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Symmetry of Incommensurate Crystal Phases. II. Incommensurate Basic Structure

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Abstract

In this second part [part I: *Acta Cryst.* (1980), A**36**, 399–408] the superspace-group approach is formulated for a class of crystals (called composite crystals) which involve a basic structure composed of subsystems, each one having three-dimensional space-group symmetry, but being mutually incommensurate. By taking into account the interaction among these subsystems, or other second-order effects, one is led to the actual structure, which very often is modulated, and in any case incommensurate. Neither the basic structure nor the actual one has a three-dimensional space-group symmetry but both allow a superspace-group characterization of their symmetry properties. The aim of the present paper is to show how these concepts apply in practice. Accordingly, two composite crystals, extensively studied in the literature, are considered from the present point of view: the organic compound $(TTF)_7I_{5-x}$, *i.e.* $C_{42}H_{28}S_{28}.I_{5-x}$, and the polymercury cation compound $Hg_{3-\delta}AsF_6$. The regularities found in these two compounds are interpreted and fit naturally with the corresponding superspace-symmetry groups.

1. Introduction

In a previous paper (Janner & Janssen, 1980), hereafter denoted by I, incommensurability was considered as existing between a so-called basic structure (which does not necessarily exist as such) with space-group symmetry and a periodic deformation (modulation) of this basic structure. In the present paper we discuss the case where it is not possible to define a basic structure with three-dimensional space-group symmetry. This happens, for example, when a crystal consists of several interpenetrating subsystems, each of which has the structure of a, possibly modulated, crystal, the basic structures of the different subsystems being mutually incommensurate. The whole crystal can then no longer be seen as arising from a modulation of a basic structure with space-group symmetry.

In the following we shall first analyze the symmetry of the basic structure (§2), which is a $(3 + d_0)$-dimensional superspace group and express the relation of superspace-group elements with those of the space groups of the subsystems. We then consider in §3 the symmetry of the modulated crystal, which is again a superspace group [now in $(3 + d)$ dimensions]. Finally, in §§4 and 5 the results obtained are applied to two examples: $(TTF)_7I_{5-x}$ and $Hg_{3-\delta}AsF_6$.

2. Symmetry of the basic structure of the composite crystal

Suppose that the basic structure consists of N subsystems labelled by ν. The positions of the atoms in the νth subsystem are

$$\mathbf{r}_0(\mathbf{n}_\nu, \nu j) = \mathbf{n}_\nu + \mathbf{r}_{\nu j}, \qquad (1)$$

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where $\mathbf{n}_\nu$ belongs to a lattice Λ_ν and $\mathbf{r}_{\nu j}$ is the position of the jth atom in the unit cell of this lattice. The basis of Λ_ν is denoted by $\mathbf{a}_{\nu 1}$, $\mathbf{a}_{\nu 2}$, $\mathbf{a}_{\nu 3}$ and its reciprocal by $\mathbf{a}^*_{\nu 1}$, $\mathbf{a}^*_{\nu 2}$, $\mathbf{a}^*_{\nu 3}$. Now choose a minimal set $\mathbf{a}^*_1, \ldots, \mathbf{a}^*_{3+d_0}$ ($3 < 3 + d_0 \leq 3N$) such that every $\mathbf{a}^*_{\nu i}$ may be expressed as

$$\mathbf{a}^*_{\nu i} = \sum_{k=1}^{3+d_0} Z^\nu_{ik}\, \mathbf{a}^*_k \tag{2}$$

with integral coefficients Z^ν_{ik}. The set $\{\mathbf{a}^*_1, \ldots, \mathbf{a}^*_{3+d_0}\}$ can be seen as the projection of $(3 + d_0)$ basis vectors spanning the superspace and the results of I can be applied.

The reciprocal lattice, Σ^*, in superspace has a basis given by

$$\begin{aligned} a^*_i &= (\mathbf{a}^*_i, 0), && i = 1, 2, 3 \\ a^*_{3+j} &= (\mathbf{a}^*_{3+j}, \mathbf{b}^*_j), && j = 1, 2, \ldots, d_0. \end{aligned} \tag{3}$$

The reciprocal basis to (3),

$$\begin{aligned} a_i &= (\mathbf{a}_i, -\mathbf{b}_{d_0+i}), && i = 1, 2, 3, \\ a_{3+j} &= (0, b_j), && j = 1, 2, \ldots, d_0, \end{aligned} \tag{4}$$

spans the lattice Σ. Moreover, expressing $\mathbf{a}^*_{3+j}$ in $\mathbf{a}^*_1$, $\mathbf{a}^*_2$, $\mathbf{a}^*_3$ one gets a matrix σ^0 by

$$\mathbf{a}^*_{3+j} = \sum_{i=1}^{3} \sigma^0_{ji}\, \mathbf{a}^*_i, \quad j = 1, 2, \ldots, d_0. \tag{5}$$

If one acts with the translations of Σ, generated by (4) on the positions (1), one obtains the atom positions of the supercrystal. We define the linear mappings π_ν by

$$\pi_\nu \mathbf{b}_j = \sum_{i=1}^{3} Z^\nu_{i3+j}\, \mathbf{a}_{\nu i}, \quad (\nu = 1, \ldots, N; j = 1, \ldots, d_0), \tag{6}$$

and it follows that

$$\exp i\mathbf{k}_I . \mathbf{t} = \exp i\mathbf{k} . \pi_\nu \mathbf{t}, \quad \text{any } \mathbf{t} \in V_I, \tag{7}$$

where $\mathbf{k} = (\mathbf{k}, \mathbf{k}_I)$ is a vector of Σ^*. Then, the positions of the atoms in the supercrystal are

$$(\mathbf{n}_\nu + \mathbf{r}_{\nu j} - \pi_\nu \mathbf{t}, \mathbf{t}), \quad \text{any } \mathbf{t} \in V_I, \mathbf{n}_\nu \in \Lambda_\nu. \tag{8}$$

