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Symmetry of Incommensurate Crystal Phases. I. Commensurate Basic Structures

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Abstract

The superspace-group approach [Janner & Janssen (1977), *Phys. Rev. B*, **15**, 643–658] is used to solve the symmetry problem of incommensurate crystal phases in the case of displacive- and occupation-wave modulation. Generalization is given to cover magnetic modulation as well. The symmetry conditions imposed by the superspace group on the crystal structure are derived and applied to the following incommensurate crystals, whose structures have been discussed in the literature independently from the present point of view: K_2SeO_4, $2H$-$TaSe_2$, $NaNO_2$ and Cr. The superspace groups describing the symmetry of these compounds are indicated and the structural implications of the corresponding symmetry elements discussed.

1. Introduction

There are crystals which at a given phase transition undergo a periodic deformation. The existence of such a deformation can be seen in their (X-ray, electron or neutron) diffraction pattern from the appearance of additional Bragg reflection peaks (called satellite reflections). When the indices of these satellites in the reference system of the other sharp peaks (the main reflections) involve irrational numbers, and this is in particular the case when the indices change continuously with temperature [see *e.g.* γ-Na_2CO_3 as reported by van Aalst, den Hollander, Peterse & de Wolff (1976)], the crystal phase is called an incommensurate modulated structure. In the case of rational indices the term superstructure is standard.

A modulated crystal does not have a three-dimensional lattice periodicity. Hence its Euclidean symmetry is not a three-dimensional space group. However, it is possible, as de Wolff (1974), (1977) and we [Janner & Janssen (1977)] have shown, to recover space-group symmetry by constructing a periodic structure in a suitably defined space such that the crystal considered appears as a three-dimensional section of it. The higher-dimensional space is called the *superspace* and the constructed periodic structure in it the *supercrystal*; the additional dimensions introduced span the *internal space*. This name has been adopted because often the additional dimensions correspond to internal degrees of freedom (like the phase of the modulation).

The Euclidean symmetry of the supercrystal is a space group of dimension higher than three. However, not all space groups of this dimension are admissible, because there are additional requirements which express the special role of the three-dimensional subspace called *position space* or *external space*, in which the positions of the modulated crystal are defined. The admitted groups are called *superspace groups*. The mathematical theory of these groups can be be found in Janner (1977), Janssen (1977) and in a more detailed paper of Janner & Janssen (1979). A brief summary of the main definitions and properties is given in §2. The loosening of the conditions leading to superspace groups is in principle possible but, up to now, no experimental evidence could be found for justifying a more general treatment.

The aim of this paper is to show the relevance of the superspace-group concept for the description of incommensurate crystal structures. To that end a number of modulated crystals are investigated. A modulated crystal structure can be characterized by a superspace group (just as a normal crystal is described by a three-dimensional space group) which is uniquely determined by the structure, up to equivalence. Moreover, this symmetry group is expected to be of importance for the study of other physical properties, but this point is not discussed here.

The concept of a supercrystal is treated in §3, and applied in further sections to a number of modulated crystal structures. The examples are chosen widely and involve displacive modulation in ionic (K_2SeO_4) or metallic layered crystals ($TaSe_2$), occupation wave modulation ($NaNO_2$) and spin wave modulation (Cr). In this first part we restrict our considerations to systems for which a basic structure can be defined having a three-dimensional space group as symmetry (commensurate basic structure). The case where this is no longer possible (incommensurate basic structure) will be treated in part II (Janner & Janssen, 1980).

