

SYMMETRY OF INCOMMENSURATE CRYSTAL PHASES
IN THE SUPERSPACE GROUP APPROACH

by

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Abstract:

The existence of incommensurate crystal phases requires a generalization of the concept of crystal symmetry. Indeed, although an incommensurate crystal has a 3-dimensional structure, its Euclidean symmetry is not a 3-dimensional space group. Furthermore this Euclidean symmetry does not give a characterization of the regularities observed in the corresponding diffraction pattern.

Enlarging the group of admitted symmetry transformations by introducing suitably defined internal degrees of freedom, one gets a symmetry group which is isomorphic to a space group in more than 3 dimensions. Accordingly this generalization can be described through an embedding of the crystal in a higher dimensional Euclidean space (the "superspace") spanned by the 3-dimensional space and by the d-dimensional internal one. The dimension of the superspace is given by the minimal number of indices needed for labelling the Bragg reflections. In particular for $d = 1$, any satellite reflection can be indexed as $h\vec{a}^* + k\vec{b}^* + l\vec{c}^* + m\vec{q}$, where $\vec{q} = \alpha\vec{a}^* + \beta\vec{b}^* + \gamma\vec{c}^*$: incommensurability then implies that at least one of the α, β, γ is irrational.

The different nature of positional and of internal space leads to additional properties of the higher dimensional space group, which is accordingly defined as a $(3+d)$ -dimensional superspace group. This generalized crystallographic group is uniquely determined (up to equivalence) by the crystal structure, and reduces to a space group for commensurate crystal phases.

A number of incommensurate crystal structures is considered like Na_2CO_3 , K_2SeO_4 , TaSe_2 , $(\text{TTF})_7\text{I}_{5-x}$ and $\text{Hg}_{3-6}\text{AsF}_6$. Their regularities are expressed and interpreted in terms of superspace group elements. These examples prove the relevance of the superspace group approach in crystal physics.

The Bravais classes for d up to 3 have been determined and a full list of inequivalent superspace groups for $d = 1$ has been established. It is a remarkable fact that the superspace group generalization allows a unified treatment of both the commensurate and the incommensurate crystal phases known so far, which emphasizes the relevant formal properties of classical crystallography.

1. Euclidean Crystallography

A crystal in the usual sense is here described by a scalar density function or matter distribution $\rho(\vec{r})$ having a Fourier decomposition as follows:

$$\rho(\vec{r}) = \sum_{\vec{k} \in \Lambda^*} \hat{\rho}(\vec{k}) e^{i\vec{k}\vec{r}} \quad (1.1)$$

with Λ^* a 3-dimensional lattice in the reciprocal space. Denoting by \vec{a}_1^* , \vec{a}_2^* , \vec{a}_3^* a basis of this lattice one has accordingly for any Fourier wave vector \vec{k} appearing in (1.1):

$$\vec{k} = \sum_{i=1}^3 z_i \vec{a}_i^* \equiv (z_1, z_2, z_3)^* \quad (1.2)$$

with z_1, z_2, z_3 a set of integers.

Denoting by $g = \{R|\vec{v}\}$ an element of the Euclidean group in 3 dimensions $E(3)$ where:

$$g\vec{r} = R\vec{r} + \vec{v} \quad (1.3)$$

the symmetry group G of the crystal described by ρ consists of those Euclidean transformations (1.3) which leave ρ invariant:

$$\rho(g\vec{r}) = \rho(\vec{r}) \quad g \in G \subset E(3) \quad (1.4)$$

The corresponding invariance condition expressed for the Fourier components $\hat{\rho}(\vec{k})$ is given by:

$$\hat{\rho}(\vec{k}) = \hat{\rho}(R\vec{k}) e^{iR\vec{k} \cdot \vec{v}} \quad (1.5)$$

One easily verifies that for ρ as in (1.1) its symmetry group G is a 3-dimensional space group: i.e. a subgroup of $E(3)$ whose translations $\vec{a} := \{1|\vec{a}\}$ are lattice translations generating the 3-dimensional space. A 3-dimensional space group G is indeed defined by:

$$(i) \quad G \subset E(3), \quad (ii) \quad G \cap T = \Lambda \simeq \mathbb{Z}^3 \quad (iii) \quad \{\Lambda\} \simeq \mathbb{R}^3 \quad (1.6)$$

where Λ is the set of vectors \vec{n} reciprocal to all $\vec{k} \in \Lambda^*$, solution of:

$$\vec{n}\vec{k} \equiv 0 \pmod{2\pi} \quad (1.7)$$

Accordingly Λ defines a 3-dimensional lattice reciprocal to Λ^* . Its elements, referred to a basis $\vec{a}_1, \vec{a}_2, \vec{a}_3$ dual to the one considered above take the form:

$$\vec{n} = \sum_{i=1}^3 n_i \vec{a}_i, \quad n_1, n_2, n_3 \text{ integers.} \quad (1.8)$$

This explains (1.6) (ii) and (iii).

