Acta Cryst. (1992). A**48**, 476-483

Unified Setting and Symbols of Superspace Groups for Composite Crystals

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(*Received* 18 *January* 1991; *accepted* 6 *January* 1992)

Abstract

A unified setting of the unit vectors in superspace groups for composite crystals is discussed. It simplifies the description of composite crystals and gives a systematic method for analyzing composite crystals in a manner similar to modulated structure analysis. The setting is generally different from the standard setting for modulated structures. The reflection conditions specific to it are given. The equivalence relation of the superspace groups for composite crystals is introduced. This is different from that for modulated substructures and leads to new symbols for the superspace groups of composite crystals.

1. Introduction

The superspace approach in crystallography was first introduced by de Wolff (1974) to describe modulated structures systematically and was applied to intergrowth compounds or misfit layer structures by Janner & Janssen (1980). These so-called composite crystals consist of two or more substructures which have mutually incommensurate periods. The superspace group is applicable to specify the symmetry of such a structure because each substructure is a modulated structure (de Wolff, Janssen & Janner, 1981). Recently it was shown that such an approach is in fact efficient for the structure analysis of composite crystals (Kato, 1990; Onoda, Kato, Gotoh & Oosawa, 1990). However, the theory of superspace groups is essentially for modulated structures. The composite crystal shows strong main reflections on two (or more) three-dimensional reciprocal lattices, part of which is overlapped but the others are incommensurate. Such a situation is not explicitly taken into account in the theory. If we take reflections belonging to one such reciprocal lattice as the main reflections, the other reflections are regarded as satellite reflections. Consequently, if we choose a different host substructure, we get a different superspace-group symbol, which is generally not equivalent to the original one in the equivalence relation for modulated structures. The substructure is modulated by the existence of the other substructure. As a result, the composite crystal consists of several modulated substructures, which penetrate each other. However, we cannot say which is the host substructure.

To treat such a structure properly, we have to introduce new symbols of superspace groups for composite crystals. This leads to a new equivalence relation and restricts a setting of the unit vectors. In this paper, we discuss the superspace groups for composite crystals and related problems, in particular, the structure-factor formula and the determination of possible modulation amplitudes for atoms in special positions. The setting of the unit vectors appropriate for composite crystals has been taken to analyze several structures based on the theory of Janner & Janssen (van Smaalen, 1989; Kato, 1990; Onoda, Kato, Gotoh & Oosawa, 1990). In this setting, the unit vectors (in the reciprocal space) are chosen from the lattice vectors of the reciprocal sublattices. It is shown that such a setting is possible for any composite crystal. The setting leads to extinction rules specific to the superspace group for the composite crystal. These are listed. Finally, we show several examples of the superspace groups for known composite crystal structures. A new version of the computer program *REMOS* (Yamamoto, 1982*a*) has been developed based on this theory. The first application of the program to a composite crystal structure will be described in a future paper (Ukei, Yamamoto, Watanabe, Shishido & Fukuda, 1992).

2. One-dimensional composite crystals

A characteristic feature of the usual modulated structure is to show strong main reflections and weak satellite ones. The main reflections define a three-dimensional reciprocal lattice and give the three-dimensionally periodic average structure. In the theory of superspace groups for modulated structures, the first three axes of the higher-dimensional reciprocal lattice are taken to be the a^*, b^* and c^* axes of the average structure and additional (fourth, fifth, ...) axes are not regarded as being equivalent to the first three (Janner & Janssen, 1979) because the strong main reflections can clearly be distinguished from the satellite reflections and higher-order satellite reflections are weak. As a result, each atom is extended continuously over the additional dimension in superspace. In composite crystals, atoms belonging to one substructure are continuous in some subspace but atoms of the other substructure

0108-7673/92/040476-08$06.00

are continuous in a different subspace as shown below.

In order to show equivalent descriptions of the composite crystal in superspace, first we consider the simplest one-dimensional composite crystal shown in Fig. 1. As in the description of the modulated structure in superspace, we take the external (physical) space along the horizontal line through the origin and the internal (complementary) space perpendicular to it (de Wolff, 1974). A composite structure in the physical space is given by the intersection of the two-dimensional crystal at the one-dimensional external space in this simple case. As seen in Fig. 1(*a*), the composite crystal includes two modulated substructures. In the first substructure, atoms are continuous along the *b* axis and in the second one they are continuous along the *a* axis. The origin of the modulation is clear in this case: the first substructure is modulated because of the interaction with the interpenetrating second substructure and the second substructure is affected by the first one. The representation of each modulated structure in Fig. 1(*a*) is different from the standard representation for the usual modulated structure. In the latter (de Wolff, 1974), each atom is continuous along the direction parallel to the internal space, while, in Fig. 1(*a*), atoms are continuous along a direction oblique to the internal space. This is, however, equivalent to the representation in which either of the two substructures is continuous along the internal space (Fig. 1*b* or *c*). It is clear that the three representations in Fig. 1 give the same atom position in the external space and therefore they are equivalent. If we consider an appropriate shear strain in Fig. 1(*a*) which leaves the external space invariant, we obtain the standard representation for a given substructure (Figs. 1*b* and *c*). But, in this case, the representation of the other modulated substructure is not standard. Consequently, there exists no standard representation for both substructures.