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2. Superspace groups

Consider a $(3 + d)$-dimensional Euclidean space which is the direct sum of two orthogonal subspaces: the three-dimensional *position space* V_E and the d-dimensional *internal space* V_I. A *superspace group*, G, is a $(3 + d)$-dimensional space group with d linearly independent translations in V_I which is a subgroup of the direct product $E(3) \times E(d)$ of Euclidean groups. The latter means that an element of a superspace group can be written as a pair: $g = (g_E, g_I)$, where g_E is a Euclidean transformation of the position space and g_I one of the internal space. We denote a Euclidean transformation by $\{R|v\}$, where R is an orthogonal transformation and v a translation, and we write

$$g = (g_E, g_I) = (\{R_E|\mathbf{v}_E\}, \{R_I|\mathbf{v}_I\}) = \{R|v\}. \quad (1)$$

The elements of the superspace $V = V_E \oplus V_I$ and, *par abus de language*, the translations in V also can be written as pairs: $v = (\mathbf{v}_E, \mathbf{v}_I)$. A basis for the lattice Σ of a superspace group can be chosen in the form

$$\text{and} \qquad \begin{aligned} a_i &= (\mathbf{a}_i, -\mathbf{b}_{d+i}), \qquad i = 1,2,3 \\ a_{3+j} &= (0, \mathbf{b}_j), \qquad j = 1,2,\ldots,d, \end{aligned} \quad (2)$$

where $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ form a basis of V_E and $\mathbf{b}_1, \ldots, \mathbf{b}_d$ one of V_I. Expressing the internal components of a_i in terms of the latter one gets a $d \times 3$ matrix σ,

$$\mathbf{b}_{d+i} = \sum_{j=1}^{d} \sigma_{ji}\, \mathbf{b}_j, \qquad i = 1, 2, 3. \quad (3)$$

Hence the lattice Σ is determined by $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ (spanning a lattice Λ in V_E), by $\mathbf{b}_1, \ldots, \mathbf{b}_d$ (spanning a lattice D in V_I) and the matrix σ.

The reciprocal lattice Σ^* has a basis

$$\text{and} \qquad \begin{aligned} a_i^* &= (\mathbf{a}_i^*, 0), \qquad i = 1, 2, 3 \\ a_{3+j}^* &= (\mathbf{a}_{3+j}^*, \mathbf{b}_j^*), \qquad j = 1, 2, \ldots, d, \end{aligned} \quad (4)$$

where $\{\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*\}$ is reciprocal to $\{\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\}$ in V_E and $\{\mathbf{b}_1^*, \mathbf{b}_2^*, \ldots, \mathbf{b}_d^*\}$ is reciprocal to $\{\mathbf{b}_1, \mathbf{b}_2, \ldots, \mathbf{b}_d\}$ in V_I. Expressing $\mathbf{a}_{3+j}^*$ in terms of $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$ one obtains the same matrix σ,

$$\mathbf{a}_{3+j}^* = \sum_{i=1}^{3} \sigma_{ji}\, \mathbf{a}_i^*, \qquad j = 1, 2, \ldots, d. \quad (5)$$

As we shall explain in the next section the reciprocal vectors $\mathbf{a}_1^*, \ldots, \mathbf{a}_{3+d}^*$ allow a characterization of the Bragg reflection peaks in crystal diffraction, which by (4) will be associated with the projection of reciprocal-lattice points in $(3 + d)$-dimensions. In direct space this corresponds to taking a section of a corresponding periodic pattern defined in superspace. In this connection the matrix σ plays a fundamental role.

The point group K of a superspace group has elements R which can be written as pairs of orthogonal transformations: $R = (R_E, R_I)$. The elements R_E form a three-dimensional crystallographic point group K_E in V_E, the elements R_I a d-dimensional one in V_I.

3. The supercrystal

Firstly we extend the concept of a (three-dimensional) crystal in order to ensure that an incommensurate crystal phase can still be considered as a crystal. We define a *crystal* as a matter distribution described by a scalar density $\rho(\mathbf{r})$ such that it admits a Fourier decomposition

$$\rho(\mathbf{r}) = \sum_{\mathbf{k}} \hat{\rho}(\mathbf{k})\, e^{i\mathbf{k}\mathbf{r}} \quad (6)$$

with wave vectors $\mathbf{k}$ of the form

$$\mathbf{k} = \sum_{i=1}^{3+d} z_i\, \mathbf{a}_i^* \equiv (z_1, z_2, \ldots, z_{3+d})_*, \quad (7)$$