Equation (8) gives the embedding of the incommensurate three-dimensional basic structure into a $(3 + d_0)$-dimensional superspace. This supercrystal has the lattice Σ as translation symmetry. Hence, its symmetry is a superspace group G_0. The elements of this group are pairs

$$g = (g_E, g_I) = (\{R_E | \mathbf{v}_E\}, \{R_I | \mathbf{v}_I\}), \tag{9}$$

such that

$$\tilde{\rho}_0(r) = \tilde{\rho}_0(g^{-1} r). \tag{10}$$

In particular, for the positions (8) the condition (10) takes the form

$$\begin{aligned} &(R_E(\mathbf{n}_\nu + \mathbf{r}_{\nu j} - \pi_\nu \mathbf{t}) + \mathbf{v}_E, R_I \mathbf{t} + \mathbf{v}_I) \\ &\quad = (\mathbf{n}'_{\nu'} + \mathbf{r}_{\nu' j'} - \pi_{\nu'} \mathbf{t}', \mathbf{t}'). \end{aligned} \tag{11}$$

The symmetry condition (11) implies the following relations:

$$R_E \Lambda_\nu = \Lambda_{\nu'} \tag{12}$$

$$R_E(\mathbf{n}_\nu + \mathbf{r}_{\nu j}) + \mathbf{v}_E + \pi_{\nu'} \mathbf{v}_I = \mathbf{n}_{\nu'} + \mathbf{r}_{\nu' j'} \tag{13}$$

and

$$R_E\, \pi_\nu \mathbf{t} = \pi_{\nu'} R_I\, \mathbf{t}. \tag{14}$$

We omit here the detailed derivation. Equation (13) implies that if a superspace-group element transforms the νth subsystem into itself, the element $\{R_E | \mathbf{v}_E + \pi_\nu \mathbf{v}_I\}$ belongs to the space group G_ν of this subsystem. This is in particular always the case when there is only one subsystem. In that case, $d_0 = 0$, $\pi_\nu \mathbf{v}_I = 0$ and (13) is equivalent with (17) of I.

3. Symmetry of the modulated composite crystal

As already mentioned in the Introduction, mutual perturbation of the atomic positions of the various subsystems leads to displacive modulation effects characterized by wave vectors belonging to the Fourier spectrum of the basic structure, but other mechanisms can occur and give rise to more general periodic deformations. We restrict our considerations to displacively modulated composite crystals.

If we include modulation, the atom positions of the composite crystal are

$$\mathbf{r}(\mathbf{n}_\nu, \nu j) = \mathbf{n}_\nu + \mathbf{r}_{\nu j} + \sum_{\mathbf{q}} \mathbf{f}_{\nu j}(\mathbf{q}) \exp\,[i\mathbf{q}(\mathbf{n}_\nu + \mathbf{r}_{\nu j})]. \tag{15}$$

Since the Fourier spectrum of such a crystal satisfies the requirements formulated in I, one can again construct the supercrystal associated with the positions (15), the construction being similar to that described in the preceding section but now in $(3 + d)$ dimensions. In this construction it is important to notice that as the coefficients Z^ν_{i3+j} in the relation generalizing (2) are zero for $j > d_0$, one has

$$\pi_\nu \mathbf{b}_j = 0 \quad \text{for } j = d_0 + 1, \ldots, d. \tag{16}$$

The atomic positions of the modulated supercrystal are given by

$$\begin{aligned} r(\mathbf{n}_\nu, \nu j, \mathbf{t}) = \{&\mathbf{n}_\nu + \mathbf{r}_{\nu j} - \pi_\nu \mathbf{t} + \sum_{\mathbf{q}} \mathbf{f}_{\nu j}(\mathbf{q}) \\ &\times \exp\,[i\mathbf{q}(\mathbf{n}_\nu + \mathbf{r}_{\nu j} - \pi_\nu \mathbf{t}) + i\mathbf{q}_I \mathbf{t}], \mathbf{t}\}, \end{aligned} \tag{17}$$

where $\mathbf{q} = \sum_{i=1}^{3+d} z_i\, \mathbf{a}^*_i$ and therefore

$$\mathbf{q}_I = \sum_{j=1}^{d} z_{3+j}\, \mathbf{b}^*_j. \tag{18}$$

Notice that for $N = 1$, and thus $d_0 = 0$, (17) reduces to that of an incommensurate displacively modulated crystal as treated in I.

For the invariance of the modulation, one gets

$$R_E\,\mathbf{f}_{vj}(\mathbf{q}) = \mathbf{f}_{v'j'}(\mathbf{q}')\exp(i\mathbf{K}\mathbf{r}_{v'j'} + iRqv), \qquad (19)$$

where the same notation has been used as in I, namely

$$g = \{R/v\},\ q = (\mathbf{q},\mathbf{q}_I) \text{ and } \mathbf{q}' = R_E\mathbf{q} + \mathbf{K}, \qquad (20)$$

but now $\mathbf{K}$ belongs to both the reciprocal lattices Λ_v^* and $\Lambda_{v'}^*$. It follows that G is a $(3+d)$-dimensional superspace group.

4. First example: $(TTF)_7I_{5-x}$

(a) *General description*

When tetrathiafulvalene molecules [*i.e.* $(C_3H_2S_2)_2$, herein called TTF] and iodine are allowed to mix by diffusion, crystals are formed with the approximate composition $(TTF)_7I_5$, which are incommensurate and involve two subsystems: one formed by the TTF molecules, the other by the I atoms. The compound, whose structure has been analyzed by Johnson & Watson (1976) can be described as a composite crystal with incommensurate basic structure. The present superspace group description is based on Johnson & Watson's paper.

The TTF subsystem ($v = 1$) has a basic structure with monoclinic space-group symmetry $G_1 = C2/m$. The I subsystem ($v = 2$) has space-group symmetry $G_2 = A2/m$. The corresponding two lattices share a basis vector along the unique axis, but in the other directions they are incommensurable. The basic structure allows an approximate supercell description with monoclinic lattice Λ_0 and 12 formula units per unit cell. As in the Johnson & Watson (1976) paper all results will here be expressed in terms of the basis **a**, **b**, **c** of the lattice Λ_0. This does not imply, however, a supercell approximation and is only done to allow a more direct comparison.