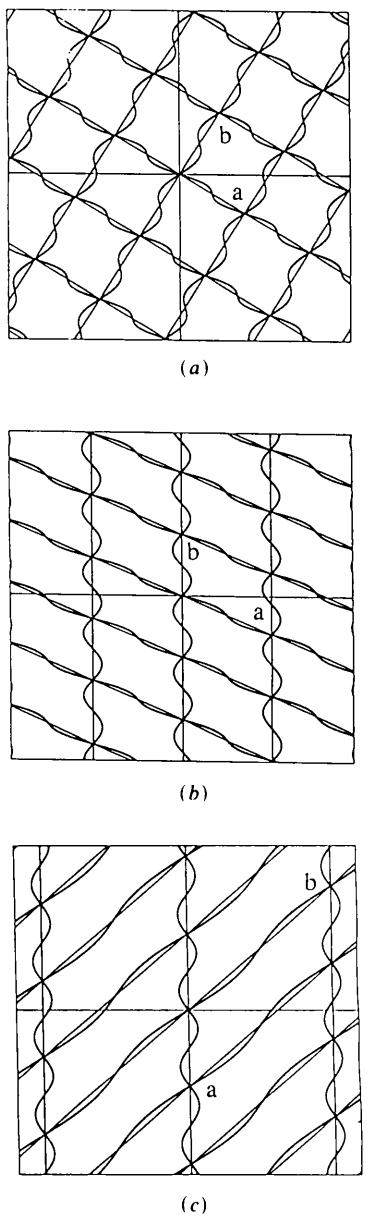

Fig. 1. Descriptions of a one-dimensional composite crystal as the intersection of a two-dimensional crystal. Horizontal and vertical lines represent the external and internal spaces. Wavy lines stand for atoms which are continuous along two directions. (*b*) and (*c*) are obtained from (*a*) by different shear strains by which the points *b* and *a* in (*a*) are shifted in the internal space. In (*c*), the scale in the internal space is different from that in (*a*) and (*b*). The shear strain used leaves the external space invariant, so that the three representations shown in (*a*)-(*c*) are equivalent to each other (see text).

The three equivalent representations give the same structure factor. This is shown for the case of harmonic modulation. We assume the Fourier amplitudes of displacement waves $\mathbf{u}^1$ and $\mathbf{u}^2$ along the external space for the first and second substructures. [The superscript j ($j=1$ or 2) denotes the jth substructure.] The atoms in the first substructure are continuous along the *b* axis and the atoms in the second one are continuous along the *a* axis, so that the coordinates of the atoms are given by

$$\begin{aligned} x^1 &= \mathbf{a}^* \cdot \mathbf{u}^1 \sin(2\pi\bar{y}^1), \\ y^1 &= \bar{y}^1 + \mathbf{b}^* \cdot \mathbf{u}^1 \sin(2\pi\bar{y}^1), \\ y^2 &= \mathbf{b}^* \cdot \mathbf{u}^2 \sin(2\pi\bar{x}^2), \\ x^2 &= \bar{x}^2 + \mathbf{a}^* \cdot \mathbf{u}^2 \sin(2\pi\bar{x}^2), \end{aligned} \tag{1}$$

where $\bar{x}^j$ and $\bar{y}^j$ are the coordinates of the jth fundamental structure from which the displacement is measured (straight lines in Fig. 1). In the above equations, $\mathbf{a}^* \cdot \mathbf{u}^j$ or $\mathbf{b}^* \cdot \mathbf{u}^j$ are invariant under the shear strain which leaves the external space invariant because the external components of $\mathbf{a}^*$ and $\mathbf{b}^*$ are unchanged under the shear strain (see Fig. 2). As a

result, the structure factor of the composite crystal

$$F(\mathbf{h}) = f^1(\mathbf{h}^e)J_{-k}(2\pi\mathbf{h}^e\cdot\mathbf{u}^1) + [f^2(\mathbf{h}^e)v^1/v^2]J_{-h}(2\pi\mathbf{h}^e\cdot\mathbf{u}^2) \qquad (2)$$

is independent of the difference in the representations in Fig. 1, where $f^j(\mathbf{h}^e)$ $(j=1,2)$ are the atomic scattering factors, the superscript e means the external component of a two-dimensional vector, $\mathbf{h}=h\mathbf{a}^*+k\mathbf{b}^*$, and J_n is the Bessel function of order n. For the first and second substructures, the volumes of the unit cell, v^1 and v^2, are equal to the periods of the average structures in the external space for the present (one-dimensional) case.

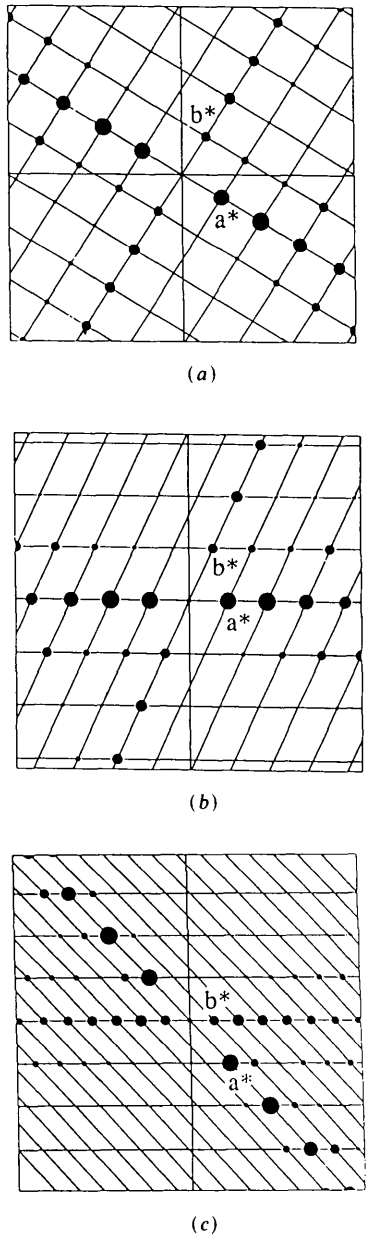

Fig. 2. Diffraction patterns of the composite crystal shown in Fig. 1. The three figures correspond to the three equivalent representations in Fig. 1.

