

Symmetry of composite crystals

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Composite crystals are crystals that consist of two or more subsystems, in first approximation each one having its own three-dimensional periodicity. The symmetry of these subsystems is then characterized by an ordinary space group. Due to their mutual interaction the true structure consists of a collection of incommensurately modulated subsystems. In this paper we derive some general properties for intergrowth structures, using the superspace-group theory as developed by Janner and Janssen [Acta Crystallogr. **A36**, 408 (1980)]. In particular, the pseudoinverse is defined of the matrices relating the subsystem periodicities to the translation vectors in superspace. This pseudoinverse is then used to reformulate the relations between the structure and symmetry in three-dimensional space and in $(3+d)$ -dimensional superspace. As an extension of the theory, subsystem superspace groups are defined, that characterize the symmetry of the individual, incommensurately modulated subsystems. The relation between a unified description of the symmetry and an independent description of the subsystems is analyzed in detail, both on the level of the basic structure (translational symmetric subsystems) and on the level of the modulated structure (incommensurately modulated subsystems). The concepts are illustrated by the analysis of the diffraction symmetry of the intergrowth compound $\text{Hg}_{3-\delta}\text{AsF}_6$.

I. INTRODUCTION

Intergrowth compounds, also called composite crystals, are crystalline compounds that do not possess three-dimensional translational symmetry. They can be characterized as a collection of subsystems, each one being translational symmetric in good approximation. Each atom belongs to one of the subsystem. The lattice characterizing the translational symmetry of one subsystem is incommensurate to the translational symmetry of all other subsystems, thus ensuring the lack of three-dimensional translation symmetry of the complete system.¹

Several examples of intergrowth compounds can be found in the literature.¹⁻³ In $\text{Eu}_{1-p}\text{Cr}_2\text{Se}_{1-p}$,² one subsystem consists of a three-dimensional net with composition $\text{Cr}_{21}\text{Se}_{36}$. Channels in this net, parallel to the hexagonal axis, accommodate either $\text{Eu}_6\text{Cr}_2\text{Se}_6$ (the second subsystem) or Eu_3Se (the third subsystem). Perpendicular to the chains the repeat distance is the same for all three subsystems. However, parallel to the channels, the Cr-Se matrix and both types of chains have a different lattice constant, providing the incommensurateness in the system.

The so-called inorganic misfit layer structures are a special kind of layer compounds.^{1,3} Contrary to periodic layer compounds (e.g., graphite), these particular compounds consist of alternating layers of different chemical composition, which provide the two subsystems. At least one of the intralayer lattice constants of one subsystem is incommensurate with the lattice constants of the other subsystem, thus providing the incommensurateness of the

complete system.

It follows, that a composite crystal can be characterized by a finite number of at least four periodicities.

In the description given above, the crystal is thought to consist of translational symmetric subsystems. This is only an approximation to the real structure, and will be called the basic structure. Due to their mutual interaction, the subsystems in the real crystal will be modulated. The modulation of one subsystem is characterized by modulation wave vectors equal to the periodicities of the other subsystems. Thus, the real crystal consists of a set of incommensurately modulated structures. The periods characterizing the complete system are a combination of the basic periodicities of the subsystems.

The symmetry of an intergrowth compound can be characterized by a higher dimensional space group (number of dimensions greater than three). This theory has been developed by Janner and Janssen,⁴ and is analogous to the theory of superspace groups as applies to incommensurately modulated structures.⁵

The goal of the present paper is to analyze the implications of this theory for the description of the symmetry and structure of composite crystals. First, a review is given of the notation and basic definitions. Second, a pseudoinverse is defined for the matrices, Z^v , relating the subsystem periodicities with the superspace lattice vectors. This pseudoinverse is subsequently used to define a set of subsystem space groups and a set of subsystem superspace groups, which, respectively, characterize the symmetry of the basic structure and modulated structure of the subsystems. These concepts are illustrated by a reanalysis of the neutron diffraction data of $\text{Hg}_{3-\delta}\text{AsF}_6$

of Pouget *et al.*⁶ Finally, the differences are derived between an approach where the symmetry of each subsystem is treated independently of the symmetry of the other subsystems and a unified treatment of the symmetry of the complete crystal (superspace group approach).

It is noted that additional modulations may occur, which are not related to any of the subsystem basic periodicities. Such a modulation can be described by adding an extra dimension to the higher dimensional space group of the complete system and to each subsystem superspace group, analogous to the way ordinary incommensurately modulated structures are described.^{4,5} These additional modulations are not considered in this paper.

II. THE BASIC STRUCTURE

First, consider the basic structure, for which the coordinates of each atom belong to a periodic point set of one of the lattices Λ_ν , $\nu=1, \dots, N$. There may be more than one atom in the unit cell of Λ_ν . The atoms belonging to any periodic point set of Λ_ν , together define the ν th subsystem. By construction, the basic structure of the ν th subsystem has symmetry according to a three-dimensional space group. Atoms belonging to different periodic point sets in Λ_ν may be found equivalent by an element of this space group.

Let $\Lambda_\nu = \{\mathbf{a}_{\nu 1}, \mathbf{a}_{\nu 2}, \mathbf{a}_{\nu 3}\}$, with its reciprocal lattice $\Lambda_\nu^* = \{\mathbf{a}_{\nu 1}^*, \mathbf{a}_{\nu 2}^*, \mathbf{a}_{\nu 3}^*\}$. Then there exists a set of reciprocal vectors, $M^* = \{\mathbf{a}_1^*, \dots, \mathbf{a}_{3+d}^*\}$, with basis $(\mathbf{a}_1^*, \dots, \mathbf{a}_{3+d}^*)$, such that⁴

$$\mathbf{a}_{\nu i}^* = \sum_{j=1}^{3+d} Z_{ij}^\nu \mathbf{a}_j^* \quad (i=1,2,3) \quad (1)$$

for each $\nu=1, \dots, N$, with Z^ν , $\nu=1, \dots, N$ is an integral $3 \times (3+d)$ matrix. The basis of M^* is chosen to contain the least possible number of elements. This means that the basis of M^* is formed by of a set of rationally independent vectors. The number of vectors in the basis of M^* is restricted to a minimum of four and a maximum of $3N$.

For convenience we choose the elements of the basis of M^* to be ordered, such that $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$ is a set of independent vectors. Then, the remaining d vectors can be written as a linear combination of the first three, thus defining a $(d \times 3)$ matrix σ :⁴

$$\mathbf{a}_{3+j}^* = \sum_{i=1}^3 \sigma_{ji} \mathbf{a}_i^* \quad (2)$$

for $j=1, \dots, d$.

The spots in the diffraction pattern of the basic structure of the ν th subsystem (main reflections) are at the positions,

$$\mathbf{S}^\nu = \sum_{i=1}^3 h_{\nu i} \mathbf{a}_{\nu i}^* \quad (3)$$

where $h_{\nu i}$ are integers. From Eq. (1) follows that all diffraction spots of the crystal can be written as an integral linear combination of the basis of M^* :

$$\mathbf{S} = \sum_{i=1}^{3+d} h_i \mathbf{a}_i^* \quad (4)$$

For the ν th subsystem the indices h_i can be obtained from $h_{\nu i}$ by application of Z^ν ,

$$(h_1, \dots, h_{3+d}) = (h_{\nu 1}, h_{\nu 2}, h_{\nu 3}) Z^\nu \quad (5)$$

The diffraction spots obtained according to Eq. (5) do not constitute the complete set of nodes of M^* . Intensity at missing points is obtained, when we allow the subsystems to be incommensurately modulated (see Sec. V).

The vectors $(\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*)$ define a lattice in three-dimensional, physical space. Identifying the remaining elements of the basis of M^* with modulation wave vectors shows the description of the diffraction pattern of an intergrowth compound [Eqs. (2) and (4)] to be formally identical to that for an incommensurately modulated compound. Therefore, as was done by Janner and Janssen,⁴ the theory of superspace groups can be applied to intergrowth compounds.⁵ That means that M^* is considered as the projection of a $(3+d)$ -dimensional reciprocal lattice Σ^* ,⁴

$$\begin{aligned} \mathbf{a}_{si}^* &= (\mathbf{a}_i^*, 0), \quad i=1,2,3, \\ \mathbf{a}_{s,3+j}^* &= (\mathbf{a}_{3+j}^*, \mathbf{b}_j^*), \quad j=1, \dots, d, \end{aligned} \quad (6)$$

where \mathbf{b}_j^* , $j=1, \dots, d$ is a set of reciprocal basis vectors perpendicular to physical space. The corresponding direct lattice Σ is

$$\mathbf{a}_{si} = \left[\mathbf{a}_i, - \sum_{j=1}^d \sigma_{ji} \mathbf{b}_j \right], \quad \mathbf{a}_{s,3+j} = (0, \mathbf{b}_j), \quad (7)$$

where \mathbf{b}_j , $j=1, \dots, d$, are the vectors reciprocal to (\mathbf{b}_j^*) .