The TTF system has a C-centered monoclinic lattice, Λ_1, with primitive basis given by

$$\mathbf{a}_{11} = \tfrac{1}{3}\mathbf{a},\quad \mathbf{a}_{12} = -\tfrac{1}{6}\mathbf{a} + \tfrac{1}{2}\mathbf{b},\quad \mathbf{a}_{13} = \tfrac{1}{7}\mathbf{c}. \qquad (21)$$

The corresponding reciprocal basis is

$$\mathbf{a}_{11}^* = (3,1,0)_*,\quad \mathbf{a}_{12}^* = (0,2,0)_*,\quad \mathbf{a}_{13}^* = (0,0,7)_*. \qquad (22)$$

The point group $2/m$ is generated by 2_y and m_y. There are two inequivalent TTF molecules in the primitive unit cell at

$$\mathbf{r}_{11} = (0,0,0) \quad \text{and} \quad \mathbf{r}_{12} = (1/6,0,1/14), \qquad (23)$$

and the non-primitive translations associated with 2_y and m_y vanish.

The iodine system has an A-centered monoclinic lattice with primitive basis

$$\mathbf{a}_{21} = (1/6,0,1/p),\quad \mathbf{a}_{22} = (0,1/2,-1/2q),\quad \mathbf{a}_{23} = (0,0,1/q), \qquad (24)$$

with $p \simeq 15$ and $q \simeq 5$. If in (24) one takes the values $p = 15$ and $q = 5$ one obtains the supercell approximation mentioned above and adopted by Johnson & Watson (1976). Without neglecting incommensurability, the reciprocal basis of (24) is

$$a_{21}^* = (6,0,0)_*,\quad \mathbf{a}_{22}^* = (0,2,0)_*,\quad \mathbf{a}_{23}^* = (6q/p,1,q)_*. \qquad (25)$$

Since in general p and q are irrational, the two lattices Λ_1 and Λ_2 are incommensurable. There is one I atom per unit cell. One can choose for its position,

$$\mathbf{r}_{21} = \tfrac{1}{2}(\mathbf{a}_{21} - \mathbf{a}_{22}) \simeq (1/12,1/4,-1/12). \qquad (26)$$

The point group is also $2/m$. The non-primitive translations associated with the point-group generators 2_y and m_y for this choice of origin are

$$\mathbf{v}_2(2_y) = \mathbf{v}_2(m_y) = \tfrac{1}{2}\mathbf{a}_{23}. \qquad (27)$$

(b) *Symmetry of the basic structure*

As a basis for the union of Λ_1^* and Λ_2^* one may choose

$$\mathbf{a}_1^* = \mathbf{a}_{11}^*,\quad \mathbf{a}_2^* = \mathbf{a}_{12}^*,\quad \mathbf{a}_3^* = \mathbf{a}_{13}^* \quad \text{and} \quad \mathbf{a}_4^* = \mathbf{a}_{23}^*. \qquad (28)$$

Indeed, every element of Λ_1^* or Λ_2^* appears as an integral linear combination of these reciprocal vectors because $\mathbf{a}_{21}^* = 2\mathbf{a}_{11}^* - \mathbf{a}_{12}^*$ and $\mathbf{a}_{22}^* = \mathbf{a}_{12}^*$. Hence the dimension of the internal space is $d_0 = 1$. From (28) it follows that the matrices Z^v defined in (2) are

$$Z^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \quad \text{and} \quad Z^2 = \begin{pmatrix} 2 & \bar{1} & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}. \qquad (29)$$

The corresponding linear mappings π_v considered in (6) are defined by

$$\pi_1\,\mathbf{b}_1 = 0 \quad \text{and} \quad \pi_2\,\mathbf{b}_1 = \mathbf{a}_{23}. \qquad (30)$$

This determines the embedding (8). Furthermore, the matrix σ^0 of (5) is

$$\sigma^0 = \left(\frac{2q}{p}, \frac{p-2q}{2p}, \frac{q}{7}\right) \equiv \left(\alpha, \frac{1-\alpha}{2}, \gamma\right), \qquad (31)$$

where $\alpha \simeq 2/3$ and $\gamma \simeq 5/7$. With respect to the conventional (non-primitive) basis for Λ_1, (1/3,0,0), (0,1,0) and (0,0,1/z), one has

$$\sigma_c^0 = (\alpha,1,\gamma). \qquad (32)$$

The lattice Σ in superspace associated with the basic structure of this composite crystal is spanned by the (primitive) basis

$$\begin{aligned} a_1 &= (\mathbf{a}_{11}, -\alpha\mathbf{b}_1) & a_3 &= (\mathbf{a}_{13}, -\gamma\mathbf{b}_1) \\ a_2 &= [\mathbf{a}_{12}, -(1-\alpha)\mathbf{b}_1/2] & a_4 &= (0,\mathbf{b}_1). \end{aligned} \qquad (33)$$

The Bravais class of Σ is denoted by $P^{C\frac{2}{\bar{1}}\frac{m}{1}}$ (Janner, Janssen & de Wolff, 1979). This symbol means that the

holohedry of Σ is generated by the point-group elements (R_E,R_I) given by

$$R_1 = (2_y,-1) \quad \text{and} \quad R_2 = (m_y, 1). \tag{34}$$

In the position space the corresponding lattice Λ spanned by $\mathbf{a}_1 = \mathbf{a}_{11}$, $\mathbf{a}_2 = \mathbf{a}_{12}$, $\mathbf{a}_3 = \mathbf{a}_{13}$ [see (28)] is C-centered monoclinic. In the internal space the lattice D is generated by $\mathbf{b}_1$.

The superspace-group symmetry of this basic structure follows from (12), (13) and (14). Since the two subsystems involve different atoms, one has necessarily $\nu = \nu'$. Furthermore, the two TTF molecules in the unit cell are non-equivalent, so that $j = j'$. The two elements 2_y and m_y are generators of both point groups of G_1 and G_2 respectively; therefore (12) is satisfied. Equation (14) is also satisfied in an evident way. For $R_E = 2_y$ one has $R_I = -1$ and (13) is fulfilled with $\mathbf{v}_E = 0$ and $\mathbf{v}_I = \frac{1}{2}\mathbf{b}_1$ because for $\nu = 1$, $\pi_1\mathbf{b}_1 = 0$ and for $\nu = 2$, $\frac{1}{2}\pi_2\mathbf{b}_1 = \frac{1}{2}\mathbf{a}_{23}$ is the corresponding non-primitive translation given in (27). The same reasoning applies to $R_E = m_y$ and $R_I = -1$. Hence, we have

$$v(2_y,-1) = v(m_y,1) = (0,\tfrac{1}{2}\mathbf{b}_1). \tag{35}$$

The first of these non-primitive translations is equivalent to zero and can be transformed away by a change of origin in the internal space. Accordingly, the superspace group of the basic structure is

$$P^{C\,\frac{2}{1}\,\frac{2/m}{s}}. \tag{36}$$

This group is generated by the translations (33) of the four-dimensional lattice Σ, and by the elements

$$\begin{aligned} g_1 &= \{(2_y,\bar{1})|\tfrac{1}{2}\mathbf{b}_1\}\colon (x,y,z,t) \to (-x, y, -z, -t + \tfrac{1}{2}),\\ g_2 &= \{(m_y,1)|\tfrac{1}{2}\mathbf{b}_1\}\colon (x,y,z,t) \to (x, -y, z, t + \tfrac{1}{2}). \end{aligned} \tag{37}$$

We recall that g_1 is equivalent to $\{(2_y,\bar{1})|0\}$ by an appropriate change in origin.