The diffraction pattern of this structure shows a characteristic feature. There are two sets of strong reflections with indices $h0$ or $0k$ along the principal axes (Fig. 2a). These are called main reflections. The $h0$ reflections mainly come from the first substructure [first term in (2)] while the $0k$ reflections come from the second one (second term). The diffraction pattern corresponding to Fig. 1(b) or (c) is obtained from Fig. 2(a) by considering an appropriate shear strain which leaves the internal space invariant (Figs. 2b and c). It should be noted that the position of the reflection in the external space (after the projection along the internal space) and the intensity remain unchanged. It is noted that an infinite number of equivalent representations corresponding to different shear strains are present.

3. Superspace groups for composite crystals

The symmetry of composite crystals can be expressed by the superspace group of the modulated structure (Janner & Janssen, 1980). This causes difficulty in some cases. As shown in the previous section, the same structure can be described in several ways. For the setting in Fig. 1(b), the first substructure gives the main reflections, which are on the external space (Fig. 2b). Corresponding to this view, we have one superspace group, while the other view in Fig. 1(c) may give a superspace group which is not equivalent to the former since the reflections coming from the second substructure are regarded as the main reflections. The one-dimensional composite crystal discussed here causes no problem because relevant superspace groups are limited. In the real case shown below, however, the first view gives the superspace group R^{P31c}_{111} while the second one gives P^{R3m}_{1s} (see § 9). These two superspace groups are non-equivalent under the equivalence relation for the modulated structure (de Wolff, Janssen & Janner, 1981). Furthermore, if we allow a setting different from these two, we may obtain another superspace group.

The symmetry of a composite crystal with two substructures is properly specified by a pair of two superspace groups which specify the symmetries of two modulated substructures. In the present case, it is written as R^{P31c}_{111}: P^{R3m}_{1s}. Similarly, in a composite crystal with three substructures, we use a triplet of the superspace-group symbols for three modulated substructures. In this notation each substructure is treated equivalently to the other because the interchange of the first and second substructures simply means the interchange of the two superspace-group symbols. Therefore these two superspace groups are called equivalent. This implies the equivalence relation of the superspace group for composite crystals:

the superspace groups obtained from each other by the interchange of substructures are equivalent. The introduced symbol of the superspace group for composite crystals is new in two ways. First, it includes two or more superspace-group symbols. Second, the setting of the superspace group for each modulated substructure can be non-standard as shown in the next section.

4. Types of composite crystal and unified setting of unit vectors

There exist several limitations for the formation of composite crystals because, if we neglect the modulation, they consist of two or more interpenetrating crystals with periods incommensurate to each other. It is clear that a one-dimensional composite crystal cannot avoid having unrealistic short interatomic distances (Fig. 1). In physically reasonable composite crystal structures, therefore, the two substructures in Fig. 1 have to be located at different positions in another dimension. Such a consideration enables us to classify all composite crystals into three types. There exists no composite crystal without a common period for some pair of substructures. (It should be noted that the common period does not exclude the case of two axes commensurate to each other.) Therefore, at least one common period for any pair of substructures has to be present.

In the simplest case, all the substructures have two common periods and periods incommensurate to each other along the one remaining direction. In this case, the a^* axis and b^* axis are common to all the substructures ($\mathbf{a}^{*1}=\mathbf{a}^{*2}=\ldots$, $\mathbf{b}^{*1}=\mathbf{b}^{*2}=\ldots$, $\mathbf{c}^{*1}, \mathbf{c}^{*2}, \ldots$). All composite crystals with four-dimensional superspace groups belong to this type. This is called the first type (or type I).

In the second type (type II), all the substructures have one common axis but have incommensurate periods along the other directions. This has a five-dimensional (or higher-dimensional) superspace group. In a crystal consisting of two substructures, there are five independent periods, $\mathbf{a}^{*1}=\mathbf{a}^{*2}$, $\mathbf{b}^{*1}$, $\mathbf{c}^{*1}$, $\mathbf{b}^{*2}$, $\mathbf{c}^{*2}$. If we consider composite crystals with more than two substructures, we can consider a structure in which all the substructures have a common period along one direction but there exists another common period among some (not all) pairs of substructures along another direction. For example, we consider a composite crystal consisting of three substructures in which the b^* axis is common to the first pair and the c^* axis to the second. Then the composite crystal has five periods, that is, $\mathbf{a}^{*1}=\mathbf{a}^{*2}=\mathbf{a}^{*3}$, $\mathbf{b}^{*1}=\mathbf{b}^{*2}$, $\mathbf{c}^{*1}$, $\mathbf{c}^{*2}=\mathbf{c}^{*3}$, $\mathbf{b}^{*3}$, and its symmetry is described by a triplet of five-dimensional superspace groups.

The composite crystal of the third type (type III) consists of more than two substructures and has common axes not for all the substructures but only for each pair of substructures. For example, we can consider a composite crystal composed of three substructures in which $\mathbf{a}^{*1}=\mathbf{a}^{*2}$, $\mathbf{b}^{*1}=\mathbf{b}^{*3}$, $\mathbf{c}^{*2}=\mathbf{c}^{*3}$ but other axes are incommensurate to each other. This has six independent periods, $\mathbf{a}^{*1}$, $\mathbf{b}^{*1}$, $\mathbf{c}^{*1}$, $\mathbf{b}^{*2}$, $\mathbf{c}^{*2}$, $\mathbf{a}^{*3}$, and its symmetry is specified by a triplet of six-dimensional superspace groups. So far types I and II have been found but type III is not known to the author's knowledge.