The homogeneous parts R of the elements of G form a subgroup of the orthogonal group $O(3)$, which is called (crystallographic) point group K : In addition to the translations $\vec{n} = \{1|\vec{n}\}$ which form a normal subgroup Λ of G , translation parts (or inhomogeneous components) $\vec{v} = \vec{v}(R)$ may occur in G for $R \neq 1$ which are not lattice translations and are thus called non-primitive translations. A set of representations $\vec{v}(K) = \{\vec{v}(R) \text{ for } R \in K\}$ of these, together with the pointgroup K and the lattice group Λ yield a full characterization of a space group G . We write:

$$G = \{K, \Lambda, \vec{v}(K)\} \quad (1.9)$$

and mean that a general element $g \in G$ can be written as:

$$g = \{R|\vec{n} + \vec{v}(R)\} \quad (1.10)$$

with $R \in K$, $\vec{n} \in \Lambda$ and $\vec{v}(R) \in \vec{v}(K)$. For more details see e.g. refs. 1 and 2. Concluding this introductory section the reader should note the following basic facts of Euclidean crystallography:

- (i) Any crystal has a space group (of same dimension) as symmetry group.
- (ii) Any matter distribution with space group symmetry is a crystal.
- (iii) The symmetry of a crystal reflects the Euclidean character of the space in which it occurs.

These fundamental properties either are no longer true or give rise to serious problems in the case of so-called incommensurate crystal phases. In the next section the experimental evidence for the existence of such phases is reviewed on the basis of a number of cases.

2. Incommensurate Crystal Phases

The symmetry of a crystal is temperature dependent, first of all because of thermal expansion, which changes the group of lattice translations and thus the whole space group:

$$\Lambda = \Lambda(T) \text{ implying } G = G(T), \quad (2.1)$$

secondly because of possible phase transitions. The space groups of a given crystal for temperatures T_1, T_2 within a same crystal phase are isomorphic, and one usually attaches to a given crystal phase a representative of the corresponding class of isomorphic space groups:

$$G(T_1) \simeq G(T_2) \simeq G. \quad (2.2)$$

This is in general not the case for space groups at temperatures belonging to different crystal phases. For transitions involving a continuous structural change (and thus of second order) very often space groups above and below the transition temperature T_c are in a group - subgroup relation:

$$G(T_0) \simeq G_0 \supseteq G_1 \simeq G(T_1), \text{ for } T_0 > T_c \text{ and } T_1 < T_c. \quad (2.3)$$

Let us consider here the case where this group - subgroup relation also occurs for the corresponding groups of lattice translations. Then we have:

$$\Lambda_1 \subset \Lambda_0 \text{ and thus } \Lambda_1^* \supset \Lambda_0^* \quad (2.4)$$

and one says that the low temperature phase ($T_1 < T_c$) forms a superstructure of the high temperature one ($T_0 > T_c$), which is then called undistorted phase. This nomenclature is based on the fact that the low temperature elementary cell is a multiple of the high temperature one and is thus called supercell.

Consider a basis $\{\vec{a}_{1i}\}$ of Λ_1 and one $\{\vec{a}_{0i}\}$ of Λ_0 . Then one can write:

$$\vec{a}_{1i} = \sum_{j=1}^3 S_{ji} \vec{a}_{0j} \quad (2.5)$$

with S_{ji} integer coefficients. The corresponding reciprocal basis transformation:

$$\vec{a}_{1i}^* = \sum_{j=1}^3 S_{ji}^* \vec{a}_{0j}^* \quad (2.6)$$

involves rational coefficients S_{ji}^* . Using the same basis $\{\vec{a}_{0j}^*\}$ for describing both the high- and low-temperature Bragg reflections, one sees that because of (2.4) all high temperature reflections have integral coefficients (indices) and also occur (in general) in the low-temperature phase. In addition to these, so-called main reflections, others appear, with rational indices now, called satellite reflections.

Equation (2.3) implies restrictions on the possible relative coordinates of the satellite reflections with respect to the main ones. Indeed, e.g. the index of Λ_1 in Λ_0 (i.e. the ratio of the corresponding unit cells) has to be temperature independent. This last property is not observed in the γ - Na_2CO_3 ³). Accordingly P.M. de Wolff et al. ⁴) considered irrational indices as well, which imply incommensurability of the periodic deformation responsible for the satellite reflections with respect to the (undeformed) basic structure one can associate with the main reflections. This first case of incommensurate modulation ⁵) leads to the concept of incommensurate crystal phase. Various examples of such phases will be considered now.

(i) First Example: Na_2CO_3

In fig 1a the various phases of Na_2CO_3 are plotted as a function of temperature. The relative position of the modulation wave vector \vec{q} with respect to a basis $\vec{a}_0^*, \vec{b}_0^*, \vec{c}_0^*$ of the lattice of main reflections is plotted in fig. 1b as a function of temperature. The continuous variation cannot be described in terms of a superstructure satisfying eq. (2.3). Indexing by rational numbers for $\vec{q} = (q_1(T), 0, q_2(T))_*$, is therefore not meaningful. This implies that in the direct space there is no elementary cell of finite volume, and the modulation, expressed in fig. 1c in terms of a set of distances among neighbouring atoms, is incommensurate with respect to the basic structure: the position of the atoms within the unit cell spanned by $\vec{a}_0, \vec{b}_0, \vec{c}_0$ varies from cell to cell in the way suggested by fig. 1d.

At -138°C there is a phase transition to a δ -phase ⁶) which is a superstructure of the β -phase characterized by a commensurate modulation. The locking of the temperature dependent indices in the temperature independent (and rational) ones of the modulation wave vector:

$$\vec{q}: (q_1(T), 0, q_3(T))_* \rightarrow \left(\frac{1}{6}, 0, \frac{1}{3}\right)_* \quad (2.7)$$

is called a "lock-in" phase transition.