(c) *Symmetry of the modulated crystal*

Both the TTF and the I subsystems are modulated. The *TTF modulation* has a translational and a librational part. If we denote the Fourier components of these two modes by $\mathbf{f}_{1j}(\mathbf{q})$ and $L_{1j}(\mathbf{q})$, respectively, one has

$$\mathbf{q} = n\mathbf{a}^*_{23}, \ (n \text{ integer}) \tag{38}$$

and

$$\text{for } n \text{ even: } \mathbf{f}_{1j}(n\mathbf{a}^*_{23}) \perp \mathbf{b},\ \mathbf{L}_{1j}(n\mathbf{a}^*_{23}) \parallel \mathbf{b} \tag{39}$$

$$\text{for } n \text{ odd: } \mathbf{f}_{1j}(n\mathbf{a}^*_{23}) \parallel \mathbf{b},\ \mathbf{L}_{1j}(n\mathbf{a}^*_{23}) \perp \mathbf{b}. \tag{40}$$

The *I modulation* has only a translational part (because of the point-atom approximation) with Fourier components $\mathbf{f}_{2j}(\mathbf{q})$ for $\mathbf{q}$ as follows,

$$\mathbf{q} = n\mathbf{a}^*_{13} \ (n \text{ integer}),\ \mathbf{f}_{2j}(\mathbf{q}) \perp \mathbf{b} \tag{41}$$

$$\mathbf{q} = \mathbf{a}^*_{11} + n\mathbf{a}^*_{13} \ (n \text{ integer}),\ \mathbf{f}_{2j}(\mathbf{q}) \parallel \mathbf{b}. \tag{42}$$

All the Fourier components of the translational modes are reported to be purely imaginary vectors, those of the librational modes being real. The corresponding origin is that leading to the non-primitive translations indicated in (35). This fixes the various phases involved in the modulation.

As the modulation $\mathbf{q}$ vectors (38), (41) and (42) belong either to Λ^*_1 or to Λ^*_2, the Fourier wave vectors of the modulated composite crystal are still expressible as integral linear combinations of the ones appearing in (28). Therefore, the dimension of the internal space remains $d = d_0 = 1$. This implies that the lattice of the modulated supercrystal is the same as that obtained for the basic structure, *i.e.* it is generated by (33) and its Bravais class is $P^{C\,\frac{2}{1}\,\frac{2/m}{1}}$.

The superspace symmetry group has to leave invariant the basic structure and the modulation. In the present case ($d_0 = d$), these two requirements imply that this group is the largest subgroup of $P^{C\,\frac{2}{1}\,\frac{2/m}{s}}$ which satisfies (19) for the observed modulation. Since the translational symmetry has already been determined, it is sufficient to consider the two generators (37).

Take g_1 first: for $\nu = 1$, one has

$$R_E\mathbf{q} = 2_y(n\mathbf{a}^*_{23}) = -\mathbf{q} + n\mathbf{a}^*_{23}. \tag{43}$$

This implies by (20) that

$$\mathbf{K} = -n\mathbf{a}^*_{22} = -n\mathbf{a}^*_2, \quad \text{thus } \mathbf{K}\mathbf{r}_{1j} = 0 \quad (j = 1, 2) \tag{44}$$

and

$$Rqa = (2_y,\bar{1})(n\mathbf{a}^*_{23},n\mathbf{b}^*_1)(0,\mathbf{b}_1/2) = -n\pi. \tag{45}$$

Substituting these results in (19), we find that the symmetry condition becomes for the translational modes

$$R_E\,\mathbf{f}_{1j}(\mathbf{q}) = (-1)^n\,\mathbf{f}^*_{1j}(\mathbf{q}) = (-1)^{n+1}\,\mathbf{f}_{1j}(\mathbf{q}), \tag{46}$$

and for the librational mode

$$R_E\,\mathbf{L}_{1j}(\mathbf{q}) = (-1)^n\,\mathbf{L}^*_{1j}(\mathbf{q}) = (-1)^n\,\mathbf{L}_{1j}(\mathbf{q}). \tag{47}$$

Because of the polarizations (39) and (40), both (46) and (47) are satisfied. The corresponding relations for $\nu = 2$ are

$$R_E\mathbf{q} = 2_y(\varepsilon\mathbf{a}^*_{11} + n\mathbf{a}^*_{13}) = -\mathbf{q} + \varepsilon\mathbf{a}^*_2 \quad \text{for } \varepsilon = 0,1, \tag{48}$$

giving by (26) and (20)

$$\mathbf{K} = -\varepsilon\mathbf{a}^*_2, \quad \mathbf{K}\mathbf{r}_{2j} = -\varepsilon\pi \tag{49}$$

and

$$Rqa = (2_y,\bar{1})(\mathbf{q},0)(0,\tfrac{1}{2}\mathbf{b}_1) = 0. \tag{50}$$

Substitution in (19) leads to the symmetry condition

$$R_E\,\mathbf{f}_{2j}(\mathbf{q}) = (-1)^\varepsilon\,\mathbf{f}^*_{2j}(\mathbf{q}) = (-1)^{1+\varepsilon}\,\mathbf{f}_{2j}(\mathbf{q}). \tag{51}$$

Again, this relation is satisfied for the polarizations (41) and (42) observed. This shows that the superspace-group element g_1 as indicated in (37) is indeed a symmetry transformation for the modulated supercrystal. In the same way, one verifies that this is

also the case for g_2. This exhausts the possibilities: therefore, the superspace group for the modulated supercrystal, *i.e.* the symmetry group of $(TTF)_7I_{5-x}$ is

$$P^{C\,\frac{2}{1}/m}_{1\;s}. \tag{52}$$

Notice that the polarizations and the phases observed are such as to allow the maximal symmetry compatible with that of the (incommensurable) basic structure. So by requiring that the modulation should be left invariant by the superspace group of the basic structure one would get for the modes involved exactly the polarization and phase relations which have been experimentally detected in this compound.