The above considerations lead to a unified setting of the unit vectors in describing a composite crystal in superspace. We take all the unit vectors from the set of reciprocal-lattice vectors for each substructure. These are recognized as the projection of the unit vectors of a higher-dimensional reciprocal lattice. For the composite crystal of type I or II, two or one of them can be common to all the substructures owing to the common periods. For example, in the simplest case of type I mentioned above, we can take $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^{*1}$ and $\mathbf{c}^{*2}$ and recognize them as the projection of the unit vectors in the four-dimensional lattice onto the external space, where $\mathbf{a}^*$ and $\mathbf{b}^*$ are the reciprocal vectors common to the two substructures and $\mathbf{c}^{*1}$ and $\mathbf{c}^{*2}$ are the third unit vectors for the first and second substructures. As stated above, each substructure is modulated by the existence of the other substructure. The modulation wave vector for the first modulated substructure is therefore $\mathbf{c}^{*2}$ while that of the second is $\mathbf{c}^{*1}$. A similar consideration can be made for the cases of types II and III.

We consider the latter case of type II mentioned above in detail because it is more general than the former and no example of type III has been found. In this case, the wave vectors of the modulation waves for the first substructure are $\mathbf{b}^{*3}$ and $\mathbf{c}^{*2}$, those for the second one are $\mathbf{b}^{*3}$ and $\mathbf{c}^{*1}$ and those for the third one are $\mathbf{b}^{*1}$ and $\mathbf{c}^{*2}$. That is, the unit vectors of the jth substructure and wave vectors of the modulation waves, $\mathbf{a}^{j*}$, $\mathbf{b}^{j*}$, $\mathbf{c}^{j*}$, $\mathbf{k}_1^{j*}$, $\mathbf{k}_2^{j*}$, are obtained from $\mathbf{a}^*$, $\mathbf{b}^{*1}$, $\mathbf{c}^{*1}$, $\mathbf{b}^{*3}$, $\mathbf{c}^{*2}$ by the permutation P^j, where $P^1=\left(\begin{smallmatrix}1,2,3,4,5\\1,2,3,4,5\end{smallmatrix}\right)=(1)$, $P^2=\left(\begin{smallmatrix}1,2,3,4,5\\1,2,5,3,4\end{smallmatrix}\right)=(3,4,5)$ and $P^3=\left(\begin{smallmatrix}1,2,3,4,5\\1,4,3,2,5\end{smallmatrix}\right)=(2,4)$. In particular, we take the identity permutation for the first substructure. This simplifies the treatment of composite crystals in superspace. We consider the five-dimensional reciprocal lattice, the unit vectors of which are projected onto the independent unit vectors selected above ($\mathbf{a}^*$, $\mathbf{b}^{*1}$, $\mathbf{c}^{*1}$, $\mathbf{b}^{*3}$, $\mathbf{c}^{*2}$). As mentioned earlier, we can consider an infinite number of such lattices but these are all equivalent. We take one of them and write its unit vectors as $\mathbf{d}_i^*$ ($i=1,2,\ldots,5$) and unit vectors reciprocal to them as $\mathbf{d}_i$ ($i=1,2,\ldots,5$) (*i.e.* $\mathbf{d}_i\cdot\mathbf{d}_j^*=\delta_{ij}$). Then, $(\mathbf{a}^{j*}, \mathbf{b}^{j*}, \mathbf{c}^{j*}, \mathbf{k}_1^{j*}, \mathbf{k}_2^{j*})=[\mathbf{d}_1^{*j}, \mathbf{d}_2^{*j}, \mathbf{d}_3^{*j}, \mathbf{d}_4^{*j}, \mathbf{d}_5^{*j}]^e=[P^j(\mathbf{d}_1^*, \mathbf{d}_2^*, \mathbf{d}_3^*, \mathbf{d}_4^*, \mathbf{d}_5^*, \mathbf{d}_6^*)]^e$ by definition, where the superscript e means the external component of the five-dimensional vector. The reflection with the diffraction vector $\mathbf{h}^e$ is regarded as the

projection of a five-dimensional vector $\mathbf{h}=\sum_{i=1}^{5} h_i\mathbf{d}_i^*$ onto the external space.

Each substructure can conveniently be described by its own coordinate system referring to $\mathbf{d}_i^j$ $(i=1, 2, \ldots, 5)$. In particular, the substructure is continuous along a two-dimensional subspace spanned by $\mathbf{d}_4^j$ and $\mathbf{d}_5^j$. The superspace-group symbol for the jth substructure (appearing in the superspace group of the composite crystal) is obtained from that of the first substructure by the permutation P^j because the permutation matrix transforms the matrix representation of a symmetry element in the first substructure into the corresponding one in the jth substructure. This means that the superspace groups of the modulated substructures are arithmetically equivalent to each other.

In the unified setting described above, the selection of the unit vectors is strongly limited because the unit vectors of each modulated substructure in the reciprocal space is chosen among a set of the reciprocal-lattice vectors of the average substructures. Furthermore, the same vector is used when an axis is common to several substructures. Therefore, the setting of the unit vectors is unique except for the ambiguity in the choice of the unit vectors in each average substructure. On the other hand, such unit vectors may lead to a superspace group in a non-standard setting as shown in § 9.

5. Structure factor and modulation wave

In the setting described above, the modulated substructure is described in the same manner as for the usual modulated structure. For an n-dimensional case, the atom coordinates x_i^j with respect to $\mathbf{d}_i^j$ $(i=1, 2, \ldots, n)$ are given by

$$\mathbf{x}_i^j=\bar{\mathbf{x}}_i^j+\mathbf{d}_i^{*j}\cdot\mathbf{u}^j \tag{3}$$

where $\bar{\mathbf{x}}_i^j$ $(i=1, 2, \ldots, n)$ are the atom coordinates for the jth substructure which are obtained from the coordinates $\bar{x}_i$ in the fundamental structure with respect to $\mathbf{d}_i$ by the permutation P^j and $\mathbf{u}^j$ is the displacement from the fundamental structure and a periodic function of $\bar{x}_{3+i}^j$ $(i=1, \ldots, n-3)$. The modulation functions of the jth modulated substructure have the same form as the corresponding ones in the usual modulated structure. The structure factor is given by