(ii) Second Example: K_2SeO_4

This compound has been investigated by Iizumi et al. ⁷). The "intermediate" incommen-

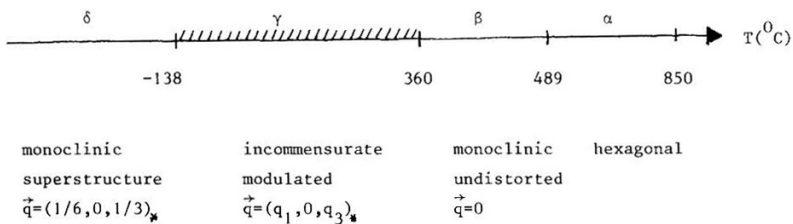


Figure 1a: Phase diagram of Na_2CO_3 .

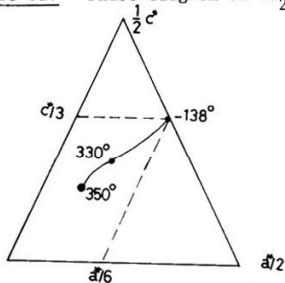


Figure 1b: Temperature dependence of the modulation wave vector.

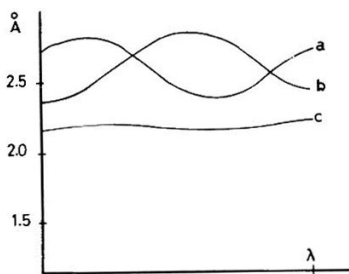


Figure 1c: Modulation of some interatomic distances in $\gamma\text{-Na}_2\text{CO}_3$.

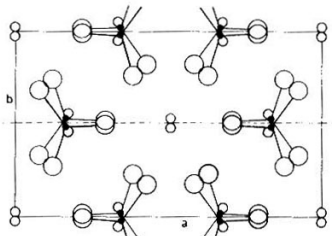


Figure 1d: Atomic positions in the average unit cell of $\gamma\text{-Na}_2\text{CO}_3$ projected along the c -direction.

surate phase indicated on fig. 2a is induced by the softening of a phonon mode as revealed by the temperature dependent dispersion branches (see fig. 2b). Again there is a continuous varying ratio of the modulation periodicity with respect to an underlying lattice periodicity as a function of the temperature (fig. 2c) which implies incommensurability. Below 53 K, in the ferroelectric phase, such a dependence disappears and the corresponding modulation wave vector shows a lock-in phase transition:

$$\vec{q}: (\frac{1-\delta(T)}{3}, 0, 0)_* \rightarrow (\frac{1}{3}, 0, 0)_* \quad (2.8)$$

(iii) Third Example: TaSe₂

This compound also shows a displacive incommensurate modulation and a lock-in transition to a (commensurate) superstructure (fig. 3a) with respect to an undistorted hexagonal high temperature phase (fig. 3b).

The interest of this example lies in the two-dimensional character of the modulation, as revealed by a set of main reflections and satellites observed (fig. 3c). The deviation from the rational value of $\frac{1}{3}$ is a continuous function of the temperature in the incommensurate phase (fig. 3d). In this example the modulation is induced by a charge density wave (CDW) in the conduction electron gas of this compound. The reported results have been taken from a paper by Moncton, Axe and DiSalvo ⁸⁾ In the same group of layered structures other examples of incommensurate crystal phases have also been reported ⁹⁾ by another team.

(iv) Fourth Example: (TTF)₇I_{5-x}

The structure of this compound can be described in terms of two subsystems. The first one formed by the tetrathiafulvalene molecules (TTF = (C₃S₂H₂)₂) with space group symmetry G₁ = C2/m and lattice A₁, and the second one consisting of Iodine atoms which has space group symmetry G₂ = A2/m and lattice A₂. The two lattices are mutually incommensurate (fig. 4): one speaks of a "composite" crystal. In addition one observes displacive modulations due to the interaction between the two subsystems. The structure including the modulation waves, has been investigated in detail by Johnson and Watson ¹⁰⁾.

(v) Fifth Example: Hg_{3-δ}AsF₆

This compound is also of the composite type and involves at low temperature three mutually incommensurate ordered subsystems. The first one, formed by the As and F atoms

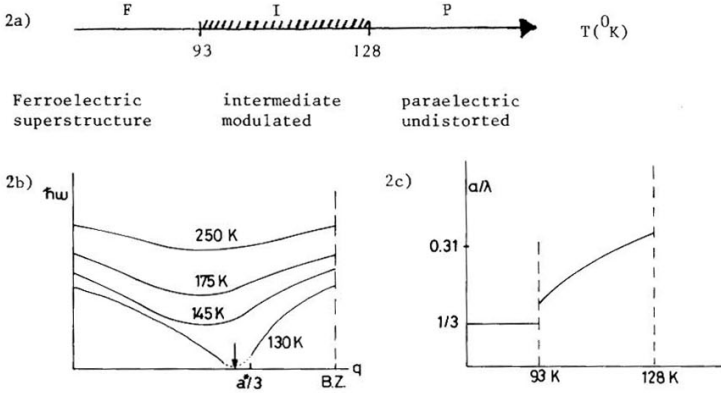


Figure 2: K_2SeO_4 a) Phase diagram. b) Softening of the dispersion branches. c) Ratio of the modulation and the lattice periodicities vs. temperature.

