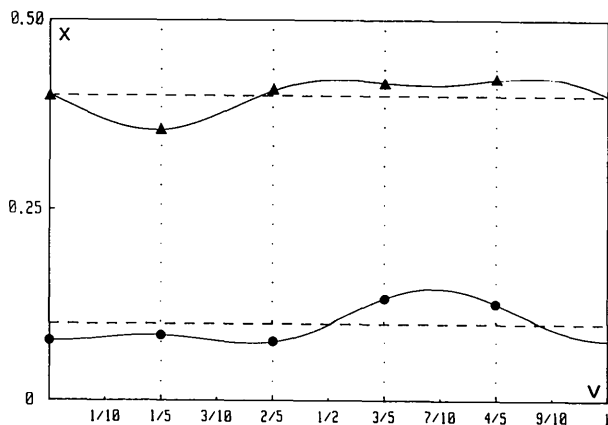

Fig. 1. Example of two AMF's related by the superspace symmetry operation $\{\sigma_x|1/2\,0\,0, 1/2\}$ [see equations (28)]. Only their components along the a axis are shown. The atomic displacements present in the commensurate modulated structure, with respect to the average structure positions given by the broken horizontal lines, are indicated by the symbols ▲ and ●. The atomic positions in the upper AMF (▲) are related to those of the lower AMF at the points $v_l' = l/5 + 1/10$, different from those structurally relevant in the lower AMF (●) at $v_l = l/5$.

displacive distortion, where no disorder exists, obviously $m_\mu = 1$ and $p(\mu, 1, \mathbf{T}) = 1$ for any μ. The expressions for $\mathbf{u}(\mu, \alpha, \mathbf{T})$, $p(\mu, \alpha, \mathbf{T})$ and the temperature tensor, which generalize (2) and (7), are then given by

$$\mathbf{u}(\mu, \alpha, \mathbf{T}) = \sum_\mathbf{n} \mathbf{u}_\mathbf{n}^{\mu,\alpha} \exp(i2\pi\mathbf{k}_\mathbf{n} . \mathbf{T}), \qquad (A2)$$

$$p(\mu, \alpha, \mathbf{T}) = p_b^{\mu,\alpha} + \sum_\mathbf{n} p_\mathbf{n}^{\mu,\alpha} \exp(i2\pi\mathbf{k}_\mathbf{n} . \mathbf{T}), \qquad (A3)$$

$$\mathbf{B}(\mu, \alpha, \mathbf{T}) = \sum_\mathbf{n} \mathbf{B}_\mathbf{n}^{\mu,\alpha} \exp(i2\pi\mathbf{k}_\mathbf{n} . \mathbf{T}), \qquad (A4)$$

where $\mathbf{n}$ represents any set of integers $(n_1, n_2, \ldots, n_d)$, and $\mathbf{k}_\mathbf{n}$ is defined by

$$\mathbf{k}_\mathbf{n} = n_1\mathbf{k}_1 + n_2\mathbf{k}_2 + \ldots + n_d\mathbf{k}_d, \qquad (A5)$$

where $\{\mathbf{k}_1, \mathbf{k}_2, \ldots, \mathbf{k}_d\}$ is a set of wave vectors incommensurate among themselves and with the basic lattice.

The average structure is described by the following atomic positions and occupational probabilities:

$$\mathbf{r}_{av}^{\mu,\alpha} = \mathbf{r}_b^{\mu,\alpha} + \mathbf{u}_0^{\mu,\alpha} \qquad (A6)$$

$$p_{av}^{\mu,\alpha} = p_b^{\mu,\alpha} + p_0^{\mu,\alpha}, \qquad (A7)$$

where $\mathbf{0}$ indicates the homogeneous term in $(A2)$ and $(A3)$.