5. Second example: $Hg_{3-\delta}AsF_6$

(*a*) *General description*

The compound $Hg_{3-\delta}AsF_6$, known for the occurrence of linear chains of mercury atoms (Brown *et al.*, 1974), has a phase transition at $T_c = 120$ K. Above this temperature the diffraction pattern shows diffuse sheets, indicating partial occupation by mercury of different crystallographic positions. Below T_c an ordered phase is observed. Its structure has been analyzed by Cutforth, Datars, Gillespie & Van Schijndel (1976), Schultz *et al.* (1978) and by Pouget *et al.* (1978): it is that of an incommensurate composite crystal. Our determination of the superspace-group symmetry of this compound is based on the last paper quoted above. It is worth noting that although in the basic structure there exist complex relations between three mutually incommensurable crystallographic subsystems, one single additional dimension suffices for its superspace description.

These three subsystems are:

(1) *the* AsF_6 *subsystem* ($\nu = 1$), with a body-centered tetragonal lattice, Λ_1, the so-called 'host lattice';

(2) a *first* Hg *subsystem* ($\nu = 2$), with mercury atoms in chains parallel to the [100] direction of the host lattice and forming an A-centered monoclinic lattice, Λ_2;

(3) a *second* Hg *subsystem* ($\nu = 3$), with mercury chains parallel to the [010] direction of Λ_1 and building a B-centered monoclinic lattice, Λ_3.

Above T_c the structure of this crystal has an average space-group symmetry $I4_1/amd$ and the phases of the Hg chains are not ordered. Below T_c phase ordering is observed together with a displacive modulation of the host lattice. This latter is neglected at first and will be taken into account later on.

As reference coordinate system we adopt that defined by the (non-primitive) conventional basis **a**, **b**, **c** of the host lattice. Accordingly, the $\nu = 1$ system has lattice Λ_1 with basis

$$\mathbf{a}_{11} = (-\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}),\quad \mathbf{a}_{12} = (\tfrac{1}{2},-\tfrac{1}{2},\tfrac{1}{2}),\quad \mathbf{a}_{13} = (\tfrac{1}{2},\tfrac{1}{2},-\tfrac{1}{2}) \tag{53}$$

and corresponding reciprocal basis

$$\mathbf{a}^*_{11} = (0,1,1)_*,\quad \mathbf{a}^*_{12} = (1,0,1)_*,\quad \mathbf{a}^*_{13} = (1,1,0)_*. \tag{54}$$

The Bragg reflections characterizing this subsystem are indexed by $(h,k,l)_*$ with $h + k + l = 2n$. It has two formula units per primitive cell: two As at Wyckoff position (b) of the space group $G_1 = I4_1/amd$, four F atoms at Wyckoff position (c) and eight at position (g). This space group is generated by (53) and by

$$\begin{aligned}
&\{4_z|(\tfrac{1}{4},\tfrac{1}{4},\tfrac{3}{4})\}\colon (x,y,z) \to (y+\tfrac{1}{4}, -x+\tfrac{1}{4}, z+\tfrac{3}{4}),\\
&\{m_z|(0,\tfrac{1}{2},0)\}\colon (x,y,z) \to (x, y+\tfrac{1}{2}, -z),\\
&\{m_x|0\}\colon (x,y,z) \to (-x,y,z).
\end{aligned} \tag{55}$$

The $\nu = 2$ mercury subsystem gives rise to Bragg reflections associated with the reciprocal lattice Λ^*_2 with basis

$$\begin{aligned}
&\mathbf{a}^*_{21} = (3-\delta, -1-\delta, 0)_*,\quad \mathbf{a}^*_{22} = (0,1,1)_*,\\
&\qquad\qquad\qquad\qquad \mathbf{a}^*_{23} = (0,1,-1)_*,
\end{aligned} \tag{56}$$

the corresponding direct basis being

$$\begin{aligned}
&\mathbf{a}_{21} = (1/(3-\delta), 0, 0),\ \mathbf{a}_{22} = ((1+\delta)/2(3-\delta), 1/2, 1/2),\\
&\qquad \mathbf{a}_{23} = ((1+\delta)/2(3-\delta), 1/2, -1/2).
\end{aligned} \tag{57}$$

This basis spans an A-centered monoclinic lattice, Λ_2, with unique axis **c**. The value of δ in (56) and (57) is the same as the one appearing in the chemical formula; $3-\delta \simeq 2.86$. There is one Hg atom per unit cell and one may choose its position at

$$\mathbf{r}_{21} = (x,\tfrac{1}{4},\tfrac{3}{4}). \tag{58}$$

The space-group symmetry of this second subsystem is $G_2 = A2/m$.

The $\nu = 3$ mercury subsystem is associated with the Bragg peaks at $(h - k\delta, k(3-\delta), l)_*$, where $h + k + l = 2n$ and h, k, l are integers. Hence, one may choose as basis for the reciprocal lattice Λ^*_3

$$\begin{aligned}
&\mathbf{a}^*_{31} = (-1-\delta, 3-\delta, 0)_*,\quad \mathbf{a}^*_{32} = (1,0,1)_*,\\
&\mathbf{a}^*_{33} = (1,0,-1)_*.
\end{aligned} \tag{59}$$

The corresponding basis for the direct lattice Λ_3 is

$$\begin{aligned}
&\mathbf{a}_{31} = (0,\ 1/(3-\delta),\ 0),\ \mathbf{a}_{32} = (1/2,\ (1+\delta)/2(3-\delta),\ 1/2),\\
&\mathbf{a}_{33} = (1/2,\ (1+\delta)/2(3-\delta),\ -1/2)
\end{aligned} \tag{60}$$

and spans a B-centered monoclinic lattice, again with unique axis **c**. There is one Hg atom per unit cell at $\mathbf{r}_{31}$, and the space group is $G_3 = B2/m$. The position of the mercury lattice array for $\nu = 3$ with respect to that for $\nu = 2$ follows from the fact that the diffraction peaks with indices $m(3-\delta, 3-\delta, 0)_*$, which belong to both Λ^*_2 and Λ^*_3, vanish for $m = 1$ and are strong for $m = 2$. There follows for $\mathbf{r}_{31} - \mathbf{r}_{21} = (x,y,z)$ the condition

$$x + y = (2n+1)/2(3-\delta),\ (n \text{ integer}). \tag{61}$$

Hence one can choose

$$\mathbf{r}_{31} = (0, \tfrac{1}{4} + x + 1/2(3-\delta), 0), \qquad (62)$$

where x has the same value as in (58).