By construction the diffraction pattern is now a projection onto physical space of intensities on the nodes of the reciprocal lattice Σ^* . Completely analogous to the situation for incommensurately modulated structures, the electron density of the composite crystal can be obtained as a section perpendicular to (\mathbf{b}_j^*) of a density function in $(3+d)$ -dimensional space. The latter has the periodicity of Σ . To describe this density function we will now construct the analog of an atom in $(3+d)$ -dimensional space.

Equation (1) expresses the elements of Λ_ν^* in the elements of M^* . Through the projection there is an one-to-one correspondence between M^* and Σ^* . Therefore, Eq. (1) also gives a relation between Λ_ν^* and Σ^* . Consider a point, $\mathbf{r}_s = \sum_{i=1}^{3+d} x_{si} \mathbf{a}_{si}$, in higher dimensional space. If \mathbf{r}_s is chosen to be in physical space, it follows that Z^ν defines the relation between the components of \mathbf{r}_s with respect to Σ and with respect to Λ_ν :

$$\begin{pmatrix} x_1^\nu \\ x_2^\nu \\ x_3^\nu \end{pmatrix} = Z^\nu \begin{pmatrix} x_{s1} \\ \vdots \\ x_{s,3+d} \end{pmatrix} \quad (8)$$

A particular embedding of physical space in the $(3+d)$ -dimensional space is chosen, once the matrices Z^ν and σ [Eqs. (1) and (2)] are defined. A pseudoinverse of Z^ν , suitable for this embedding, can then be defined as

$$Y^v = \begin{pmatrix} (Z_3^v + Z_d^v \sigma)^{\text{inv}} \\ \sigma(Z_3^v + Z_d^v \sigma)^{\text{inv}} \end{pmatrix}, \quad (9)$$

where the matrix $Z^v = (Z_3^v Z_d^v)$ is written as the juxtaposition of a 3×3 matrix Z_3^v and a $3 \times d$ matrix Z_d^v . It is easily verified that $Z^v Y^v$ is the 3×3 unit matrix.

An atom of subsystem v , together with its translational equivalents is defined by the positions

$$\begin{pmatrix} \bar{x}_1^v \\ \bar{x}_2^v \\ \bar{x}_3^v \end{pmatrix} = \begin{pmatrix} x_1^0 \\ x_2^0 \\ x_3^0 \end{pmatrix} + \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix} \quad (10)$$

for all $n_i \in \mathbb{Z}$, $i=1,2,3$. The inverse of Eq. (8) then gives the corresponding coordinates in $(3+d)$ -dimensional space,

$$\begin{pmatrix} x_{s1} \\ \vdots \\ x_{s,3+d} \end{pmatrix} = Y^v \begin{pmatrix} x_1^0 \\ x_2^0 \\ x_3^0 \end{pmatrix} + Y^v \begin{pmatrix} n_1 \\ n_2 \\ n_3 \end{pmatrix}. \quad (11)$$

Because $Z^v Y^v$ is the 3×3 unit matrix and Z^v is an integral matrix, it follows that $Y^v \mathbf{n}$ can be written as the sum of a lattice vector of Σ and a vector in the d -dimensional subspace given by $Z^v \mathbf{r}_s = 0$. If Z^v contains components different from 1, the possibility arises that a fraction of a lattice vector of Σ should be added: the superspace lattice then is centered. Again, because all components of Z^v are integers, a basis for the d -D subspace $Z^v \mathbf{r}_s = 0$ can be chosen as d lattice vectors of Σ , which we denote by $\{\mathbf{e}_{s4}^v, \dots, \mathbf{e}_{s,3+d}^v\}$. The incommensurability in σ ensures that the components of \mathbf{e}_{si}^v in $Y^v \mathbf{n}$ are irrational. Then the periodicity of the density in superspace, determines that the higher dimensional equivalent of an atom in subsystem v , is given by the d -D subspace $Z^v \mathbf{r}_s = 0$.⁷

It is possible now, to choose three lattice vectors of Σ , such that all lattice points are part of the d -D subspace, or any of its translational equivalents. These vectors are denoted by $\{\mathbf{e}_{s1}^v, \mathbf{e}_{s2}^v, \mathbf{e}_{s3}^v\}$. Then, the point set is obtained, equivalent to Eq. (8) in Ref. 4, which represents the equivalent in higher-dimensional space of a point atom in physical space:

$$A_{ncj}^v = \left\{ \mathbf{r}_s \mid \mathbf{r}_s = \mathbf{x}_s^0 + \mathbf{c}_s + \sum_{i=1}^3 n_i \mathbf{e}_{si}^v + \sum_{i=4}^{3+d} x_i \mathbf{e}_{si}^v, n_i \in \mathbb{Z}, x_i \in \mathbb{R} \right\}, \quad (12)$$

where $\mathbf{x}_s^0 = Y^v \mathbf{x}^0$, and $\mathbf{c}_s = (c_{s1}, \dots, c_{s,3+d})$ represents the components of centering translations in $(3+d)$ -dimensional space, which in any case include the null vector. The components of \mathbf{r}_s with respect to the standard basis of Σ are obtained when the \mathbf{e}_{si}^v are expressed by their (integer) components with respect to $\{\mathbf{a}_{si}\}$. Note that Eq. (12) does not include the modulations.

Physical, three-dimensional space is a section through $(3+d)$ -dimensional space perpendicular to the d extra di-

mensions. Thus, each section can be represented by d numbers t_1, \dots, t_d through the relation

$$\begin{pmatrix} x_{s4} \\ \vdots \\ x_{s,3+d} \end{pmatrix} = \sigma \begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \end{pmatrix} + \begin{pmatrix} t_1 \\ \vdots \\ t_d \end{pmatrix}. \quad (13)$$

Equation (13) represents d linear equations between the $(3+d)$ variables x_{sj} . The form of the superspace atoms as d -dimensional subspaces then leads to exactly one solution for the section of an atom [Eq. (12)] with any given three-dimensional subspace. That is, the atom A_{ncj}^v gives rise to point atoms in physical space. Furthermore, the way of construction of A_{ncj}^v shows that application of Eq. (8) to this section gives indeed an atom of subsystem v .

In Fig. 1 we give an illustration for $d=1$ and two subsystems. The incommensurateness is defined by the matrix $\sigma = (\alpha, 0, 0)$, with $\alpha \simeq 0.6$ is irrational. The first subsystem is described by

$$Z^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}.$$

The 1D, continuous subspace then has basis vector $\mathbf{e}_{s4}^1 = \mathbf{a}_{s4}$; the three discrete directions can be chosen as $\mathbf{e}_{si}^1 = \mathbf{a}_{si}$, $i=1,2,3$. This implies that the atoms of the first subsystem are point sets parallel to \mathbf{a}_{s4} . The second subsystem is defined by

$$Z^2 = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}.$$

The discrete directions are $\mathbf{e}_{s1}^2 = \mathbf{a}_{s4}$, and $\mathbf{e}_{si}^2 = \mathbf{a}_{si}$, $i=2,3$. The continuous direction now is $\mathbf{e}_{s4}^2 = \mathbf{a}_{s1}$. This corre-

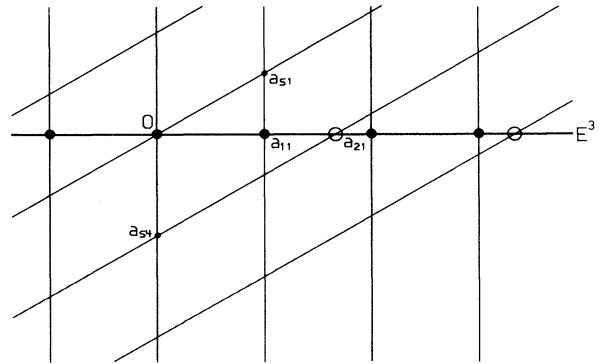


FIG. 1. Projection of the higher-dimensional density function along \mathbf{a}_{s2} and \mathbf{a}_{s3} , of a composite crystal with two subsystems and $d=1$. For each subsystem, there is one atom in the subsystem unit cell. \mathbf{a}_{11} and \mathbf{a}_{21} are parallel, but have incommensurate length ratio, they correspond to \mathbf{a}_{s1} and \mathbf{a}_{s4} , respectively. The intersection with physical space (E^3) is shown to consist of point atoms belonging to two incommensurate lattices: solid circles constitute subsystem 1, open circles define subsystem 2.

sponds to superspace atoms which are 1D point sets parallel to \mathbf{a}_{s1} (Fig. 1).