$$F_{\mathbf{h}}=\sum_j (v^1/v^j)F_{\mathbf{h}}^j \tag{4}$$

$$\begin{aligned}F_{\mathbf{h}}^j=\sum_{\{R^j|\tau^j\}}\sum_{\mu} P^{\mu_j}\int_0^1 \mathrm{d}\bar{x}_{1+m}^j\ldots\int_0^1 \mathrm{d}\bar{x}_n^j f^{\mu_j}(\mathbf{h})P^{\mu_j}\\ \times\exp\left\{-\sum_{ik=1}^{n} h_i^j(R^jB^{\mu_j}R^j)_{ik}h_k^j\right.\\ \left.+2\pi i\sum_{i=1}^{n} h_i^j(R^j\mathbf{x}^{\mu_j})_i+h_i^j\tau_i^j\right\}\end{aligned} \tag{5}$$

where h_i^j and τ_i^j are the ith components of $P^j(h_1, h_2, \ldots, h_n)$ and $P^j(\tau_1, \tau_2, \ldots, \tau_n)$. The matrix representation of the rotation operator R^j is obtained from that of the first substructure by the permutation of rows and columns according to P^j. The structure factor of the jth substructure [(5)] has the same form as the corresponding formula for the usual modulated structure (Yamamoto, 1982*a*) because each modulated substructure is the usual modulated structure. The structure factor of the total structure [(4)] is the summation of the structure factors of the modulated substructures with the weight proportional to the inverse of the unit-cell volume of the average substructure v^j. The computer program for the refinement of the composite crystal has been developed on the basis of (4) and (5) by the modification of a previous program *REMOS* for modulated structures (Yamamoto, 1982*a*).

In the modulated structure analysis, the amplitudes of possible modulation waves are limited when atoms are located at the special position in the average structure. (The average structure of the jth substructure is obtained by the projection along the subspace spanned by $\mathbf{d}_4^j, \ldots, \mathbf{d}_n^j$. This is inferred from Fig. 1 because the jth substructure is continuous in such a subspace.) Then the possible modulation waves are constrained by the site symmetry as in the modulated structure. In order to find possible modulation waves, we can apply the same method as in the modulated structure (Yamamoto & Nakazawa, 1981; Yamamoto, 1982*b*; van Smaalen, 1989; Kato, 1990).

In conclusion, if we use the unified setting and the coordinate system for each substructure, the substructure can be treated in the same way as the usual modulated structure and we can apply the method used in the modulated structure analysis to the analysis of the composite crystal.

6. Additional symbols of superspace groups

We confine ourselves to the symbols and superspace groups of composite crystals of type I with two substructures because their symmetry is specified by a four-dimensional superspace group and the list of five- and six-dimensional superspace groups has not yet been given. As shown above, the choice of the unit vectors is restricted in the unified setting. As a result, the setting may be non-standard not only for the superspace group of the modulated substructure but also for the space group of the average substructure. We may have to use, for example, a face-centered lattice for a monoclinic structure in some cases and a wave vector such as $\mathbf{k}=\mathbf{a}^*+\mathbf{b}^*+\gamma\mathbf{c}^*$ for which the symbol of the superspace group is not given (see § 9). Therefore, we introduce several symbols for the superspace groups in addition to those introduced by de Wolff *et al.* (1981). Additional rational components of the wave vector $\mathbf{k}$ are $(1/2, 1, 0)$, $(1/2, 0, 1)$,

Table 1. *Additional prefixes and corresponding rational components (RC) of the modulation wave vector appearing in the unified setting of superspace groups for composite crystals*

Prefix	*D*	*E*	*F*	*G*	*H*
RC	$(\frac{1}{2}, 1, 0)$	$(\frac{1}{2}, 0, 1)$	$(0, \frac{1}{2}, 1)$	$(1, \frac{1}{2}, 0)$	$(1, 0, \frac{1}{2})$
Prefix	*I*	*X*	*Y*	*Z*	
RC	$(0, 1, \frac{1}{2})$	$(0, 1, 1)$	$(1, 0, 1)$	$(1, 1, 0)$	

$(0, 1/2, 1)$, $(1, 1/2, 0)$, $(1, 0, 1/2)$, $(0, 1, 1/2)$, $(0, 1, 1)$, $(1, 0, 1)$ and $(1, 1, 0)$. These cases are specified by the prefixes given in Table 1. They are also available for the superspace-group symbol of the usual modulated structure with a non-standard setting.

7. Reflection conditions

The unified setting for composite crystals leads to additional reflection conditions which have not been listed in the table of de Wolff, Janssen & Janner (1981). (The indices *hklm* are used instead of $h_1h_2h_3h_4$ hereafter for convenience.) All the reflection conditions for general reflections due to the Bravais lattice are listed in Table 2. It should be noted that the same reflection condition appears in different settings. The reflection conditions for general reflections imply the centering translations. For example, $h+k+l=2n$, $h+l+m=2n$, $k+m=2n$ for *FB* in the table imply the centering translations of $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0)$, $(\frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2})$ and $(0, \frac{1}{2}, 0, \frac{1}{2})$. It should be noted that, when the rational component of the wave vector is $\frac{1}{2}$, the corresponding axis is doubled in the centered lattice compared with the unit cell describing the average structure according to the theory of superspace groups. [*WP* in the tetragonal system is exceptional (see de Wolff *et al.*, 1981).]