(b) Symmetry of the basic structure

All elements of Λ_1^*, Λ_2^* and Λ_3^* can be written as integral linear combinations of the following four vectors,

$$\mathbf{a}_1^* = (0,1,1)_*, \quad \mathbf{a}_2^* = (1,0,1)_*, \quad \mathbf{a}_3^* = (1,1,0)_*$$
$$\text{and } \mathbf{a}_4^* = (-\delta, -\delta, 0)_*. \qquad (63)$$

This implies that the incommensurate basic structure has a four-dimensional superspace group as symmetry. Hence, $d_0 = 1$. Expressing the bases (54), (56) and (59) in terms of (63), one gets the matrices Z^ν defined in (2):

$$Z^1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad Z^2 = \begin{pmatrix} \bar{2} & 2 & 1 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & \bar{1} & 1 & 0 \end{pmatrix},$$

$$Z^3 = \begin{pmatrix} 2 & \bar{2} & 1 & 1 \\ 0 & 1 & 0 & 0 \\ \bar{1} & 0 & 1 & 0 \end{pmatrix} \qquad (64)$$

and the matrix σ^0 expressing $\mathbf{a}_4^*$ in $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$ as in (5):

$$\sigma^0 = (0,0,-\delta), \qquad (65)$$

or, with respect to the non-primitive basis $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$,

$$\sigma_c^0 = (-\delta,-\delta,0).$$

The lattice Σ_0 of the superspace group of the basic structure is spanned by

$$a_{01} = (\mathbf{a}_1,0), \quad a_{02} = (\mathbf{a}_2,0), \quad a_{03} = (\mathbf{a}_3,\delta\mathbf{b}_1), \quad a_{04} = (0,\mathbf{b}_1), \qquad (66)$$

where $\mathbf{a}_i = \mathbf{a}_{1i}$, $i = 1, 2, 3$ and $\mathbf{b}_1$ is a vector of the internal space.

The holohedry of Σ_0 is determined by $\Lambda = \Lambda_1$ and σ^0. The matrix σ^0 (or σ_c^0) is not compatible with tetragonal symmetry (Janner, Janssen & de Wolff, 1979). Transforming the reference basis **a**, **b**, **c** to the following new one, we get

$$\mathbf{A} = \mathbf{a} + \mathbf{b}, \quad \mathbf{B} = \mathbf{b} - \mathbf{a}, \quad \mathbf{C} = \mathbf{c}, \qquad (67)$$

which spans an F-centered lattice, one obtains $\mathbf{a}_4^* = -2\delta\mathbf{A}^*$; this is compatible with orthorhombic symmetry. Indeed, the Bravais class of Σ_0 is

$$P^F \begin{matrix} \bar{1} & 1 & 1 \end{matrix}^{m\,m\,m} \qquad (68)$$

and the corresponding holohedry is generated by the three point-group elements

$$R_{01} = (m_I,-1)\colon (x,y,z,t) \to (-y,-x,z,-t),$$
$$R_{02} = (m_{II},1)\colon (x,y,z,t) \to (y,x,z,t), \qquad (69)$$
$$R_{03} = (m_{III},1)\colon (x,y,z,t) \to (x,y,-z,t),$$

where the coordinates refer to the **a**, **b**, **c**, $\mathbf{b}_1$ basis of the superspace, as we shall continue to do in what follows: $(x,y,z,t) = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} + t\mathbf{b}_1$. Since the holohedry is orthorhombic and not tetragonal, one expects a distortion of the host lattice. This has indeed been observed: the angle between **a** and **b** deviates slightly from 90°. The embedding of the basic structure is given by (6) and (8) with

$$\pi_1\mathbf{b}_1 = 0, \quad \pi_2\mathbf{b}_1 = \mathbf{a}_{21}, \quad \pi_3\mathbf{b}_1 = \mathbf{a}_{31}. \qquad (70)$$

So a translation in the internal space leaves the first subsystem invariant but moves the Hg chains by an equal interval along their respective chain direction. Accordingly, the phase relationship expressed in (61) is conserved in such a transformation. Elements of the superspace-symmetry group of the supercrystal have to satisfy the conditions (12), (13) and (14), and their homogeneous part has to belong to the holohedry of Σ_0; so we consider the three generators (69). The subsystem AsF_6 is necessarily mapped into itself: so $\nu = 1$ implies $\nu' = 1$. Furthermore, since π_1 is the zero mapping the condition $R_E\mathbf{r}_{1j} + \mathbf{v}_E \equiv \mathbf{r}_{1j'} \pmod{\Lambda_1}$ implies that for the translation $\mathbf{v}_E$ one has to take a non-primitive translation associated with R_E in the space group $G_1 = I4_1/amd$.

For $R_E = m_I$, $R_I = -1$, one has $\mathbf{v}_E = \mathbf{v}_E(R_{01}) = (\frac{3}{4},\frac{1}{4},\frac{3}{4})$. The subsystems 2 and 3 are interchanged: $\nu = 2$ implies $\nu' = 3$ and $\nu = 3$ gives $\nu' = 2$. So the symmetry conditions become

$$R_E\Lambda_1 = \Lambda_1, \quad R_E\Lambda_2 = \Lambda_3 \quad \text{and} \quad R_E\Lambda_3 = \Lambda_2. \qquad (71)$$