III. SPACE GROUP SYMMETRY IN SUPERSPACE

The higher-dimensional equivalent of the electron density function has translational symmetry according to the lattice Σ . In particular, the higher-dimensional equivalent of an atom was constructed [Eq. (12)], which distributed over the nodes of the lattice Σ leads to a periodic arrangement of atoms on Λ_v . This means that the symmetry of a composite crystal can be characterized by a $(3+d)$ -dimensional space group,⁴ here denoted by G_s .

A determination of the higher-dimensional space group can be done, in part, through analysis of the symmetry and systematic extinctions of the diffraction pattern. This is done analogous to the analysis for ordinary structures and modulated structures. Equation (5) gives the $(3+d)$ -dimensional indices of all subsystem reflections. Analysis of the point symmetry of the resulting reflection positions (h_1, \dots, h_{3+d}) , and of the systematic absences, then must lead to the rotational and translational parts of the elements of the higher-dimensional space group. An example of such a derivation is given in Sec. VII (see also Ref. 8).

IV. SUBSYSTEM SPACE GROUP SYMMETRY

The analysis was started with the proposition of an intergrowth compound made of the number of subsystems, each of which has three-dimensional translational symmetry. Thus, each subsystem has symmetry according to a three-dimensional space group, denoted as the subsystem space group G_v .⁴ This neglects the mutual interaction of the subsystems, which will be treated in the following sections. Here, we will show how the subsystem space group can be obtained from the higher-dimensional space group for the complete system.

Define $(R_s|\tau_s)$ to be the matrix representation on Σ of the superspace group operator $\{R_s|\tau_s\}$, for active transformation on the coordinates in $(3+d)$ -dimensional space.⁹ Analogously, $(R^v|\tau^v)$ and $\{R^v|\tau^v\}$ are defined on Λ_v in physical space.

Let $\mathbf{x}^v = (x_1^v, x_2^v, x_3^v)$ be the coordinates of an atom of Λ_v . Then $Y^v \mathbf{x}^v$ gives the corresponding coordinates in superspace [Eq. (11)], which belong to an atom A_{ncj}^v . Because $(R_s|\tau_s)$ is a symmetry operator, $R_s Y^v \mathbf{x}^v + \tau_s$ must be coordinates belonging to some atom $A_{n'c'j'}^v$ equivalent to A_{ncj}^v . There are only two possibilities. First, $v' = v$, then $A_{n'c'j'}^v = A_{ncj}^v$ belongs also to subsystem v , and $Z^v(R_s Y^v \mathbf{x}^v + \tau_s)$ is again an atom of Λ_v . Define R^v as the 3×3 matrix:

$$R^v = Z^v R_s Y^v \quad (14a)$$

and define τ^v as the vector in three-dimensional space:

$$\tau^v = Z^v \tau_s \quad (14b)$$

Then, we have shown that for $\mathbf{x}^v \in \Lambda_v$, $(R^v \mathbf{x}^v + \tau^v)$ is in Λ_v . Thus $(R^v|\tau^v)$ is the matrix representation of a sym-

metry operator $\{R^v|\tau^v\}$ of subsystem v , in physical space.

When $v' \neq v$, applying Z^v to $R_s Y^v$ is not meaningful. As $A_{n'c'j'}^v$ now belongs to another subsystem, R_s does not define some symmetry operator in subsystem v .

Thus, we find that each element of G_s gives rise to a three-dimensional space group element in all, in part, or in none of the subsystems. The collection of operators $(R^v|\tau^v)$ so obtained for subsystem v , gives the subsystem space group G_v .¹⁰

A more easy test for $(R^v|\tau^v)$ as calculated from Eq. (14), being an element of G_v is that $(R^v|\tau^v) \in G_v$ if and only if $\mathbf{n} = R^v \mathbf{n}$ is a triplet of integers for all triplets of integers \mathbf{n} .

V. THE COMPLETE STRUCTURE

The interaction between the different subsystems leads to a modulation of each subsystem, with modulation wave vectors determined by the periodicities of the other subsystems. There are $3+d$ periodicities present in the system [expressed by the basis of M^* (Sec. II)] so that each subsystem has a d -dimensional incommensurately modulated structure.

Disregarding systematic extinctions and nonmeasurable intensities, the diffraction of a single modulated subsystem can have intensity at all nodes of M^* ,

$$\mathbf{S} = \sum_{i=1}^{3+d} h_i \mathbf{a}_i^* \quad (15)$$

This means that the intensity at each diffraction position in principle has a contribution of all subsystems. However, the main reflections of one subsystem coincide with the, usually much weaker, satellites of the others, implying that the dissection of the diffraction pattern into parts arising from the different subsystems can often be made in good approximation.^{3,11}

Because the number of possible reflection positions [Eq. (4)] does not increase when the modulation is allowed, the same higher-dimensional space group applies to the complete structure as the one derived for the basic structure (Sec. III). It follows that the higher-dimensional equivalent of the density function still has to obey the symmetry of the higher-dimensional space group. However, the subsystems do not need to have translational symmetry.

For the basic structure, defined by the subsystems having translational symmetry, the higher-dimensional equivalent of the point atoms are d -dimensional subspaces [Eq. (12); Fig. 1]. Removing the condition of three-dimensional periodicity means that the $(3+d)$ -dimensional atoms are represented as a collection of wavy d -dimensional patterns.⁴ This wavyness can be a value of the points belonging to that atom different from Eq. (12) (displacive modulation), or it can mean a periodic variation of some other aspect of the atoms (atom number, orientation of magnetic moment). The periods of this multidimensional wave are those determined by the lattice Σ (Fig. 2).

For a given subsystem, let $\bar{\mathbf{r}}_i$ represent the basic structure position as defined in Eq. (12), and with components

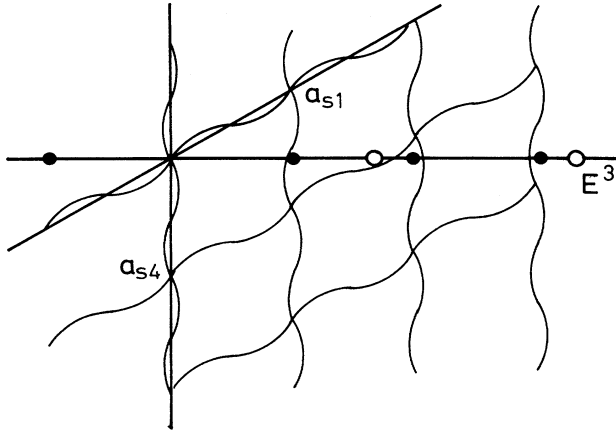


FIG. 2. The same projection as in Fig. 1, but for modulated subsystems. The atoms in superspace are now wavy lines, representing a displacive modulation in the subsystems, parallel to E^3 . The actual intersections of these superspace "atoms" with E^3 correspond to the modulated positions of the subsystem atoms.

$$\bar{x}_{sk} = x_{sk}^0 + c_{sk} + \sum_{i=1}^3 n_i e_{sik}^v + \sum_{i=4}^{3+d} x_i e_{sik}^v \quad (16)$$

for $k=1, \dots, 3+d$. x_i runs over all values in \mathbb{R} . e_{sik}^v are the $(3+d)$ integer coefficients of e_{si}^v with respect to the $\{\mathbf{a}_{sk}\}$ basis of Σ . A single atom is characterized by one set of numbers $n_i \in \mathbb{Z}$, $c_i \in \mathbb{Q}$, and $x_i^0 \in \mathbb{R}$, $i=1,2,3$. For a displacive modulation, the position, \mathbf{r}_s , of an atom in the real structure then is,

$$\mathbf{r}_{sk} = \bar{x}_{sk} + \mathbf{u}_{sk}(\bar{x}_{s1}, \dots, \bar{x}_{s,3+d}), \quad k=1, \dots, 3+d, \quad (17)$$

$\mathbf{u}_s(\bar{x}_{s1}, \dots, \bar{x}_{s,3+d})$ represents the modulation function, which is periodic with periodicity 1 in each of its arguments.