8. Description of the composite crystals

In order to describe the composite crystal structure, it is sufficient to specify the lattice constants of the first substructure and the modulation wave vector for it, the permutation matrix for the second (third, fourth, ... if any) substructure(s), the superspace group, the number of formula units in the unit cell for each substructure and the description of the modulated substructure with reference to the unit vectors for each substructure. The lattice constants and wave vectors for the other substructures can be calculated from those of the first substructure and the permutation matrix. The superspace-group symbol implies the permutation matrix in many cases. In the case of type I with two substructures, the permutation is taken only on two parallel axes among $\mathbf{d}_1^{*e}, \mathbf{d}_2^{*e}, \mathbf{d}_3^{*e}, \mathbf{d}_4^{*e}$ for the monoclinic, orthorhombic, tetragonal and hexagonal systems. Then the description of the permutation matrix is neglected.

Table 2. *Reflection conditions due to the Bravais lattice*

PA etc. in the first column means the prefix of the two-line symbol and the Bravais type of the average substructure. The reflection condition for the general reflection *hklm* is written in the convention of *International Tables for Crystallography* (1983). The wave vector specific to the type in the first column is given in the third column. For the type *WP*, the reflection condition in the tetragonal Bravais lattice is different from that of the others, so two cases are listed.

Type	Reflection condition	Wave vector
PA	$k+l=2n$	
PB	$h+l=2n$	
PC	$h+k=2n$	
PI	$h+k+l=2n$	
PF	$h+k=2n, k+l=2n, h+l=2n$	
PR	$-h+k+l=3n$	$(0, 0, \gamma)$
AP	$h+m=2n$	$(\frac{1}{2}, \beta, 0), (\frac{1}{2}, 0, \beta), (\frac{1}{2}, \alpha, \beta)$
BP	$k+m=2n$	$(\alpha, \frac{1}{2}, 0), (0, \frac{1}{2}, \gamma), (\alpha, \frac{1}{2}, \gamma)$
CP	$l+m=2n$	$(\alpha, 0, \frac{1}{2}), (0, \beta, \frac{1}{2}), (\alpha, \beta, \frac{1}{2})$
UP	$k+m=2n, l+m=2n$	$(\alpha, \frac{1}{2}, \frac{1}{2})$
VP	$h+m=2n, l+m=2n$	$(\frac{1}{2}, \beta, \frac{1}{2})$
WP	$h+k+m=2n$ (tetragonal)	$(\frac{1}{2}, \frac{1}{2}, \gamma)$
WP	$h+m=2n, k+m=2n$ (others)	$(\frac{1}{2}, \frac{1}{2}, \gamma)$
AA	$h+m=2n, k+l=2n$	$(\frac{1}{2}, \beta, 0), (\frac{1}{2}, 0, \gamma), (\frac{1}{2}, \beta, \gamma)$
DA	$h+k+l=2n, k+l+m=2n, h+m=2n$	$(\frac{1}{2}, 1, \gamma)$
EA	$h+k+l=2n, k+l+m=2n, h+m=2n$	$(\frac{1}{2}, \beta, 1)$
MA	$k+l+m=2n$	$(0, 1, \gamma), (\alpha, 1, \gamma)$
NA	$k+l+m=2n$	$(0, \beta, 1), (\alpha, \beta, 1)$
BB	$h+l=2n, k+m=2n$	$(\alpha, \frac{1}{2}, 0), (0, \frac{1}{2}, \gamma), (\alpha, \frac{1}{2}, \gamma)$
FB	$h+k+l=2n, h+l+m=2n, k+m=2n$	$(\alpha, \frac{1}{2}, 1)$
GB	$h+k+l=2n, h+l+m=2n, k+m=2n$	$(1, \frac{1}{2}, \gamma)$
LB	$h+l+m=2n$	$(1, \beta, 0), (1, \beta, \gamma)$
NB	$h+l+m=2n$	$(0, \beta, 1), (\alpha, \beta, 1)$
CC	$h+k=2n, l+m=2n$	$(\alpha, 0, \frac{1}{2}), (0, \beta, \frac{1}{2}), (\alpha, \beta, \frac{1}{2})$
HC	$h+k+l=2n, h+k+m=2n, l+m=2n$	$(1, \beta, \frac{1}{2})$
IC	$h+k+l=2n, h+k+m=2n, l+m=2n$	$(\alpha, 1, \frac{1}{2})$
LC	$h+k+m=2n$	$(1, \beta, 0), (1, \beta, \gamma)$
MC	$h+k+m=2n$	$(\alpha, 1, 0), (\alpha, 1, \gamma)$
LI	$h+k+l+m=2n$	$(1, \beta, 0), (1, 0, \gamma), (1, \beta, \gamma)$
MI	$h+k+l+m=2n$	$(\alpha, 1, 0), (0, 1, \gamma), (\alpha, 1, \gamma)$
NI	$h+k+l+m=2n$	$(\alpha, 0, 1), (0, \beta, 1), (\alpha, \beta, 1)$
LF	$h+k+m=2n, k+l=2n, h+l+m=2n$	$(1, \beta, 0), (1, 0, \gamma), (1, \beta, \gamma)$
MF	$h+k+m=2n, k+l+m=2n, h+l=2n$	$(\alpha, 1, 0), (0, 1, \gamma), (\alpha, 1, \gamma)$
NF	$h+k=2n, k+l+m=2n, h+l+m=2n$	$(0, \beta, 1), (\alpha, 0, 1), (\alpha, \beta, 1)$
XF	$h+k+m=2n, h+l+m=2n, k+l=2n$	$(\alpha, 1, 1)$
YF	$h+k+m=2n, h+l=2n, k+l+m=2n$	$(1, \beta, 1)$
ZF	$h+k=2n, h+l+m=2n, k+l+m=2n$	$(1, 1, \gamma)$
RP	$-h-k-m=3n$	$(\frac{1}{3}, \frac{1}{3}, \gamma)$

9. Examples of composite crystals and superspace groups

In this section we show examples of composite crystals with triclinic, monoclinic, orthorhombic, trigonal and tetragonal superspace groups and their simple

description except for the structural parameters. In the following, each substructure is enclosed by square brackets in the chemical formula.