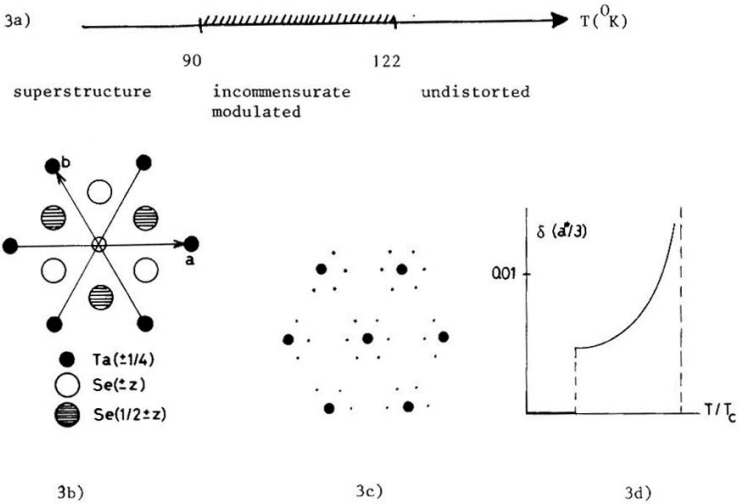


Figure 3: $TaSe_2$ a) Phase diagram. b) Undistorted structure. c) Diffraction pattern. d) Change in the modulation wave vector vs. temperature.

has space group symmetry $G_1 = I4_1/amd$; the second one involves a set of parallel chains of mercury atoms along the $[100]$ direction perpendicular to the previously mentioned tetragonal axis and has space group symmetry $G_2 = A2/m$. The third subsystem consists of the mercury chains along the $[010]$ direction defined by the AsF_6 subsystem, and has space group symmetry $G_3 = B2/m$ (fig. 5a). Incommensurability arises because the periodicity along the Hg chains (a_{Hg}) does not fit with that of the AsF_6 lattice (a_{AsF_6}) (fig. 5b). One has:

$$(3 - \delta)a_{Hg} \approx a_{AsF_6} \quad (2.9)$$

with $\delta \approx 0.18$ at room temperature and temperature dependent ($\delta = \delta(T)$): the same δ -value also appears in the (nonstoichiometric) unit formula of this compound. This only describes the gross structure: small deviations from tetragonality and induced modulation waves are also observed ¹¹).

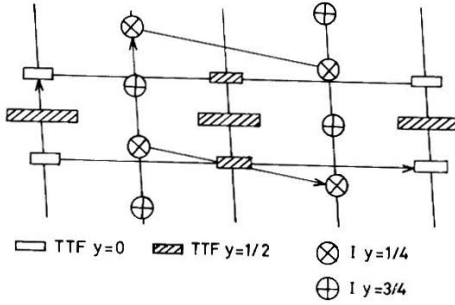
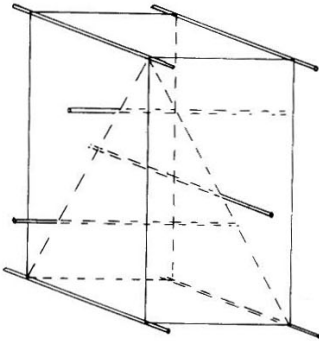
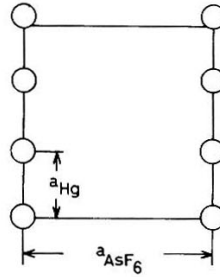


Figure 4: The structure of the composite compound $\text{TTF}_x\text{I}_{5-x}$



5a)



5b)

Figure 5: $\text{Hg}_{3-0}\text{AsF}_6$ a) Schematic representation of the mercury chain arrays. b) Incommensurability between the lattice constants of the AsF_6 lattice and the mercury chain lattice.

3. Problems

Incommensurability of a crystal phase implies that:

- The crystal symmetry is not one of the 230 3-dimensional space groups.
- The Fourier wave vectors occurring in the crystal density are not necessarily elements of a reciprocal lattice (in 3-dimensions). Nevertheless the physical properties of incommensurate crystal phases are essentially the same as those typical for a (normal or commensurate) crystal. It is even difficult to indicate which properties depend in a critical way on incommensurability. Accordingly this naturally leads to the basic question: "What is a crystal?"
- The Euclidean symmetry of an incommensurate crystal phase is fairly low (e.g. no 3-dimensional lattice periodicity is possible) and does not explain the regularities of the diffraction pattern: main reflections, satellites, systematic extinctions, a.s.o. Therefore the 3-dimensional Euclidean symmetry is a bad characterization of the crystal in question. But then the second basic question arises: "Which symmetry is a "good" one?". In order to give an answer to this question the concept of internal dimension is introduced.

4. Internal Dimensions

The concept of internal dimension is illustrated here by two typical examples. A first one involving a displacive modulation of a 1-dimensional periodic chain; a second one based on a simple model for a 2-dimensional composite crystal.

(i) First Example: Displacive modulation

The modulated crystal considered is obtained from a basic structure with space group symmetry (fig. 6a) by a periodic deformation called modulation (fig. 6b). The characteristic diffraction pattern shows main reflections and satellites (fig. 6c).