Because the effect of the modulation can only be seen through the displacement of the atoms in physical space, we require the modulation to be parallel to physical space. Then, restrictions on the functions $u_{si}(\bar{x}_{s1}, \dots, \bar{x}_{s,3+d})$ follow from [Eq. (13)]:

$$\begin{pmatrix} u_{s4}(\bar{x}_{sk}) \\ \vdots \\ u_{s,3+d}(\bar{x}_{sk}) \end{pmatrix} = \sigma \begin{pmatrix} u_{s1}(\bar{x}_{sk}) \\ u_{s2}(\bar{x}_{sk}) \\ u_{s3}(\bar{x}_{sk}) \end{pmatrix}. \quad (18)$$

Equations (16), (17), and (18) together define a d -dimensional collection of points which represents an atom of subsystem v in higher-dimensional space, and thus replaces Eq. (12). Of course, for a given structure the values of x_i^0 and the form of the functions $u_{si}(\bar{x}_{s1}, \dots, \bar{x}_{s,3+d})$ still have to be specified.

A description, which relates this collection of points more directly to the structure in physical space is obtained as follows. As inferred before, physical space is obtained by taking any section perpendicular to $(\mathbf{a}_{s4} \cdots \mathbf{a}_{s,3+d})$. Such a section is represented by d real

numbers (t_1, \dots, t_d) , defining d relations between the coordinates in superspace,

$$\begin{pmatrix} x_{s4} \\ \vdots \\ x_{s,3+d} \end{pmatrix} = \begin{pmatrix} t_1 \\ \vdots \\ t_d \end{pmatrix} + \sigma \begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \end{pmatrix}. \quad (13')$$

Substitution of Eqs. (17) and (18) gives

$$\begin{pmatrix} \bar{x}_{s4} \\ \vdots \\ \bar{x}_{s,3+d} \end{pmatrix} = \begin{pmatrix} t_1 \\ \vdots \\ t_d \end{pmatrix} + \sigma \begin{pmatrix} \bar{x}_{s1} \\ \bar{x}_{s2} \\ \bar{x}_{s3} \end{pmatrix}. \quad (19)$$

Substitution of Eq. (16) for \bar{x}_{sk} and expressing x_{sk}^0 in the three parameters x_i^0 [Eq. (11)], makes it possible to employ Eq. (19) to express the d parameters x_i in the parameters x_i^0 , n_i , and c_i , characterizing an atom, and the d parameters t_i . The collection of points in $(3+d)$ -dimensional space given by the continuous variation of the x_i , is equally well represented by allowing the t_i , $i=1, \dots, d$ to assume all real values.

Substitution of $\bar{x}_{sk}(\bar{x}_i^v; t_i)$ into the argument of the modulation functions [Eq. (17)] shows them to depend only on the subsystem basic structure positions, and a set of real numbers t_1, \dots, t_d , in a linear way. Each set of values of (t_1, \dots, t_d) selects one section representing physical space. The coordinates of the atoms in physical space are then obtained through Eq. (8) as

$$\begin{pmatrix} x_1^v \\ x_2^v \\ x_3^v \end{pmatrix} = \mathbf{Z}^v \begin{pmatrix} \bar{x}_{s1} + u_{s1}(\bar{x}_i^v; t_i) \\ \vdots \\ \bar{x}_{s,3+d} + u_{s,3+d}(\bar{x}_i^v; t_i) \end{pmatrix}. \quad (20)$$

For \bar{x}_{sk} given by Eq. (16) or Eq. (12), this indeed describes an incommensurately modulated structure for the v th subsystem.

VI. THE SUBSYSTEM SUPERSPACE GROUP

In the previous section we have described the composite crystal as a collection of d -dimensionally incommensurately modulated subsystems. It was argued that this gives the true structure of such a crystal, with the symmetry given by a single $(3+d)$ -dimensional space group. This higher-dimensional space group is the same as is necessary to describe the basic structure (Sec. III).

In Sec. IV a space group, G_v , was defined, which gives the symmetry of subsystem v . Each subsystem, in the basic structure, has its own space group, but all the subsystems space groups can be derived from the higher-dimensional space group in a unique way.

Completely analogous, for each subsystem we can define a subsystem superspace group, G_s^v , which gives the symmetry of its incommensurately modulated structure. They can also be derived from the higher-dimensional space group of the complete system, as we will do here.

The fundamental periodicities of subsystem ν are obtained from M^* through application of Z^ν [Eq. (1)]. The modulation of this subsystem is given by the periodicities in M^* which are missing in Λ_ν^* . So, we can define a set of modulation wave vectors \mathbf{q}^{vj} , $j=1, \dots, d$, by

$$\mathbf{q}^{vj} = \sum_{i=1}^{3+d} V_{ji}^\nu \mathbf{a}_i^* , \quad (21)$$

where V^ν is an integral $dx(3+d)$ matrix. Juxtaposition of Z^ν and V^ν gives a square matrix of order $(3+d)$,

$$W^\nu = \begin{bmatrix} Z^\nu \\ V^\nu \end{bmatrix} . \quad (22)$$

To ensure that the set (\mathbf{q}^{vj}) describes the modulation in subsystem ν , it is sufficient to require that W^ν is a non-singular matrix, i.e., its inverse exists.

Analogous to the definition of Σ^* [Eq. (6)] we can lift the set of points $(\mathbf{a}_{\nu 1}^*, \mathbf{a}_{\nu 2}^*, \mathbf{a}_{\nu 3}^*, \mathbf{q}^{\nu 1}, \dots, \mathbf{q}^{\nu d})$ to a reciprocal basis Σ_ν^* in $(3+d)$ -dimensional space. It follows from Eqs. (1), (6), (21), and (22) that Σ_ν^* can be obtained from Σ^* by a coordinate transformation defined by W^ν :

$$\mathbf{a}_{si}^{\nu*} = \sum_{j=1}^{3+d} W_{ij}^\nu \mathbf{a}_{sj}^* . \quad (23)$$

The structure and symmetry of the composite crystal are equivalently described on Σ as well as on Σ_ν . The elements of the higher-dimensional space group on basis $\Sigma_\nu(G_s^\nu)$ can be obtained from the elements of G_s by the similarity transform

$$R_s^\nu = W^\nu R_s (W^\nu)^{\text{inv}} , \quad (24a)$$

$$\tau_s^\nu = W^\nu \tau_s . \quad (24b)$$

The elements $(R_s^\nu | \tau_s^\nu)$ in G_s^ν which are in a $3-d$ reduced form image Λ_ν onto itself. Only these belong to the subsystem superspace group G_s^ν . As discussed before, there may be elements in G_s which do not fulfill this requirement for all or for part of the subsystems. It follows that the subsystem superspace group is a subgroup of the complete system higher-dimensional space group, when the latter is defined on the basis Σ_ν . Its elements are obtained from the elements of G_s defined with respect to Σ by Eq. (24), with the additional requirement that they are in a $3-d$ reduced form.

For the operators which map subsystem ν onto subsystem ν' matrices of the following form can be defined:

$$R_s^{\nu\nu'} = W^{\nu'} R_s (W^\nu)^{\text{inv}} , \quad (25a)$$

$$\tau_s^{\nu\nu'} = W^{\nu'} \tau_s . \quad (25b)$$

Application of such an operator to the coordinates of an atom with respect to Σ_ν , gives the coordinates with respect to $\Sigma_{\nu'}$, of a symmetry related atom of the other subsystem, ν' . Of course, the matrices $R_s^{\nu\nu'}$ do not constitute a symmetry operator of the intergrowth compound, or of any of its subsystems.