From $(A3)$ and $(A1)$ it can be easily seen that the Fourier amplitudes $p_\mathbf{n}^{\mu,\alpha}$ satisfy

$$\sum_{\alpha=1}^{m_\mu} p_\mathbf{n}^{\mu,\alpha} = 0. \qquad (A8)$$

Equation (5) becomes

$$\mathbf{H} = (h_1, h_2, h_3, m_1, m_2, \ldots, m_d) = \mathbf{G} + \mathbf{k}_\mathbf{m}, \qquad (A9)$$

where $\mathbf{k}_\mathbf{m}$ is defined according to $(A5)$.

The AMF's are now defined along a d-dimensional 'internal' space, in which again any point $\mathbf{v} = (v_1, v_2, \ldots, v_d)$ represents in principle a definite cell in the infinite crystal, according to the rule

$$\mathbf{T} \to \mathbf{v_T} = (\mathbf{k}_1 . \mathbf{T}, \mathbf{k}_2 . \mathbf{T}, \ldots, \mathbf{k}_d . \mathbf{T}). \qquad (A10)$$

The AMF's can then be written as

$$\Delta p^{\mu,\alpha}(v) = \sum_\mathbf{n}' p_\mathbf{n}^{\mu,\alpha} \exp(i2\pi\mathbf{n} . \mathbf{v}), \qquad (A11)$$

$$\mathbf{u}^{\mu,\alpha}(v) = \sum_\mathbf{n}' \mathbf{u}_\mathbf{n}^{\mu,\alpha} \exp(i2\pi\mathbf{n} . \mathbf{v}), \qquad (A12)$$

$$\mathbf{B}^{\mu,\alpha}(v) = \sum_\mathbf{n}' \mathbf{B}_\mathbf{n}^{\mu,\alpha} \exp(i2\pi\mathbf{n} . \mathbf{v}), \qquad (A13)$$

where $\mathbf{n} . \mathbf{v}$ is a short symbol for the 'scalar product' $\sum n_i v_i$, and the primes in the sums indicate that the term $\mathbf{0} = (0, 0, \ldots, 0)$ is excluded.

The structure factor (9) is now

$$F(\mathbf{H}) = \sum_\mu f^\mu(H) \sum_\alpha p_{av}^{\mu,\alpha} g^{\mu,\alpha}(\mathbf{H})$$

$$\times \exp(-\tilde{\mathbf{H}} . \mathbf{B}_0^{\mu,\alpha} . \mathbf{H}) \exp(i2\pi\mathbf{H} . \mathbf{r}_{av}^{\mu,\alpha}),$$
$$(A14)$$

the atomic modulation factors $g^{\mu,\alpha}(\mathbf{H})$ being

$$g^{\mu,\alpha}(\mathbf{H})$$

$$= \int_0^1 dv_1 \ldots \int_0^1 dv_d \Delta p^{\mu,\alpha}(\mathbf{v}) \exp[-\tilde{\mathbf{H}} . \mathbf{B}^{\mu,\alpha}(\mathbf{v}) . \mathbf{H}]$$

$$\times \exp\{i2\pi[\mathbf{H} . \mathbf{u}^{\mu,\alpha}(v) + \mathbf{m} . \mathbf{v}]\} \qquad (A15)$$

where $\mathbf{m} = (m_1, m_2, \ldots, m_d)$ corresponds to the indexation of the reflexion $\mathbf{H}$ in $(A9)$.

The generalization of equations (13) is immediate, adding a new equation for the corresponding occupation probability modulation:

$$\Delta p_{tr}^{\mu,\alpha}(\mathbf{v}) = \Delta p^{\mu,\alpha}(\mathbf{v} + \boldsymbol{\tau}), \qquad (A16)$$

where $\boldsymbol{\tau}$ is the shift in the internal d-dimensional space corresponding to the superspace symmetry operation $\{\mathbf{R}|\mathbf{t}, \boldsymbol{\tau}\}$. The restrictions on the AMF's imposed by such an operation are also direct generalizations of equations (15) with an additional condition

$$\Delta p'^{\nu,\xi}(\mathbf{R}_I \mathbf{v} + \boldsymbol{\tau}_0) = \Delta p'^{\mu,\alpha}(\mathbf{v}), \qquad (A17)$$