where the z_i are integers, the $\mathbf{a}_i^*$ $(i = 1, 2, \ldots, 3 + d)$ span the three-dimensional space and d is minimal. Clearly, for $d = 0$ this definition reduces to the ordinary one and then describes a *commensurate crystal phase*. If $d > 0$ one gets an *incommensurate crystal phase*. We adopt the convention that $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$ form a basis for the main reflections. Then $\mathbf{a}_4^*, \ldots, \mathbf{a}_{3+d}^*$ determine the matrix σ *via* (5).

With the function $\rho(\mathbf{r})$ describing a crystal in V_E we associate, in the way indicated below, a function $\tilde{\rho}(\mathbf{r}, \mathbf{t})$ in V which defines what we call a *supercrystal*. We first assume that one can distinguish in (7) main reflections from satellites and that the former belong to a lattice Λ^* spanned by $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$. Then a matrix σ is determined *via* (5) by the remaining vectors $\mathbf{a}_4^*$, ..., $\mathbf{a}_{3+d}^*$. One can then choose a lattice D^* in the internal space and construct, in the way indicated in §2, a lattice Σ^* with basis given as in (4). To each vector $\mathbf{k}$ of (7) there corresponds now exactly one element k of Σ^* by

$$k = \sum_{i=1}^{3+d} z_i\, a_i^* = (\mathbf{k}, \mathbf{k}_I),$$

with

$$\mathbf{k}_I = \sum_{j=1}^{d} z_{3+j}\, \mathbf{b}_j^*. \quad (8)$$

Writing $r = (\mathbf{r}, \mathbf{t})$ for a general vector in V, the supercrystal associated with (6) is defined by

$$\tilde{\rho}(r) = \sum_{k} \tilde{\rho}(k)\, e^{ikr}, \quad (9)$$

where $\hat{\rho}(k) \overset{\text{def}}{=} \hat{\rho}(\mathbf{k})$ and $k \in \Sigma^*$. Note that the crystal appears as the $\mathbf{t} = 0$ section of the associated supercrystal.

The superspace group of $\tilde{\rho}$ is uniquely determined by $\tilde{\rho}$ (up to equivalency) and the symmetry condition for $\tilde{\rho}$ by g as in (1),

$$\tilde{\rho}(g_E\,\mathbf{r}, g_I\,\mathbf{t}) = \tilde{\rho}(\mathbf{r}, \mathbf{t}), \tag{10}$$

is also expressible in terms of the Fourier coefficients of ρ by

$$\hat{\rho}(\mathbf{k}) = \hat{\rho}(\mathbf{k}')\, e^{iRk.v}, \tag{11}$$

where $k = (\mathbf{k}, \mathbf{k}_I)$ and $Rk = (\mathbf{k}', \mathbf{k}'_I)$.

4. Displacive modulation

Consider a commensurate basic structure, *i.e.* a distribution of points with space-group symmetry. Hence the position of these points can be written as

$$\mathbf{r}_0(\mathbf{n}, j) = \mathbf{n} + \mathbf{r}_j, \tag{12}$$

where $\mathbf{n}$ labels the cell ($\mathbf{n} \in \Lambda$) and $\mathbf{r}_j$ the position of the jth point in the unit cell. If g_0 is an element of the space group G_0, one has the relation

$$g_0\, \mathbf{r}_0(\mathbf{n}, j) = \mathbf{r}_0(\mathbf{n}', j'). \tag{13}$$

A crystal phase with displacive modulation occurs if the atomic positions can be described by

$$\mathbf{r}(\mathbf{n}, j) = \mathbf{r}_0(\mathbf{n}, j) + \sum_{\mathbf{q}} \mathbf{f}_j(\mathbf{q}) \exp[i\mathbf{q}(\mathbf{n} + \mathbf{r}_j)]. \tag{14}$$