For completeness the matrix, σ^ν , expressing the modulation wave vectors (\mathbf{q}^{vj}) in Λ_ν^* is given:

$$\begin{bmatrix} \mathbf{q}^{\nu 1} \\ \vdots \\ \mathbf{q}^{\nu d} \end{bmatrix} = (V_3^\nu + V_d^\nu \sigma) (Z_3^\nu + Z_d^\nu \sigma)^{\text{inv}} \begin{bmatrix} \mathbf{a}_{\nu 1}^* \\ \mathbf{a}_{\nu 2}^* \\ \mathbf{a}_{\nu 3}^* \end{bmatrix} , \quad (26)$$

where $V^\nu = (V_3^\nu V_d^\nu)$.

Each subsystem is an incommensurately modulated structure, with a modulation of dimension d . Therefore, the $(3+d)$ -dimensional space group, G_s^ν , describing its symmetry, must be one of the $(3+d)$ -dimensional superspace groups as defined by Janner, Janssen, and De Wolff.⁵ Characteristic for the subclass of superspace groups is that the first three coordinates are not mixed with the d extra coordinates by any element of the superspace group. For the intergrowth compounds each subsystem has at least one periodicity in Λ_ν^* which is incommensurate to the lattices $\Lambda_{\nu'}^*$, of all other subsystems ν' . It follows that there can be at most one subsystem which has Λ_ν^* equal to $\{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*\}$. For this subsystem the subsystem superspace group is a subgroup of G_s . The basic periodicities, $\Lambda_{\nu'}^*$, of all other subsystems contain at least one of the $\mathbf{a}_j^* \in M^*$, with $j=4, \dots, 3+d$. The corresponding operator W^ν is one that mixes the extra coordinates with the first three. Thus it is an operator not allowed for superspace groups. It follows that all other subsystem superspace groups are a subgroup of a higher-dimensional space group which is equivalent to G_s as a higher-dimensional space group, but not necessarily as a superspace group. This opens the possibility that two subsystem superspace groups are equivalent as higher-dimensional space groups, but not as superspace groups.

VII. APPLICATION TO $\text{Hg}_{3-\delta}\text{AsF}_6$

At higher temperature ($T > T_c = 120$ K) $\text{Hg}_{3-\delta}\text{AsF}_6$ ($\delta \approx 0.18$) crystallizes in the tetragonal space group $G_{\text{HT}} = I4_1/amd$.^{12,13} The structure is built of a lattice of AsF_6 octahedra, in which channels parallel to $[100]$ and $[010]$ are occupied by mercury atoms (Fig. 3). Long-range order within the individual chains exists, expressed by the interatomic Hg-Hg distance of 2.64 Å. Correlation between the positions along the chain of the mercury atoms in different chains is absent. The interatomic Hg-Hg distance is incommensurate with the periodicity of the host lattice ($a = 7.534$ Å). Slightly less than three Hg fit along the unit cell axis. This incommensurability between the mercury subsystems and the AsF_6 subsystem is expressed by the parameter δ in $\text{Hg}_{3-\delta}\text{AsF}_6$.

Below T_c , the structure becomes completely ordered. New reflections in the diffraction pattern appear at positions $(h(3 \pm \delta), k \pm h\delta, l)$ and $(h \pm k\delta, k(3 \pm \delta), l)$, with $\delta = 0.21$. In each case only those with $h+k+l = \text{even}$ are observed.⁶ On basis of the experimental observation of an additional extinction: $(3-\delta, 3-\delta, 0)$ is absent, Pouget *et al.*⁶ were able to devise a model for the ordering of the Hg chains with respect to each other. The superspace group symmetry for the structure was given by Janner and Janssen,⁴ and reviewed by Buiting *et al.*¹⁴

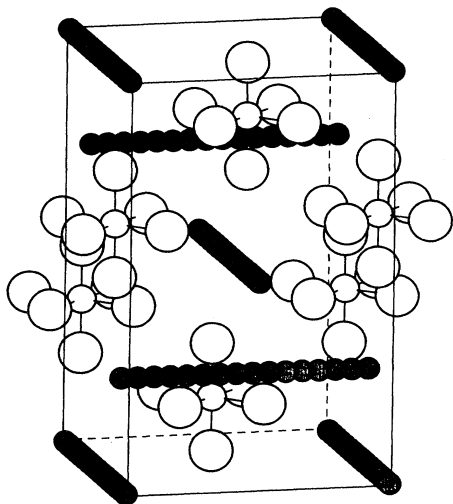


FIG. 3. Perspective view of one unit cell of the structure of $\text{Hg}_{3-\delta}\text{AsF}_6$. Large and small circles denote As and F atoms, respectively. The positions of the Hg atoms in the AsF_6 sublattice are given schematically by the small solid circles. The two distinct channels filled by Hg are clearly shown.

Here, the superspace group symmetry will be derived, starting from the observed extinction conditions rather than from the structure model proposed by Pouget *et al.*⁶ For this analysis the extinctions in the neutron diffraction spectrum as reported by Pouget *et al.*⁶ will be used.

A. Superspace and subsystem symmetry

The ordering transition at T_c is observed in the diffraction pattern by the occurrence of additional reflection positions, accompanied by a lowering of the diffraction symmetry to orthorhombic. The mirror planes retained at low temperature are parallel to the high temperature diagonal d -glides and the a -glide. Pouget *et al.*⁶ show that the diffraction pattern can be divided in two sets, arising from two different domains. For a single domain the additional diffraction positions are $(h(3-\delta), k-h\delta, 1)_I$ and $(h-k\delta, k(3-\delta), 1)_I$, where the indexing with respect to the reciprocal of the I -centered tetragonal unit cell is indicated by a subscript I . All reflections with $h+k+l=\text{odd}$ were reported to be extinct.⁶

Integer indices for all reflections can be obtained when three reciprocal unit cells are used, indicated by $\Lambda_v^* = \{\mathbf{a}_{v1}^*, \mathbf{a}_{v2}^*, \mathbf{a}_{v3}^*\}$ (see Sec. II). The \mathbf{a}_{v3}^* axes correspond to the \mathbf{c}^* axis of the high-temperature phase, with $\mathbf{a}_{13}^* = \mathbf{a}_{23}^* = -\mathbf{a}_{33}^* = \mathbf{c}^*$. The relation between the other axes is given in Fig. 4. It was shown that Λ_1 corresponds to the ordering of the AsF_6 octahedra, which then constitute subsystem 1. The second subsystem comprises the mercury atoms in the channels parallel to $[1\ 0\ 0]$. They are the origin of the reflections at Λ_2^* . The mercury atoms in the channels parallel to $[0\ 1\ 0]$ give rise to the reflections at Λ_3^* , and thus form the third subsystem.

The subsystem reciprocal lattices can be written as integral linear combinations of only four vectors,⁴ implying

$d=1$. The set $M^* = \{\mathbf{a}_1^*, \dots, \mathbf{a}_{3+d}^*\}$ can be defined by $\mathbf{a}_i^* = \mathbf{a}_{1i}^*$, for $i=1,2,3$, and $\mathbf{a}_4^* = -2\delta\mathbf{a}_1^*$. Then the (3×4) matrices Z^ν are [Eq. (1)]

$$\begin{aligned} Z^1 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \\ Z^2 &= \begin{pmatrix} 3 & \bar{3} & 0 & 1 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \\ Z^3 &= \begin{pmatrix} 3 & 3 & 0 & 1 \\ 1 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \end{pmatrix}. \end{aligned} \quad (27)$$

The σ matrix is 1×3 , and immediately follows as [Eq. (2)]

$$\sigma = (-2\delta, 0, 0). \quad (28)$$

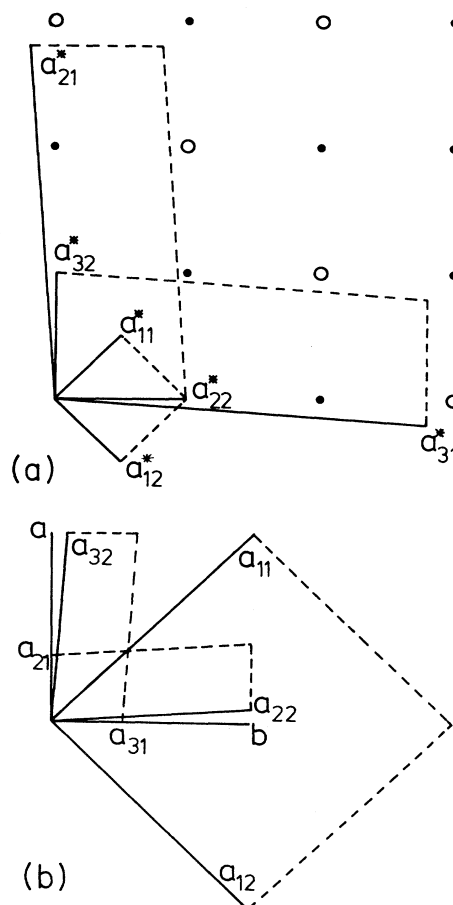


FIG. 4. Subsystem unit cells compared with the high-temperature tetragonal unit cell. The plane perpendicular \mathbf{a}_{v3}^* is given. (a) gives the reciprocal lattice vectors. \mathbf{a}_{vi}^* , $i=1,2$, denote the basis vectors of Λ_v^* ; $\mathbf{a}^* = \mathbf{a}_{32}^*$ and $\mathbf{b}^* = \mathbf{a}_{22}^*$ correspond to high-temperature I -centered unit cell. Solid and open circles represent the extinct and present Bragg reflections of the I -centered cell. (b) gives the lattice vectors for the corresponding direct unit cells.