In order to recover lattice periodicity the diffraction pattern is considered as belonging to the projection of a reciprocal lattice Σ^* defined in a superspace by adding to the positional dimensions the necessary internal ones. This corresponds to view the modulated crystal as intersection of a pattern with lattice periodicity Σ and the position (sub)space (fig. 6d). Typical elements of Σ^* are of the form:

$$\mathbf{k} = (\vec{\mathbf{K}} + \vec{\mathbf{q}}, \vec{\mathbf{q}}_{\mathbf{I}}) \in \Sigma^* \quad (4.1)$$

with $\vec{\mathbf{K}}$ the wave vector of a main reflection ($\vec{\mathbf{K}} \in \Lambda^*$), $\vec{\mathbf{q}}$ that of a satellite and $\vec{\mathbf{q}}_{\mathbf{I}}$ the corresponding internal component. Giving to the superspace an Euclidean structure one gets from (4.1) the corresponding expressions for elements of the lattice Σ :

$$\mathbf{s} = (\vec{\mathbf{n}}, -\vec{\mathbf{n}}_{\mathbf{I}} + \vec{\mathbf{d}}_{\mathbf{I}}) \in \Sigma \quad (4.2)$$

with $\vec{\mathbf{n}}$ a symmetry translation of the basic structure ($\vec{\mathbf{n}} \in \Lambda$), and $-\vec{\mathbf{n}}_{\mathbf{I}}$ the corresponding internal component related to $\vec{\mathbf{q}}_{\mathbf{I}}$ by the condition:

$$\vec{\mathbf{n}} \cdot \vec{\mathbf{q}} = \vec{\mathbf{n}}_{\mathbf{I}} \cdot \vec{\mathbf{q}}_{\mathbf{I}} \quad (4.3)$$

The vectors $\vec{\mathbf{d}}_{\mathbf{I}}$ generate a lattice D expressing (in the internal space) the periodicity of the modulation (fig. 6e). From the atomic positions of the modulated crystal one gets by Σ the corresponding ones of the (periodic) pattern in superspace called super-crystal. Typical situations arising from commensurate and from incommensurate modulations are given in fig. 6f. Note that the number of translational inequivalent atoms in the supercell of the position subspace is the same as that in the unit cell in superspace. The corresponding analytic expression for a supercrystal $\rho_{\mathbf{S}}$ is:

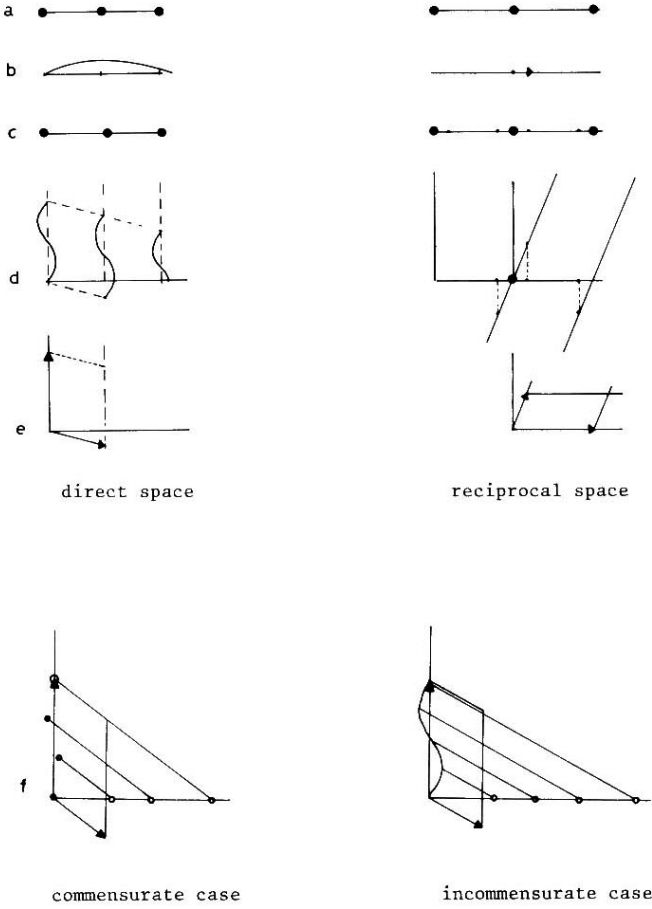


Figure 6: One-dimensional modulated crystal. a) Basic structure. b) Modulation. c) Modulated crystal and typical diffraction pattern. d) Superspace description. e) Superspace lattices. f) Atomic positions in the supercrystal.

$$\rho_S(\vec{r}_O, \vec{r}_I) = \sum_{\vec{k}} \hat{\rho}(\vec{k}) e^{i(\vec{k}\vec{r}_O + \vec{k}_I\vec{r}_I)} \quad (4.4)$$

when the crystal ρ is defined by:

$$\rho(\vec{r}_O) = \sum_{\vec{k}} \hat{\rho}(\vec{k}) e^{i\vec{k}\vec{r}_O} \quad (4.5)$$

Here \vec{r}_O indicates a general vector in the position space, \vec{r}_I one in the internal space; the Fourier coefficient $\hat{\rho}(\vec{k})$ is correspondingly the same in (4.4) and (4.5): One verifies that indeed:

$$\rho(\vec{r}_O) = \rho_S(\vec{r}_O, 0) \quad (4.6)$$

(ii) Second Example: Composite crystal

The model considered consists of two subsystems, each one having lattice periodicity (Λ_1 and Λ_2 , respectively). In the example Λ_1 is generated by \vec{a}_1 and \vec{b}_2 ; Λ_2 by \vec{a}_2 and \vec{b}_1 ; such that one has:

$$\vec{b}_1 = \vec{b}_2 \quad \text{and} \quad \vec{a}_1, \vec{a}_2 \quad \text{incommensurate} . \quad (4.7)$$

Applying to this model the same definition of supercrystal as in (4.4) and (4.5) by defining, e.g.:

$$(\vec{a}_1^*)_I = (\vec{b}_1^*)_I = 0 \quad \text{and} \quad (\vec{a}_2^*)_I \neq 0 \quad (4.8)$$

one gets a supercrystal as pattern of lines in 3-dimensions whose 2-dimensional intersection (with the position space) gives the composite crystal (fig. 7a,b). The additional internal dimension allows shifts in the relative position of the two subsystems. Yet sections at different value of the internal coordinates yield equivalent (i.e. the same) composite crystal: this because of the incommensurability between \vec{a}_1 and \vec{a}_2 . In the commensurate case the supercrystal would here also consist of discrete points as in the previous example.