where the shifted AMF's are defined with an equation analogous to (16) but substituting $\mathbf{k} . \mathbf{r}_0^\mu$ by the corresponding d-dimensional vector $(\mathbf{k}_1 . \mathbf{r}_0^\mu, \ldots, \mathbf{k}_d . \mathbf{r}_0^\mu)$. The atomic 'parts' (μ, α) and (ν, ξ) in $(A16)$ are related in the average structure in the form

$$\mathbf{R}\mathbf{r}_{av}^{\mu,\alpha} + \mathbf{t} = \mathbf{r}_{av}^{\nu,\xi} + \mathbf{T}^{\mu,\alpha}, \qquad (A18)$$

$$p_{av}^{\mu,\alpha} = p_{av}^{\nu,\xi}. \qquad (A19)$$

The internal translation $\boldsymbol{\tau}_0$ is the direct generalization of τ_0, $[\boldsymbol{\tau} + (\mathbf{k}_1 . \mathbf{T}, \ldots, \mathbf{k}_d . \mathbf{T})]$, and the coefficients $\mathbf{R}_I(\mathbf{R})_{ij}$ of the $d \times d$ matrix $\mathbf{R}_I(\mathbf{R})$ are integers defined by the equation (de Wolff, Janssen & Janner, 1981; Perez-Mato, Madariaga & Tello, 1986)

$$\mathbf{R}^{-1}\mathbf{k}_i = \sum \mathbf{R}_I(\mathbf{R})_{ij}\mathbf{k}_j + \mathbf{G}. \qquad (A20)$$

This expression makes explicit the condition that the action of $\mathbf{R}^{-1}$ (or $\mathbf{R}$) on any wave vector $\mathbf{k}_j$ results in a linear combination with integer coefficients of the independent set of wave vectors.

Finally, the symmetry equation for the structure factor (23) is also valid, substituting $\mathbf{m} . \boldsymbol{\tau}$ for $m\tau$.

In the preceding expressions, we have considered occupation probability modulation functions describing positional disorder in the structure, such that a given atom occupies with a certain probability several positions in each basic cell. However, these results can easily be transformed to the case of occupational disorder, in which several different atoms can occupy with a certain probability a given position. We need only reinterpret the labels μ and α. μ now indicates a certain atomic position, subject to the displacive modulation, and α the different atoms that can occupy it. The subsequent changes in the expressions above are then immediate.

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Rigid-Link Constraints and Rigid-Body Molecules

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Abstract

The rigid-bond condition for harmonic thermal parameters states that the difference of the mean-square displacements of atoms A and B along the covalent bond $A-B$ is negligible. In this paper, the corresponding condition for non-bonded intramolecular distances is called a rigid link. Rigid-body motion according to the TLS formalism requires *all* intramolecular links to be rigid. Conversely, a complete set of rigid links is not necessarily equivalent to rigid-body motion. An algorithm is presented for the determination of the maximum number Q_N of independent rigid links of an N-atom molecule. In general for site symmetry 1, $Q_N = N-1$ for linear and $3N-6$ for planar molecules. For three-dimensional molecules, $Q_N = N(N-1)/2$, $N \le 8$ and $6N-20$, $N \ge 8$. For particular geometries, Q_N may be smaller. For many molecules, Q_N rigid links are equivalent to rigid-body motion. Notable exceptions are most linear and planar molecules, and all molecules with six or seven atoms. Higher site symmetries reduce and often eliminate these differences between rigid links and rigid-body motion. The use of rigid-link restraints in crystallographic least squares is recommended. They provide a computationally simple means of relaxing the constraints imposed on the displacement parameters by the TLS model for any molecular site symmetry.

Introduction

For many chemical bonds, the contribution of bond-stretching vibrations to the atomic thermal displacement parameters can be expected to be relatively small in comparison with angle bending, torsional and intermolecular vibrations. This is the basis of the *rigid-bond criterion* for the physical soundness of independently refined anisotropic displacement parameters (Hirshfeld, 1976). If we define the coordinate system by the unit translations of the crystal lattice