Note that here we use centered unit cells, instead of referring all vectors to a primitive lattice, as was done by Janner and Janssen.⁴

The indices with respect to the subsystem reciprocal unit cells can be obtained from the Pouget-indexing by $(h_{11}, h_{12}, h_{13}) = (h+k, k-h, l)_1$ for the $(h, k, l)_I$ reflections; $(h_{21}, h_{22}, h_{23}) = (h, k, l)_2$ for the $(h(3-\delta), k-h\delta, l)_I$ reflections; and $(h_{31}, h_{32}, h_{33}) = (k, h, -l)_3$ for the $(h-k\delta, k(3-\delta), l)_I$ reflections. Indexing with respect to the subsystem reciprocal lattices Λ_v^* is indicated by an additional subscript $v=1,2,3$. Transforming the extinction condition $h+k+l=\text{odd}$ is absent accordingly, shows that Λ_1 is described by an F -centered lattice basis, whereas Λ_2 and Λ_3 have I -centered settings.

The indexing on the superspace reciprocal lattice Σ^* is identical to the indexing on M^* , and thus can be obtained from Eq. (5). The main reflections of each subsystem constitute a 3D sublattice of Σ^* , which is expressed by an additional condition on the indices. The result for the (h_1, h_2, h_3, h_4) reflection is

$$\begin{aligned} \nu=1: & (h_{11}, h_{12}, h_{13}, h_4) \text{ with } h_4=0, \\ \nu=2: & (3h_{21}+h_{22}, h_{22}-3h_{12}, h_{23}, h_{21}) \\ & \text{with } h_1-h_2-6h_4=0, \quad (29) \\ \nu=3: & (3h_{31}+h_{32}, 3h_{31}-h_{32}, -h_{33}, h_{31}) \\ & \text{with } h_1+h_2-6h_4=0. \end{aligned}$$

There are two kinds of extinction condition conditions reported by Pouget *et al.*⁶ for the low temperature phase. One pertains to the centering of the sublattices, and is already referred to above. The second was stated as $(3(3-\delta), 3(3-\delta), 0)_I$ is absent, while $(6(3-\delta), 6(3-\delta), 0)_I$ is present. The only structural effect reported for the phase transition was an ordering of the Hg atoms. Therefore, it is expected that the high-temperature symmetry is retained as much as possible in the low temperature structure. To be able to make the superspace group determination, we assume the extinctions of the high-temperature space group, $I4_1/amd$, which point toward $Fddd$ symmetry for Λ_1 to be retained at low temperature. Performing the two steps of transformation of the indices then gives extinction conditions valid for either one of the subsets defined in Eq. (29).

The conditions for the three subsets can be combined, in order to obtain extinction conditions for the complete 4D diffraction pattern. It should be noted that such a generalization still has to be checked against satellite reflections, whose measurement might be possible in the future. For the centering of the 4D lattice we obtain

$$(h_1, h_2, h_3, h_4): \\ h_1+h_2=2n; h_1+h_3=2n; h_2+h_3=2n. \quad (30)$$

Translational components for the three mirror planes follow from

$$(h_1, h_2, 0, h_4): h_1=2n; h_2=2n; h_1+h_2+2h_4=4n, \quad (31)$$

$$(h_1, 0, h_3, h_4): h_1=2n; h_3=2n; h_1+h_3=4n, \quad (32)$$

$$(0, h_2, h_3, 0): h_2=2n; h_3=2n; h_2+h_3=4n. \quad (33)$$

In each case n is an arbitrary integer. To derive Eq. (32), it was necessary to extend the condition for the $(3(3-\delta), 3(3-\delta), 0)$ reflection to similar reflections with nonzero l . The validity still has to be checked against part of the diffraction pattern not reported by Pouget *et al.*⁶

The superspace group in accordance with the extinctions Eqs. (30)–(33) and with the orthogonal mmm symmetry is $G_2 = P:FDDD:\bar{1}1s(-2\delta, 0, 0)$, the same as found by Janner and Janssen.⁴ To be compatible with the high-temperature space group G_{HT} , a nonstandard setting is used, given by the symmetry operators in Table I.

It is easy to check that all elements of G_s leave subsystem 1 invariant, while the subgroup generated by the translations and by $(m_x \bar{1} | 0, \frac{1}{4}, \frac{3}{4}, \frac{1}{2})$ and $(m_y 1 | \frac{3}{4}, 0, \frac{1}{4}, 0)$ maps subsystem 2 onto 3, and vice versa.⁴ The subsystem space groups can then be obtained by application of Eq. (14) to the appropriate symmetry operators (Table I); the result is given in Table II. With an appropriate unit cell transformation, it can be shown that G_2 and G_3 are equivalent to the $A2/m$ and $B2/m$, as given by Janner and Janssen.⁴ It is interesting to note that G_2 and G_3 are equivalent, but that they are obtained in a different setting: the position of the mirror planes is at $z=\frac{1}{4}$ and $z=0$, respectively. This expresses the fact that these two subsystems have atoms only at $z=\frac{1}{4}$ and $z=0$, respectively.

To derive the subsystem superspace groups, the modulation wave vectors in each subsystem need to be defined, i.e., the matrix V^v has to be chosen [Eqs. (21) and (22)]. Appropriate choices for the modulation wave vector \mathbf{q}^v are a primitive vector taken from the common reciprocal lattice points of the other two subsystems, but not belonging to Λ_v^* . Any primitive reciprocal lattice vector of Λ_v^* may be added. The following choice for the matrices V^v and W^v is a possibility:

$$\begin{aligned} W^1 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \\ W^2 &= \begin{pmatrix} 3 & \bar{3} & 0 & 1 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 2 & 0 & 0 \end{pmatrix}, \\ W^3 &= \begin{pmatrix} 3 & 3 & 0 & 1 \\ 1 & \bar{1} & 0 & 0 \\ 0 & 0 & \bar{1} & 0 \\ 0 & 2 & 0 & 0 \end{pmatrix}. \end{aligned} \quad (34)$$

Now, Eq. (24) gives the elements of the subsystem superspace groups. For subsystem 1, $G_s^1 = P:FDDD:\bar{1}1s(-2\delta, 0, 0)$ is identical to G_s , as W^1 is the

TABLE I. Symmetry operators of the superspace group of $\text{Hg}_{3-\delta}\text{AsF}_6$.

$(E \frac{1}{2}, \frac{1}{2}, 0, 0)$	$(E \frac{1}{2}, 0, \frac{1}{2}, 0)$
$(E 0, \frac{1}{2}, \frac{1}{2}, 0)$	
$(E n_1, n_2, n_3, n_4)$	$(i\bar{1} 0, 0, 0, 0)$
$(2^x 1 0, \frac{3}{4}, \frac{3}{4}, \frac{1}{2})$	$(m_x \bar{1} 0, \frac{3}{4}, \frac{3}{4}, \frac{1}{2})$
$(2^y \bar{1} \frac{3}{4}, 0, \frac{3}{4}, 0)$	$(m_y 1 \frac{3}{4}, 0, \frac{3}{4}, 0)$
$(2^z \bar{1} \frac{1}{4}, \frac{1}{4}, 0, \frac{1}{2})$	$(m_z 1 \frac{1}{4}, \frac{1}{4}, 0, \frac{1}{2})$

unit matrix. For the other two subsystems, $G_s^2 = P: I2_1/m: \bar{1}s(\alpha, 2-3\alpha, 0)$ and $G_s^3 = P: I2/m: \bar{1}s(\alpha, 3\alpha-2, 0)$ are obtained (Table III). The subsystem modulation wave vectors are defined by the subsystem σ matrix σ^ν . The latter are obtained as

$$\begin{aligned}\sigma^1 &= (-2\delta, 0, 0), \\ \sigma^2 &= (\alpha, 2-3\alpha, 0), \\ \sigma^3 &= (\alpha, 3\alpha-2, 0),\end{aligned}\quad (35)$$

with $\alpha = 1/(3-\delta)$.