5. Crystal definition and crystal symmetry revised

The two examples of section 4 are here formalized in order to get an answer to the questions formulated in section 3.

A crystal is defined by requiring for its density function $\rho(\vec{r})$ a Fourier decomposition of the form:

$$\rho(\vec{r}) = \sum_{\vec{k} \in M^*} \hat{\rho}(\vec{k}) e^{i\vec{k}\vec{r}} \quad (5.1)$$

with $M^* \approx \mathbb{Z}^{3+d}$, a so called \mathbb{Z} -module of rank $3+d$ and dimension 3. The rank is the number of linearly independent (with respect to the integral linear combination) vectors generating the module M^* (basis vectors). The dimension is that of the vector space spanned (over the real numbers) by these basis vectors. For example in the classical case of eq. (1.1): $M^* = \Lambda^* \approx \mathbb{Z}^3$: The basis of M^* is $\vec{a}_1^*, \vec{a}_2^*, \vec{a}_3^*$ (rank 3) which is also basis of the (reciprocal) vector space (dimension 3). Thus $d = 0$.

In the previous example (fig. 6) of one-dimensional modulated crystal with incommensurate \vec{q} one has: $M^* \approx \mathbb{Z}^2$; Basis of M^* :

$\vec{k} = \vec{a}^*, \vec{q}$ (rank 2). The reciprocal space is generated by \vec{a}^* (dimension 1). Thus $d = 1$.

In the example of the composite crystal of fig. 7 one has: $M^* \approx \mathbb{Z}^3$; Basis of M^* :

$\vec{a}_1^*, \vec{a}_2^*, \vec{b}_1^* = \vec{b}_2^*$ (rank 3). The reciprocal space is spanned by \vec{a}_1^*, \vec{a}_2^* (dimension 2).

Thus $d = 1$. Quite in general: We call a crystal commensurate if $\text{rank } M^* = \dim. M^*$ and incommensurate if $\text{rank } M^* > \dim. M^*$.

In order to define the symmetry of a crystal one admits (reducible) Euclidean transformations in the position and in the internal space. Thus:

$$g = (g_0, g_I) \in E(3) \times E(d) \quad (5.2)$$

where we use the same notation as in section 1:

$$g_0 = \{R_0 | v_0\} \in E(3), \quad (5.3)$$

$$g_I = \{R_I | \vec{v}_I\} \in E(d)$$

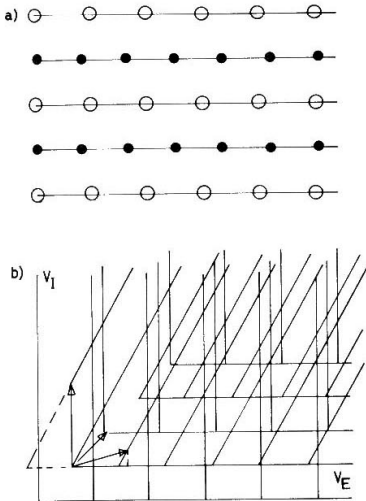


Fig. 7 a) Two dimensional composite crystal. b) Corresponding supercrystal description.

One then chooses a basis $\vec{a}_1^*, \vec{a}_2^*, \dots, \vec{a}_{3+d}^*$ of M^* such that $\vec{a}_1^*, \vec{a}_2^*, \vec{a}_3^*$ spans a 3-dim lattice Λ^* (describing the main reflections in the modulated case, and an appropriate set of reflections in the composite crystal case), and a basis $\vec{b}_1^*, \vec{b}_2^*, \dots, \vec{b}_d^*$ in the internal space. (This basis is taken formally at first and subject to crystallographic restrictions afterwards. The reader is referred to a set of papers on the subject for more details^{12, 13}). Then for any $\vec{k} \in M^*$ appearing in (5.1), which can always be written as:

$$\vec{k} = \sum_{i=1}^{3+d} z_i \vec{a}_i^* \quad , \quad z_1 \dots, z_{3+d} \text{ integers} \quad , \quad (5.4)$$

a corresponding internal component \vec{k}_I is defined by:

$$\vec{k}_I = \sum_{j=1}^d z_{3+j} \vec{b}_j^* \quad (5.5)$$

with coefficients as in (5.4).