(*a*) $[LaS]_x[CrS_2]$. This is a so-called misfit layer structure which consists of LaS and CrS_2 layers (Kato, 1990). The first substructure consists of LaS and the second of CrS_2. Each substructure has a triclinic average structure but the structure was analyzed based on the non-standard setting in which the *C*-centered lattice is taken: $L^{C\bar{1}}_{\bar{1}}: L^{C\bar{1}}_{\bar{1}}$, $a = 5.936$, $b = 5.752$, $c = 11.036$ Å, $\cos\alpha = -0.0058$, $\cos\beta = -0.0924$, $\cos\gamma = -0.0003$, $\mathbf{k} = \mathbf{a}^* + 1.67441\mathbf{b}^* + 0.16666\mathbf{c}^*$, $P^2 = (2, 4)$, $Z_1 = 2$, $Z_2 = 2$. When we take $\mathbf{A}^* = \mathbf{a}^*$, $\mathbf{B}^* = \mathbf{c}^*$, $\mathbf{C}^* = \mathbf{a}^* + \mathbf{b}^*$, this becomes $P^{P\bar{1}}_{\bar{1}}: P^{P\bar{1}}_{\bar{1}}$, $P^2 = (3, 4)$, $\mathbf{k} = -0.67441\mathbf{A}^* + 0.166666\mathbf{B}^* + 1.67441\mathbf{C}^*$, $Z_1 = 1$, $Z_2 = 1$. All the atoms are located in the general position.

(*b*) $[PbS]_x[VS_2]$. This is a misfit layer structure similar to the previous one but with a different superspace group (Onoda *et al.*, 1990). Each substructure is monoclinic (de Wolff *et al.*, 1981) but the first substructure has the face-centered lattice because of the restriction in the choice of unit vectors mentioned before: $L^{F2}_{1}: H^{C2}_{1}$, $a = 5.728$, $b = 5.789$, $c = 23.939$ Å, $\cos\beta = -0.1556$, $\mathbf{k} = \mathbf{a}^* + 1.778\mathbf{b}^*$. [The permutation matrix $P^2 = (2, 4)$ is implied by the superspace group.] In this case, only the V atom in the second substructure is located at the special position 2(*b*) with site symmetry $\binom{2}{s}$.

(*c*) $[(Bi, Ca, Sr)_2Cu_2O_3]_x[CuO_2]$. This is an intergrowth structure with two substructures (Kato, 1990). Each substructure has the same orthorhombic superspace group: $Z^{F2\,2\,2}_{1\,1\,1}: Z^{F2\,2\,2}_{1\,1\,1}$, $a = 12.811$, $b = 11.3446$, $c = 3.9035$ Å, $\mathbf{k} = \mathbf{a}^* + \mathbf{b}^* + 1.4169\mathbf{c}^*$. [The superspace group implies $P^2 = (3, 4)$.] In the first substructure, Bi, Ca and Sr atoms occupy the same Wyckoff position 8(*e*) at random with site symmetry $\binom{2}{1}$, Cu(1) and O(1) are at 8(*f*) with site symmetry $\binom{2}{1}$ and O(2) is at 4(*b*) with $\binom{2\,2\,2}{1\,1\,1}$. Similarly, Cu(2) in the second substructure is at 4(*c*) with $\binom{2\,2\,2}{1\,1\,1}$ and O(3) is at 8(*i*) with $\binom{2}{1}$.

(*d*) $[Ba]_x[(Cu, Pt)O_3]$. This is also an intergrowth structure in which the $(Cu, Pt)O_3$ forms a framework structure and Ba atoms are located in tunnels (Ukei *et al.*, 1992). The first Ba substructure has a hexagonal lattice while the second one has a rhombohedral lattice: $R^{P31c}_{111}: P^{R3m}_{1s}$, $a = 5.817$, $c = 4.233$ Å, $\cos\gamma = -0.5$, $\mathbf{k} = (\mathbf{a}^* + \mathbf{b}^*)/3 + 1.519\mathbf{c}^*$. [$P^2 = (3, 4)$.] All the atoms are in special positions: Ba in the first substructure is at 2(*b*) with site symmetry $\binom{3}{t}$ while (Cu, Pt) in the second is at 3(*a*) with site symmetry $\binom{3m}{1s}$ and O is at 9(*b*) with site symmetry $\binom{m}{s}$.

(*e*) $[Ba]_x[FeS_2]$. This is the third example of an intergrowth structure consisting of two substructures but these have periods commensurate to each other (Onoda & Kato, 1991). It was, however, analyzed on the basis of an approximate superspace-group symmetry. The second substructure FeS_2 forms the framework structure and the Ba atoms are located in tunnels. Both substructures have the body-centered tetragonal lattice: $L^{I4mm}_{1\,s\,s}: L^{I4bm}_{1\,s\,s}$, $a = 7.776$, $c = 4.986$ Å, $\mathbf{k} = \mathbf{a}^* + 0.9\mathbf{c}^*$. [$P^2 = (3, 4)$.] The space group of the second average substructure is *I*4*cm* but the symbol *I*4*bm* is used because the former leads to an ambiguous superspace-group symbol (Yamamoto, Janssen, Janner & de Wolff, 1985). Ba atoms in the first substructure are at 2(*a*) with site symmetry $\binom{4mm}{1\,s\,s}$. In the second substructure, Fe is at 4(*b*) with site symmetry $\binom{mm2}{s\,s\,1}$, where the mirror *m* is normal to $\mathbf{a} \pm \mathbf{b}$, while S is at 8(*c*) with site symmetry $\binom{m}{s}$.