B. The structure in superspace

The one-dimensional point sets representing the superspace atoms for the basic structure [Eq. (12)] follow from $Z^\nu \mathbf{r}_s = 0$, for each subsystem, respectively. For the first subsystem, it immediately follows that the superspace atoms are lines parallel to $\mathbf{e}_{s4}^1 = \mathbf{a}_{s4}$. The discrete directions \mathbf{e}_{si}^1 can be chosen as \mathbf{a}_{si} , for $i=1,2,3$, respectively. For the second subsystem we find lines parallel to $\mathbf{e}_{s4}^2 = (\bar{1}, 1, 0, 6)$ (the coordinates refer to the standard basis of Σ [Eq. (7)]). The same set of vectors as for subsystem 1 can be used for the discrete directions. However, for

TABLE II. The subsystem space groups for the three subsystems of $\text{Hg}_{3-\delta}\text{AsF}_6$.

$G_1 = Fddd$	
$(E \frac{1}{2}, \frac{1}{2}, 0)$	$(E \frac{1}{2}, 0, \frac{1}{2})$
$(E 0, \frac{1}{2}, \frac{1}{2})$	
$(E n_1, n_2, n_3)$	$(i 0, 0, 0)$
$(2^x 0, \frac{3}{4}, \frac{3}{4})$	$(m_x 0, \frac{3}{4}, \frac{3}{4})$
$(2^y \frac{3}{4}, 0, \frac{3}{4})$	$(m_y \frac{3}{4}, 0, \frac{3}{4})$
$(2^z \frac{1}{4}, \frac{1}{4}, 0)$	$(m_z \frac{1}{4}, \frac{1}{4}, 0)$
$G_2 = I2_1/m$	$G_3 = I2/m$
$(E n_1, n_2, n_3)$	$(E n_1, n_2, n_3)$
$(E \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	$(E \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$
$(i 0, 0, 0)$	$(i 0, 0, 0)$
$(2^z 0, 0, 0.5)$	$(2^z 0, 0, 0)$
$(m_z 0, 0, 0.5)$	$(m_z 0, 0, 0)$

TABLE III. Subsystem superspace groups for $\text{Hg}_{3-\delta}\text{AsF}_6$. Note that G_s^1 is identical to G_s (see Table I). $\alpha = 1/(3-\delta)$.

$G_s^2 = P: I2_1/m: \bar{1}s(\alpha, 2-3\alpha, 0)$		$G_s^3 = P: I2/m: \bar{1}s(\alpha, 3\alpha-2, 0)$	
$(E n_1, n_2, n_3, n_4)$	$(E n_1, n_2, n_3, n_4)$	$(E n_1, n_2, n_3, n_4)$	$(E n_1, n_2, n_3, n_4)$
$(E \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0)$	$(E \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0)$	$(E \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0)$	$(E \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0)$
$(i\bar{1} 0, 0, 0, 0)$	$(i\bar{1} 0, 0, 0, 0)$	$(i\bar{1} 0, 0, 0, 0)$	$(i\bar{1} 0, 0, 0, 0)$
$(2^z \bar{1} 0, 0, 0.5, 0.5)$	$(2^z \bar{1} 0, 0, 0.5, 0.5)$	$(2^z \bar{1} 0, 0, 0.5, 0.5)$	$(2^z \bar{1} 0, 0, 0.5, 0.5)$
$(m_z 1 0, 0, 0.5, 0.5)$	$(m_z 1 0, 0, 0.5, 0.5)$	$(m_z 1 0, 0, 0.5, 0.5)$	$(m_z 1 0, 0, 0.5, 0.5)$

$\mathbf{e}_{s1}^2 = \mathbf{a}_{s4}$, $\mathbf{e}_{s2}^2 = \mathbf{a}_{s2} + 3\mathbf{a}_{s4}$, and $\mathbf{e}_{s3}^2 = \mathbf{a}_{s3}$, a lattice translation $\sum_{i=1}^3 n_i \mathbf{e}_{si}^2$ corresponds to a lattice translation $(n_1, n_2, n_3)_2$ with respect to Λ_2 . The atoms of the third subsystem are formed by lines parallel to $\mathbf{e}_{s4}^3 = (1, 1, 0, \bar{6})$. Now, $\mathbf{e}_{s1}^3 = \mathbf{a}_{s4}$, $\mathbf{e}_{s2}^3 = -\mathbf{a}_{s2} + 3\mathbf{a}_{s4}$, and $\mathbf{e}_{s3}^3 = -\mathbf{a}_{s3}$ is a possible choice. Again, the lattice translation $\sum_{i=1}^3 n_i \mathbf{e}_{si}^3$ corresponds to a lattice translation $(n_1, n_2, n_3)_3$ with respect to Λ_3 .

The coordinates for Hg were given with respect to the high-temperature unit cell as $(x', \frac{3}{4}, \frac{1}{4})$ for chains parallel to $[1, 0, 0]$ (subsystem 2), and as $(0, y', 0)$ for subsystem 3. In the ordered phase, the values of x' and y' differ from one unit cell to the other. It is not difficult to deduce from Fig. 4 and Eq. (27), that the coordinates with respect to Λ_2 then are $(x, \frac{3}{4}, \frac{1}{4})_2$. The size of the subsystem unit cell is such that it should contain one mercury atom in each of the two chains per cell. Application of the elements of G_2 (Table II) shows that $(x, \frac{3}{4}, \frac{1}{4})$ is invariant under m_z , but that other operators map this position onto $(\frac{1}{2}-x, \frac{3}{4}, \frac{1}{4})$ and $(\frac{1}{2}\pm x, \frac{1}{4}, \frac{3}{4})$. The latter two positions belong to the other chain. The first position gives a second atom in the unit cell for the first chain. This would be possible if we assume a disordered, partial occupation of both positions. However, it is more likely that a single position is fully occupied, which is only possible for $x = \frac{1}{4}$.

Thus, it is found that the chains parallel to $[1\ 0\ 0]$ are described by a single Hg atom at the two-fold special position $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})_2$ of G_2 , where the coordinates refer to the subsystem lattice Λ_2 .

Now, it is interesting to consider the operators in G_s which map one subsystem onto another. For example, $(2^x 1| 0, \frac{1}{4}, \frac{3}{4}, \frac{1}{2})$ maps subsystem 2 onto subsystem 3. The coordinates of an atom of $\nu=3$ with respect to Λ_3 are obtained from the coordinates of an atom of $\nu=2$ with respect to Λ_2 , by application of the following matrix [Eq. (25)]:

$$R_s^{23} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & \bar{1} \end{pmatrix}, \quad \tau_s^3 = (\frac{1}{4}, \frac{3}{4}, \frac{1}{4}, \frac{1}{2}). \quad (36)$$

For the position $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})$ of $\text{Hg}(\nu=2)$, the coordinates of $\text{Hg}(\nu=3)$ are obtained as $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, which is indeed in one

of the chains parallel to $[0\ 1\ 0]_I$.

In summary, combination of the knowledge of the high temperature structure with the symmetry of the low temperature phase, leads to the conclusion that the Hg atoms in the second subsystem occupy the twofold position $(\frac{1}{4}, \frac{3}{4}, \frac{1}{4})_2; (\frac{3}{4}, \frac{1}{4}, \frac{3}{4})_2$. The Hg atoms of the third subsystem have coordinates $(0, 0, 0)_3$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})_3$. This model for the positions of the mercury atoms is the same as the one proposed by Pouget *et al.* However, the *ad hoc* derivation by Pouget *et al.*⁶ is replaced by a general symmetry analysis of the diffraction pattern. The symmetry analysis given here shows that there must be an additional extinction condition for the reflections as compared to the conditions reported by Pouget *et al.*⁶

C. Modulations

In this paper it is proposed that, in principle, each subsystem is modulated with modulation wave vectors equal to the periodicities in M^* , which are missing in Λ_v^* . For $\text{Hg}_{3-8}\text{AsF}_6$ this means that each subsystem should have a one-dimensionally modulated structure. The corresponding modulation wave vectors are defined in Eqs. (34) and (35). Satellite reflections, which would arise because of these modulations, have never been reported.