A transformation $g \in E(3) \times E(d)$ is a symmetry for the crystal ρ as in (5.1) if and only if the relation:

$$\hat{\rho}(\vec{k}) = \hat{\rho}(R_O \vec{k}) e^{iR_O \vec{k} \cdot \vec{v}_O} + iR_I \vec{k}_I \cdot \vec{v}_I \quad , \quad (5.6)$$

is satisfied for each of its Fourier coefficients. Note that $\{R_O | \vec{v}_O\}$ is in general not a Euclidean symmetry for $\rho(\vec{r})$. One can recover the Euclidean character of the symmetry group of G by embedding the \mathbb{Z} module M^* as a $(3+d)$ -dimensional lattice Σ^* in the superspace:

$$\vec{k} = \sum_{i=1}^{3+d} z_i \vec{a}_i^* \Rightarrow k = \sum_{i=1}^{3+d} z_i a_i^* \quad (5.7)$$

where $\{a_i^*\}$ is a basis for $V_S = V_E \oplus V_I$, V_E being the position (sub)space and V_I the internal one. The integral coefficients in the two expressions of (5.7) are correspondingly the same. The supercrystal is then defined by:

$$\rho_S(r) = \sum_{k \in \Sigma^*} \hat{\rho}(k) e^{ikr} \quad (5.8)$$

with $r = (\vec{r}_E, \vec{r}_I) \in V_S$, $k = (\vec{k}_E, \vec{k}_I)$, $\vec{k}_E = \vec{k}$ and \vec{k}_I as in (5.5). Furthermore

$$\hat{\rho}(k) = \hat{\rho}(\vec{k}) \quad \text{if } k \text{ corresponds to } \vec{k} \text{ as in (5.7)}. \quad (5.9)$$

The symmetry of ρ_S is the Euclidean one and expressed by the condition:

$$\rho_S(g_E \vec{r}_E, g_I \vec{r}_I) = \rho_S(\vec{r}_E, \vec{r}_I) \quad , \quad (5.10)$$

$g_E \in E(3)$ and $g_I \in E(d)$.

Note that writing $g_E = g$, using (5.8) and (5.9) the condition (5.10) is equivalent with the previous one (5.6) formulated in terms of Fourier coefficients. As (by construction) ρ_S has lattice symmetry the symmetry group G of ρ_S (and thus of ρ also) is a $(3+d)$ -dimensional space group. This group has additional properties because of the special rôle played in V_S by the positional subspace $V_O = V_E$. Accordingly G is called a $(3,d)$ -dimensional superspace group ¹²⁾.

6. Application

The main results of the extension of crystal definition and of crystal symmetry given in the previous section can be formulated as follows:

(i)

A full classification of all symmetries of commensurate as well as incommensurate crystal phases is possible.

(ii)

The symmetry of a crystal having n positional dimensions and d internal dimensions is a $(n+d)$ -dimensional space group having additional properties and which is therefore called an (n,d) -dimensional superspace group.

(iii)

There is a finite number of inequivalent symmetry groups of given dimensions.

Without going into details let us call equivalent two superspace groups such that:

- They have the same (n,d) -dimension.

- There is a crystal structure having these two superspace groups as symmetry group.

The usual concepts appearing in the Euclidean crystallography allows a natural generalization in the superspace formulation. So in particular one also gets Bravais classes for the classification of (n,d) dimensional lattices Σ . These classes have been determined for n and d up to 3. Their number for $n = 3$ is indicated on the following table (see also ref. 14):

Number of inequivalent Bravais classes

dimension (n,d)	$(3,0)$	$(3,1)$	$(3,2)$	$(3,3)$
total number	14	24	83	215

The $(3,1)$ -dimensional superspace groups have been classified and a full list will be published soon ¹⁵⁾. Furthermore the superspace groups of the incommensurate crystal phases exemplified in section 2 have been determined ¹³⁾. We do not indicate these here in order to avoid a lengthy explanation of the notation used. Instead of that a glimpse of the geometrical and structural meaning of superspace symmetries will be given in the following section: on the basis of a specific example attention is drawn to the fact that this type of symmetry may be relevant in the case of a commensurate crystal as well.

7. Structural Properties and Superspace Symmetries

Four particular cases are reported here: one occurring in Na_2CO_3 as exemplification of a displacive modulated crystal; two involving composite crystals $(\text{TTF})_{7-5-x}\text{I}_{5-x}$ and $\text{Hg}_{3-\delta}\text{AsF}_6$ for which the basic characteristics have been presented in section 2 and finally an example of a not incommensurate phase where a case of so called "diffraction enhancement of symmetry" is analysed in terms of superspace symmetries.

(i) Displacive modulated crystal: $\gamma\text{-Na}_2\text{CO}_3$

In the γ -phase of Na_2CO_3 (see fig 1a) the general form of the Fourier wave vector is:

$$\vec{k} = z_1 \vec{a}^* + z_2 \vec{b}^* + z_3 \vec{c}^* + z_4 \vec{q} \quad (7.1)$$

with \vec{a}^* , \vec{b}^* , \vec{c}^* spanning the conventional monoclinic unit cell of the basic structure, \vec{q} the modulation wave vector and z_1, \dots, z_4 integer coefficients. Accordingly $M^* \approx \mathbb{Z}^4$ and the internal dimension is $d = 1$. Furthermore systematic extinctions in the x-ray diffraction pattern are observed ⁵⁾ for:

$$(h, 0, l, m), m \text{ odd, or in the notation (7.1) for } (z_1, 0, z_3, z_4)_* \text{ and } z_4 \text{ odd.} \quad (7.2)$$

The symmetry of the basic structure is $G_o = C2/m$, with unique axis \vec{b} . In this setting the modulation wave vector (in the mirror plane) is:

$$\vec{q} = (\alpha, 0, \gamma)_* \quad (7.3)$$

with α, γ real coefficients (and temperature dependent). The polarization of the displacive modulation waves is transverse, along the unique axis \vec{b} .