10. Discussion

So far we have avoided the exceptional case of $[AsF_6][Hg]_x[Hg]_x$ which has been discussed by Janner & Janssen (1980). This is composed of three substructures, one of which consists of AsF_6 and the other two of Hg (Pouget, Shirane, Hastings, Heeger, Miro & MacDiarmid, 1978). The first substructure AsF_6 forms a body-centered tetragonal lattice. The other two substructures (Hg) have *A*-centered and *B*-centered monoclinic sublattices, in which the a^* and b^* axes are incommensurate to each other but one of these is common to the a^* or b^* axis of the first substructure and their c^* axes are the same as the first one: $\mathbf{a}^{*1} = \mathbf{a}^{*3}$, $\mathbf{a}^{*2} = (3 - \delta)\mathbf{a}^{*1} + (-1 - \delta)\mathbf{b}^{*1}$, $\mathbf{b}^{*1} = \mathbf{b}^{*2}$, $\mathbf{b}^{*3} = (-1 - \delta)\mathbf{a}^{*1} + (3 - \delta)\mathbf{b}^{*1}$ and $\mathbf{c}^{*1} = \mathbf{c}^{*2} = \mathbf{c}^{*3}$, where δ is a small irrational number. Therefore, there are five independent periods defined by $\mathbf{a}^{*1}$, $\mathbf{b}^{*1}$, $\mathbf{c}^{*1}$, $\mathbf{a}^{*2}$, $\mathbf{b}^{*3}$ with $\mathbf{a}^{*2} \cdot \mathbf{b}^{*2} \neq 0$ and $\mathbf{a}^{*3} \cdot \mathbf{b}^{*3} \neq 0$. Because of the symmetry of the Hg substructures, the superspace-group symmetry common to all the substructures is monoclinic. The Hg substructures are, however, related by a glide plane. As a result, total diffraction symmetry is orthorhombic and higher than the symmetry of the substructure (Fig. 10 of Pouget *et al.*, 1978). Such a situation is not taken into account in the previous sections. We discuss this case briefly in order to show the applicability of the theory to such a case.

This structure is an example of a composite crystal of type II and can be treated within the framework of the superspace-group theory in which the five-dimensional superspace group is applied to the *merged* Hg and AsF_6 substructures. In the present theory, such a merged substructure is not considered because Hg really forms two substructures giving two sets of main reflections. Instead of generalizing the theory within the framework of the group theory to treat such a structure, we can use the groupoid (Sadanaga & Ohsumi, 1979). The superspace groupoid **T** is given by $\{\mathbf{h}_i\mathbf{G}\mathbf{h}_j^{-1} | \mathbf{h}_i, \mathbf{h}_j^{-1} \in \mathbf{H}\}$, where **G** is the superspace group of the substructure and **H** is the set of operations $\mathbf{h}_i$ superimposing the first substructure into the *i*th substructure and operating only on the first substructure and its inverse operator $\mathbf{h}_i^{-1}$ operating on the *i*th substructure and superimposing

it into the first one. ($\mathbf{h}_1$ is the identity operator.) The groupoid **T** is therefore the set of operations which superposes each substructure onto itself (diagonal terms) or onto the other substructure (off-diagonal terms). The superspace group **G** is called the kernel and **H** the hull of the superspace groupoid. The structure analysis can be made within the framework of the present theory if we use the operators in **G** and **H**.

It is possible to classify the structure into two groups of substructures, one of which consists of the second substructure of Hg and part of the first substructure and the other consists of the third substructure of Hg and the remaining part of the first substructure. The two groups are transformed into each other by the glide plane normal to $\mathbf{a}^{*1}-\mathbf{b}^{*1}$ which transforms $\mathbf{a}^{*1}$ into $\mathbf{b}^{*1}$. In the first substructure, each part has a tetragonal lattice but with monoclinic symmetry. These two parts have no common atoms because they are related by the glide plane. We can apply the groupoid theory to these two groups by recognizing the groups as the substructures in the above discussion. The two structure groups have a five-dimensional superspace group with monoclinic symmetry. When the structure factor of the first group $F_0(\mathbf{h}^e)$ and $\mathbf{h}_2=\{R|\tau\}$ transforming the first part into the second one are considered, the structure factor of the total structure is given by $F(\mathbf{h}^e)=F_0(\mathbf{h}^e)+\exp(2\pi\mathbf{h}^e\tau)F_0(R^{-1}\mathbf{h}^e)$. In the present case, $\mathbf{h}_2$ is the glide plane so that $R^{-1}=R$. Then the diffraction pattern shows the rotational symmetry due to $\mathbf{h}_2$: $F(R\mathbf{h}^e)=\exp(2\pi R\mathbf{h}^e\tau)F(\mathbf{h}^e)$ because $\{R|\tau\}^2=\{E|\tau+R\tau\}=\{E|0\}$ and therefore $\exp(2\pi R\mathbf{h}^e\tau)=\exp(-2\pi\mathbf{h}^e\tau)$, where E is the identity operator. This ensures orthorhombic diffraction symmetry. Thus, instead of applying the superspace group for the merged Hg substructure, we can use the superspace groupoid as given in a previous paper (Yamamoto & Ishihara, 1988). This shows the applicability of the present theory to all cases.

The author thanks Dr K. Kato and Dr M. Onoda, National Institute for Research in Inorganic Materials, for valuable discussions and for supplying test data in the development of the new version of *REMOS*.

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On Quantitative Relations among Crystal Structures

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(*Received* 25 *September* 1991; *accepted* 3 *January* 1992)

Dedicated to Professor Dr W. Fischer on the occasion of his 60*th birthday*

Abstract

A procedure for the quantitative evaluation of structural relationships among crystal structures is introduced based on the concept of mappings represented by pairs of matrices (**A**, **S**). Lattice relationships, symmetry relationships, local atomic deviations and mapping failures are distinguished and for each type of relationship, a figure of merit is constructed. The different figures are combined in a figure of misfit

0108-7673/92/040483-08$06.00