Still, there are some experimental indications that the mercury atoms should have values different from the fixed basic structure positions. More precisely, different Hg along one chain should have different deviations from their fixed basic structure z position.^{13,15} Such a variation in the mercury position can be explained by assuming a displacive modulation for the Hg atoms.

For the special position as occupied by Hg, the symmetry restrictions are as follows: $u_x = u_y = 0$ for the first (odd) harmonics, and $u_z = 0$ for the second (even) harmonics. Assuming the first harmonics to be the most important ones, the modulation is obtained as mainly a z displacement, in accordance with the structure determination by Schultz *et al.*¹³

The occurrence of another type of additional reflections, the so-called 2δ satellites, was reported by Pouget *et al.*⁶ These were observed at the positions $(h \pm 2\delta, 0, 1)_I$. They cannot be indexed on the basis of the four reciprocal vectors defined previously [Eq. (27)]. An additional modulation wave vector is needed, which would then result in a five-dimensional superspace group.⁴ An alternative interpretation of these reflections is obtained when the other domain is taken into account. The second domain gives reflections of the third subsystem at $(h + k\delta, k(3 - \delta), l)_I$, as compared with the first domain with reflections at $(h - k\delta, k(3 - \delta), l)_I$. Subtracting these reflections precisely gives the 2δ satellite. The presence of an ordered array of domains, with the two different domains alternating, would give the 2δ satellites as a result of diffraction against the ordered array of domain walls. Then, the structure of a single domain can still be described by the four-dimensional superspace group. The complete structure is too complicated for simply assigning a 5D superspace group.

VIII. DISCUSSION

The basic structure of an intergrowth compound can be described as a collection of subsystems, each one with a translational symmetric structure. In this approximation, the symmetry of each subsystem is given by a three-dimensional space group, G_v . This description has been successfully applied to the determination of the structure of inorganic misfit layer structures by Wieggers and co-workers.^{3,11}

Problem in such an analysis is that the subsystems are considered independently, and that there are apparently no rules for the combinations of subsystem space groups which are possible. In this paper we have shown that the higher-dimensional space group uniquely defines the subsystem space groups. It immediately follows which combinations of G_v are allowed. Furthermore, the higher-dimensional space group may contain elements which relate one subsystem to another, thus giving symmetry of the intergrowth compound which is not described by the collection of subsystem space groups (Secs. III and IV). Application of this higher-dimensional space group analysis to particular inorganic misfit layer structures made it possible to rule out certain subsystem symmetries which could not be discarded on basis of an independent analysis of the diffraction of the different subsystems.^{8,11}

The real structure can be described as a family of interpenetrating incommensurately modulated structures. The basic periods of one subsystem occur as modulation periods of others. For a complete mutual interaction, the modulation in each subsystem is of dimension d , when there are $(3+d)$ elements in the basis of M^* . Again, the subsystems can be considered independently, each one with its own symmetry according to the $(3+d)$ -dimensional subsystem superspace group G_s^v . As for the subsystem space groups, the complete system $(3+d)$ -dimensional space group is needed to obtain the relation between the G_s^v , as well as that the higher-dimensional space group may contain elements which relate one subsystem to another.

Apart from the relation between subsystem symmetries, the higher-dimensional space group of the complete system also defines relations of more direct importance for the structure. As we know from the superspace group analysis of incommensurately modulated crystals, the structure is independent of the choice of the phase of the modulation function. When the N subsystems are considered independently, we are free in the choice of Nd phases. However, when the subsystems occur together in one intergrowth compound, the choice of the d phases in one subsystem will fix the phases in all others. There are only d phases free to choose. It is easy to show that the structure is independent of the relative orientation of the sublattices along a mutual incommensurate direction. However, the specific form of the relation between the phases does depend on this relative orientation. It is the complete system higher-dimensional space group which gives the relations between the initial phases of the modulation in the different subsystems, and their dependence on the relative orientation of the sublattices. In this way, the higher-dimensional space group of the complete system leads to a reduction of the number of parameters

needed to describe the structure, as compared to the description as independent subsystems.

Finally, we like to point out that it is only G_s which gives the symmetry of the intergrowth compound. The correctness of each analysis making use of the subsystem symmetries, has to be shown by making use of the relation between G_s , G_s^v , and G_v , as defined in this paper.

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APPENDIX: GLOSSARY OF SYMBOLS

$\mathbf{a}_{vi}, \mathbf{a}_{vi}^*$	Basis vector (and reciprocal) of the lattice Λ_v (Λ_v^*) of subsystem v ($i=1,2,3$).
\mathbf{a}_k^*	Element of the set M^* ($k=1, \dots, 3+d$).
$\mathbf{a}_{sk}, \mathbf{a}_{sk}^*$	Basis vector (and reciprocal) of the superspace lattice Σ (Σ^*) ($k=1, \dots, 3+d$).
$\mathbf{a}_{sk}^v, \mathbf{a}_{sk}^{v*}$	Basis vector (and reciprocal) of the subsystem superspace lattice Σ_v (Σ_v^*) ($k=1, \dots, 3+d$).
$\mathbf{b}_j, \mathbf{b}_j^*$	Vector (and reciprocal) perpendicular to physical space ($j=1, \dots, d$).
\mathbf{e}_{sk}^v	Lattice vectors of Σ ($k=1, \dots, 3+d$).
h_{vi}	Reflection indices with respect to Λ_v^* .
h_i	Reflection indices with respect to M^* and Σ_v^* .
\mathbf{q}^{vj}	Modulation wave vector of subsystem v ($j=1, \dots, d$).
G_s	Superspace group for the intergrowth compound.
G_s^v	Subsystem superspace group.
G_v	Subsystem space group.
M^*	Set of $(3+d)$ reciprocal vectors in physical space.
R_s	Rotational part of a symmetry operator in superspace, and its $(3+d) \times (3+d)$ -matrix representation with respect to Σ^* .
R_s^v	$(3+d) \times (3+d)$ -matrix representation with respect to Σ_v^* of the rotational part of a symmetry operator in superspace.
R^v	3×3 -matrix representation with respect to Λ_v^* of the rotational part of a symmetry operator for subsystem v .
\mathbf{S}	Diffraction wave vector in physical space.
\mathbf{S}^v	Diffraction wave vector for subsystem v .
V^v	$d \times (3+d)$ -matrix defining \mathbf{q}^{vj} in terms of the elements of M^* .
V_3^v	Leftmost $d \times 3$ part of V^v .
V_d^v	Rightmost $d \times d$ part of V^v .
W^v	$(3+d) \times (3+d)$ matrix relating the subsystem periodicities with M^* .
Y^v	$(3+d) \times 3$ matrix, the pseudoinverse of Z^v .
Z^v	$3 \times (3+d)$ matrix, defining Λ_v^* in terms of M^* .
Z_3^v	Leftmost 3×3 part of Z^v .
Z_d^v	Rightmost $3 \times d$ part of Z^v .
σ	$d \times 3$ matrix relating the last d elements of M^* to the first three.
σ^v	$d \times 3$ matrix giving the elements of \mathbf{q}^{vj} in terms of Λ_v^* .
ν	Subscript or superscript enumerating the subsystems.
τ_s	$(3+d)$ -dimensional vector defining the translational part of the symmetry operator in superspace.
τ_s^v	$(3+d)$ -dimensional vector defined by $W^v \tau_s$.
τ^v	Three-dimensional vector defined by $Z^v \tau_s$.
Σ	Lattice in $(3+d)$ -dimensional space, with basis vectors \mathbf{a}_{sk} .
Σ_v	Lattice in $(3+d)$ -dimensional space, with subsystem basis.
Σ^*	Reciprocal lattice in $(3+d)$ -dimensional space, with basis vectors \mathbf{a}_{sk}^* .
Σ_v^*	Reciprocal lattice in $(3+d)$ -dimensional space, defined as $W^v \Sigma^*$.
Λ_v	Lattice, defining the average periodicity of subsystem v .
Λ_v^*	Reciprocal lattice for subsystem v .

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