The superspace symmetry group is (3,1)-dimensional, and contains as element ^{5) 16)}:

$$g = \{R|v\} = \left\{ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \right\} \{ (000\frac{1}{2}) \} \quad (7.4)$$

where the transformation matrices refer to a basis reciprocal to the one adopted in (7.1) for describing the Fourier spectrum. According to eq. (5.6) one gets from the symmetry (7.4) the observed systematic extensions (7.2). Furthermore this same symmetry element is consistent with the transverse polarization of the modulation.

(ii) Composite crystals $(\text{TTF})_{7-5-x}\text{I}_{5-x}$ and $\text{Hg}_{3-\delta}\text{AsF}_6$

As already mentioned in section 2, $(\text{TTF})_{7-5-x}\text{I}_{5-x}$ is a composite crystal (at room tempera-

ture) involving two incommensurate subsystems: the TTF-subsystem and the Iodine-subsystem, with lattices Λ_1 and Λ_2 , respectively. The superspace group of the basic structure is (3,1)-dimensional and given by $P_{Ts}^{C2/m}$. (see ref. 13 for more details). The actual structure can be obtained by considering in addition displacive modulation waves, which have been determined in great detail in the structural investigation by Johnson and Watson (ref. 10). There are two sets of modulation waves:

- one with lattice periodicity Λ_1 produced by the TTF subsystem on the iodine-subsystem
- one with periodicity Λ_2 due to the action of the iodine subsystem on the array of TTF-molecules.

The remarkable fact is that all these modulation waves have the symmetry imposed by the superspace group $P_{Ts}^{C2/m}$, so that in this case basic structure and modulated one have the same superspace symmetry.

In the case of $Hg_{3-6}AsF_6$ there are three incommensurate subsystems (see section 2 and fig. 5). Choosing as origin a conventional one on the basis of the AsF_6 subsystem (space group $G_1 = I4_1/amd$), representatives of the other two subsystems, say $Hg(1)$ and $Hg(2)$, have position at:

$$O_2 = (x, \frac{1}{2}, \frac{1}{2}) \quad \text{and} \quad O_3 = (0, y, 0) \quad (7.5)$$

respectively, where the coordinates are expressed in the tetragonal unit cell of G_1 . At low temperature ordering in the mercury chains occur such that:

$$2(x - y + \frac{1}{2}) = \frac{1}{3-\delta} \quad (7.6)$$

and this phenomenon is revealed by extinctions of the Bragg reflections at: $(3-\delta, 3-\delta, 0)_*$, where the lattice Λ_1^* of the AsF_6 subsystem has been used as reference system. The same extinctions and the same structural relations among the three subsystems are required by (3,1)-dimensional superspace group symmetries. These symmetries are mirrors mapping mercury subsystems onto each other associated with relative shifts of these subsystems. Therefore these are not Euclidean 3-dimensional symmetries for the composite crystal. This shows the relevance of the approach proposed. Again interaction among the subsystems gives rise to additional displacive modulation which in terms of crystallographic symmetries requires an additional internal dimension leading to a (3,2)-dimensional space group. (see ref. 13 for more details).

(iii) Diffraction enhancement of symmetry

Consider a 2-dimensional crystal with atoms arranged according to a space group symmetry $G_0 = p3$. As indicated in fig. 8 there are three inequivalent types of atoms, which

in the unit cell have location:

$$P_1 \text{ at } (\frac{2}{3}, \frac{1}{3}), \quad P_2 \text{ at } (\frac{1}{3}, \frac{2}{3}) \quad \text{and} \quad (7.7)$$

$$P_3 \text{ at } (x, y), \quad (\bar{y}, x-y) \text{ and } (y-x, \bar{x}) \quad \text{for } x = \frac{1}{3} \quad \text{and } y = 0.$$

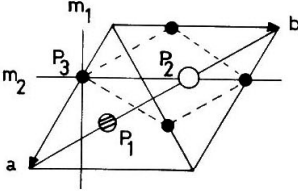


Fig. 8: Example of 2-dim.crystal showing diffraction enhancement of symmetry

As pointed out by T. Matsumoto ¹⁷⁾ such a crystal structure gives rise to an enhancement of diffraction symmetry in the sense that its diffraction pattern has point group symmetry $K_{di} = 6mm$, whereas the point group of the structure is $K_o = 3$. Let us label the Bragg reflections by $(hk)_*$ in a basis of the reciprocal lattice of $p3$, and consider the reflections $(1,1)_*$ and $(\bar{1},2)_*$ as generators of main reflections and the reflections at $(1,0)_*$ and $(0,1)_*$ as satellite reflections. One can then apply the superspace approach by adding to these latter a component in a 2-dimensional internal space. One then finds for the structure indicated above a superspace group

$$G = \begin{matrix} p3ml \\ p \\ p3ml \end{matrix}$$

with among the generators:

$$g_1 = \{(3,3) | (0,0,\frac{2}{3},\frac{1}{3})\} \text{ and } g_2 = \{(m_1, m_1) | (0,0,0,\frac{1}{2})\}$$

implying a point group $K \approx 3m$ and thus a Laue point group symmetry $6mm$. In this example the "accidental" value $x = \frac{1}{3}$ and $y = 0$ for the coordinates of atoms of type P_3 is connected with the presence of superspace symmetries, which would not be present for more general values of x and y . Note that in this example these "non-Euclidean" symmetries appear even though the crystal has a space group symmetry.

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