Furthermore, (14) is also satisfied. One also requires

$$R_E\mathbf{r}_{21} + \mathbf{v}_E + \pi_3\mathbf{v}_I \equiv \mathbf{r}_{31} \pmod{\Lambda_3}$$
$$\text{and } R_E\mathbf{r}_{31} + \mathbf{v}_E + \pi_2\mathbf{v}_I \equiv \mathbf{r}_{21} \pmod{\Lambda_2}, \qquad (72)$$

which are both satisfied by $\mathbf{v}_E = \mathbf{v}_E(R_{01})$ and $\mathbf{v}_I = [\delta/2 + 2x(3-\delta)]\mathbf{b}_1$. Hence, $R_{01} = (m_I,-1)$ belongs to the point group and is associated with the non-primitive translation

$$v(R_{01}) = (\tfrac{3}{4}, \tfrac{1}{4}, \tfrac{3}{4}, \delta/2 + 2x(3-\delta)). \qquad (73)$$

For $R_E = m_{II}$, $R_I = 1$, one has $\mathbf{v}_E = \mathbf{v}_E(R_{02}) = (\frac{1}{4},\frac{1}{4},\frac{3}{4})$. This element also interchanges the subsystems 2 and 3 and (14) and (71) are again verified. Furthermore, (72) is now fulfilled for $\mathbf{v}_I$ given by

$$\mathbf{v}_I(R_{02}) = \tfrac{1}{2}\delta\mathbf{b}_1, \qquad (74)$$

so that R_{02} is also an element of the point group and has associated the non-primitive translation

$$v(R_{02}) = (\tfrac{1}{4},\tfrac{1}{4},\tfrac{3}{4},\delta/2). \tag{75}$$

Finally, one considers $R_E = m_{III}$, $R_I = 1$ and $\mathbf{v}_E = (0,\frac{1}{2},0)$. In this case, $v = v'$ for each subsystem. Equations (12) and (14) are verified immediately. Equation (13) is also solved by taking for $\mathbf{v}_I$

$$\mathbf{v}_I(R_{03}) = (1 + \delta)\mathbf{b}_1/2. \tag{76}$$

It is convenient to shift the origin of the internal space by $-[\delta/4 + x(3 - \delta)]\mathbf{b}_1$, so that the non-primitive translations take the simpler form

$$\begin{aligned} v(R_{01}) &= a_{01} + \tfrac{3}{2}a_{02} + a_{03} = (\tfrac{3}{4},\tfrac{1}{4},\tfrac{3}{4},\delta),\\ v(R_{02}) &= a_{01} + a_{02} + \tfrac{1}{2}a_{03} = (\tfrac{1}{4},\tfrac{1}{4},\tfrac{3}{4},\delta/2),\\ v(R_{03}) &= \tfrac{1}{2}(a_{01} + a_{03} + a_{04}) = (0,\tfrac{1}{2},0,(1+\delta)/2). \end{aligned} \tag{77}$$

Hence, the superspace group of the basic structure of $Hg_{3-\delta}AsF_6$ is

$$G_0 = P^F{}_{\bar{1}}{}^{d}{}_{1}{}^{d}{}_{s}{}^{d}. \tag{78}$$

This group is generated by the translations (66) and by the following three elements:

$$\begin{aligned} g_{01}\,(x,y,z,t) &\to (-y + \tfrac{3}{4}, -x + \tfrac{1}{4}, z + \tfrac{3}{4}, -t + \delta),\\ g_{02}\,(x,y,z,t) &\to (y + \tfrac{1}{4}, x + \tfrac{1}{4}, z + \tfrac{3}{4}, t + \delta/2),\\ g_{03}\,(x,y,z,t) &\to (x, y + \tfrac{1}{2}, -z, t + (1+\delta)/2). \end{aligned} \tag{79}$$

This superspace group is non-symmorphic and gives rise to several systematic extinctions: those arising from the F centering and those from the non-primitive translations associated with the generators g_{0i}. In particular, the diffraction spots at $(h,k,l,m)_* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{a}_4^*$ are left invariant for $l = 0$ by $R_{03} = (m_z, 1)$. Accordingly, $h + k$ even and m even are conditions imposed by the superspace-group symmetry on the Bragg peaks. This explains the extinction at $(3 - \delta, 3 - \delta, 0)_*$.

(c) *Symmetry of the modulated structure*

In addition to the reflections at positions which correspond to integral linear combinations of the vectors given at (63) there are satellite reflections which have their origin in the modulation of the subsystems. These spots appear at positions $(h \pm 2\delta, 0, l)_*$ with $(h + l)$ even in the k zone and at position $(0, k \pm 2\delta, l)_*$, with $(k + l)$ even in the h zone. These additional Fourier wave vectors can be expressed as integral linear combinations of $\mathbf{a}_1^*, \ldots, \mathbf{a}_4^*$ as in (63) and

$$\mathbf{a}_5^* = (\delta,-\delta,0)_*. \tag{80}$$

Accordingly, a two-dimensional internal space is required, and in this second example $d = 2 > d_0 = 1$. The symmetry group will then be a (3 + 2)-dimensional superspace group. To determine its lattice, Σ, one notices that now

$$\sigma = \begin{pmatrix} 0 & 0 & -\delta \\ -\delta & \delta & 0 \end{pmatrix}, \tag{81}$$

or, with respect to the non-primitive basis $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$,

$$\sigma_c = \begin{pmatrix} -\delta & -\delta & 0 \\ \delta & -\delta & 0 \end{pmatrix}. \tag{82}$$

The first row of these matrices describes $\mathbf{a}_4^*$, the second one $\mathbf{a}_5^*$. From the lattice $\Lambda = \Lambda_1$ spanned by $\mathbf{a}_{11}$, $\mathbf{a}_{12}$, $\mathbf{a}_{13}$ and from the matrix σ_c (or σ) it follows that the Bravais class of the lattice Σ is

$$P^{I\,4/m\,\dot{m}\,\dot{m}\,\dot{m}}_{p\,4\;1\;\ddot{m}\;m} \tag{83}$$

for Λ tetragonal. If Λ is orthorhombic, as it is in the present case because $T < T_c$, the Bravais class of Σ is given by

$$P^{F\,m\,m\,m}_{p\,m\,m\,1}. \tag{84}$$

The most general σ matrix compatible with this Bravais class is

$$\begin{pmatrix} 0 & 0 & \gamma \\ \mu & -\mu & 0 \end{pmatrix}. \tag{85}$$

Hence, the relation $\mu = \gamma = -\delta$ is accidental, or, alternatively, the δ appearing in the second row of (81) differs slightly from the δ of the first row. This seems to be compatible with experiment. In any case, we go on using the matrix (81). The lattice Σ is then generated by the five basis vectors:

$$\begin{aligned} &a_1 = (\mathbf{a}_1,\delta\mathbf{b}_2), \quad a_2 = (\mathbf{a}_2,-\delta\mathbf{b}_2), \quad a_3 = (\mathbf{a}_3,\delta\mathbf{b}_1),\\ &a_4 = (0,\mathbf{b}_1), \quad a_5 = (0,\mathbf{b}_2), \end{aligned} \tag{86}$$

where, as for the basic structure, $\mathbf{a}_i = a_{1i}$ $i = 1, 2, 3$, and now $\mathbf{b}_1$ and $\mathbf{b}_2$ are perpendicular vectors spanning the internal space. The holohedry of Σ is generated by

$$\begin{aligned} R_1 &= (R_{01},1) = (m_1,m_1)\colon (x,y,z,t,u) \to (-y,-x,z,-t,u),\\ R_2 &= (R_{02},-1) = (m_{1\bar{1}},m_2)\colon (x,y,z,t,u) \to (y,x,z,t,-u)\\ R_3 &= (R_{03},1) = (m_{III},1)\colon (x,y,z,t,u) \to (x,y,-z,t,u), \end{aligned} \tag{87}$$

where $(x,y,z,t,u) = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} + t\mathbf{b}_1 + u\mathbf{b}_2$. Notice that the restriction to the (3 + 1)-dimensional subspace defines correspondingly the same transformation as in (69).

Pouget *et al.* (1978) only found modulation of the Hg chain. No evidence could be detected for a modulation of the AsF_6 subsystem. The modulation vectors are

$$\mathbf{q}_2 = (0,2\delta,0)_* \quad \text{and} \quad \mathbf{q}_3 = (2\delta,0,0)_* \tag{88}$$

for the displacive modulation in the subsystem $v = 2$ and $v = 3$, respectively. The polarization observed is perpendicular to the chain direction and to the $\mathbf{c}$ axis. Thus,

$$\mathbf{f}_{21}(\mathbf{q}_2) = (0,f,0) \quad \text{and} \quad \mathbf{f}_{31}(\mathbf{q}_3) = (f,0,0). \tag{89}$$

To determine the superspace-group symmetry of the modulated supercrystal, one examines whether or not (19) is satisfied for the three generators R_1, R_2 and R_3 of the holohedry of Σ, keeping in mind that the invariance of the basic structure imposes a condition on the (3 + 1)-dimensional component of the associated non-primitive translation $v = v(R_i)$, namely

$$v(R_i) = [v(R_{0i}), \ldots], \quad i = 1, 2, 3, \tag{90}$$

with $v(R_{0i})$ given as in (77). Let us also indicate the internal components one gets for the modulation vectors $\mathbf{q}_1$ and $\mathbf{q}_2$ by the embedding defined by (63), (80) and (86):

$$\mathbf{q}_{2I} = -\mathbf{b}_1^* - \mathbf{b}_2^*, \quad \mathbf{q}_{3I} = -\mathbf{b}_1^* + \mathbf{b}_2^*. \tag{91}$$

We first consider R_1 as in (87) which transforms $v, j = 2, 1$ into $v', j' = 3, 1$ and *vice versa*. Then, provided that $\mathbf{f}_{v1}(-\mathbf{q}_v) = -\mathbf{f}_{v1}(\mathbf{q}_v)$, a property that can be obtained by an appropriate shifting of the origin in the internal space along $\mathbf{b}_2$, one verifies the validity of (19) when the associated non-primitive translation is chosen to be $v(R_1) = a_1 + (3/2)a_2 + a_3$. Comparison with (77) shows that (90) is also fulfilled. In the same way, $R_2 = (R_{02}, -1)$ also transforms $v, j = 2, 1$ into $v', j' = 3, 1$ and *vice versa*. The corresponding **K** vectors are zero. The non-primitive translation that solves (19) and (90) is given by $v(R_2) = a_1 + a_2 + \frac{1}{2}a_3$. Finally, for R_3 one has $R_3 q_i = q_i$, $i = 1, 2$ and $v', j' = v, j$, and for the associated non-primitive translation one gets $v(R_3) = \frac{1}{2}(a_1 + a_3 + a_4 + a_5)$.

These calculations imply that the superspace group for the modulated crystal $Hg_{3-\delta}AsF_6$ is

$$G = P^{Fddd}_{pmmd} \tag{92}$$

which is generated by the five translations (86) and the three elements

$$\begin{aligned} &g_1 = \{R_1 | \tfrac{1}{2}a_2\}, \quad g_2 = \{R_2 | \tfrac{1}{2}a_3\} \\ \text{and} \quad &g_3 = \{R_3 | \tfrac{1}{2}(a_1 + a_3 + a_4 + a_5)\}, \end{aligned} \tag{93}$$

with R_i as in (87)

Notice that in this case, as in all the preceding ones with commensurate or incommensurate basic structure, the $(3 + d_0)$-dimensional component of the superspace group of the modulated structure is the full symmetry group of the basic structure; one can say that modulation which occurs takes into account this underlying symmetry.

Nevertheless, we still have the feeling that in the present case the presence of the 2δ peaks is not completely understood [as already stated in Pouget *et al.* (1978)]. Not so much because of lack of knowledge of the detailed mechanism leading to the modulation of the mercury chains, but more because the increase in dimension of the internal space suggests the presence of a mechanism in addition to the more geometric one expressed by the parameter δ. Unexpectedly, however, as already mentioned above, this δ is the only parameter appearing in the matrix σ. Despite that, the superspace group symmetry of $Hg_{3-\delta}AsF_6$ reveals the presence of rather sophisticated structural relations still fitting in a general frame of properties.

6. Concluding remarks

On the basis of the experimental data available for two compounds with intriguing crystallographic properties, the superspace-group symmetry description gives a consistent and coherent overall view of the structural implications of geometric invariance. The same type of laws governing crystal physics in the commensurate phases apply to the incommensurate ones, provided the right language is used. In deriving the results presented here, and in part I, the knowledge of the full list of (3 + 1)- and (3 + 2)-dimensional Bravais classes played an important role (Janner, Janssen & de Wolff, 1979, 1980) together with a knowledge of the basic properties of superspace groups (Janner & Janssen, 1979).

The superspace-group approach gives a working scheme within which crystal structural analysis can be performed without being restricted by a commensurate supercell approximation.

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