The modulation is incommensurate if at least one of the vectors $\mathbf{q}$ does not have a multiple belonging to the reciprocal lattice Λ^* of the basic structure. Application of (9) gives for the atom positions of the supercrystal

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

The symmetry condition for this supercrystal is expressible in the form

$$gr(\mathbf{n}, j, \mathbf{t}) = r(\mathbf{n}', j', \mathbf{t}'), \qquad \text{for } g = (g_E, g_I). \tag{16}$$

This equation implies invariance of the basic structure, *i.e.* the condition

$$R_E(\mathbf{n} + \mathbf{r}_j) + \mathbf{v}_E = \mathbf{n}' + \mathbf{r}_{j'}, \tag{17}$$

thus $g_E \in G_0$, and a corresponding invariance of the modulation

$$R_E\, \mathbf{f}_j(\mathbf{q}) = \mathbf{f}_{j'}(\mathbf{q}') \exp(iRq.v + i\mathbf{K}\mathbf{r}_{j'}), \tag{18}$$

where $q = (\mathbf{q}, \mathbf{q}_I)$, $\mathbf{q}' = R_E\,\mathbf{q} + \mathbf{K}$ for some vector $\mathbf{K}$ of the reciprocal lattice Λ^* (note that $\mathbf{K}$ may depend on $\mathbf{q}$ and R), and $v = (\mathbf{v}_E, \mathbf{v}_I)$. Equation (18) is the same as (3.16) in Janner & Janssen (1977) if one replaces $\mathbf{f}_j(\mathbf{q})$ by $\mathbf{f}_j(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}_j)$.

If the crystal contains rigid molecules it is sometimes convenient to describe the displacement of each molecule by two vectors: one for the displacement of the center of mass, one for the rotation around this point. The rotation vectors form an axial vector field with Fourier components $\mathbf{R}_j(\mathbf{q})$. The invariance condition for such a modulation is

$$R_E\, \mathbf{R}_j(\mathbf{q}) = (\det R_E)\, \mathbf{R}_{j'}(\mathbf{q}') \exp(iRq.v + i\mathbf{K}\mathbf{r}_{j'}). \tag{19}$$

The symmetry conditions (17) and (18) imply that the symmetry group G is a superspace group. The external components g_E form a three-dimensional space group, called the *basic space group* G_E. Because of (17), G_E is a subgroup of the space group G_0 of the basic structure. Very often both groups G_E and G_0 coincide. The internal components g_I do not form a d-dimensional space group. It is possible to extract from these a d-dimensional space group, but we do not need it here. Let us only remark that the homogeneous transformations R_I form a d-dimensional crystallographic point group leaving D invariant.

5. One-dimensional displacive modulation: K_2SeO_4

In this section we analyze the structure of K_2SeO_4 using the superspace-group concept. Our analysis is based on Iizumi, Axe, Shirane & Shimaoka (1977). The compound K_2SeO_4 has an incommensurable modulated phase between 93 and 128 K. The modulation is of the displacive type and can be described starting from a basic structure with space-group symmetry *Pnam*. This group is generated by an orthorhombic lattice Λ and by the space-group elements

$$\begin{aligned} &\{m_x|\mathbf{v}_E(m_x)\} : (x,y,z) \to (-x + \tfrac{1}{2}, y + \tfrac{1}{2}, z + \tfrac{1}{2}),\\ &\{m_y|\mathbf{v}_E(m_y)\} : (x,y,z) \to (x + \tfrac{1}{2}, -y + \tfrac{1}{2}, z),\\ &\{m_z|\mathbf{v}_E(m_z)\} : (x,y,z) \to (x, y, -z + \tfrac{1}{2}). \end{aligned} \tag{20}$$

There are four formula units per unit cell: eight oxygens [O(1)] are in general position (d), all other atoms are at Wyckoff positions (e): O(2), O(3), K_α, K_β and Se. The modulation is described in the rigid SeO_4 approximation and involves 12 displacive modulation waves $\mathbf{f}_j(\mathbf{r})$, ($j = 1, 2, \ldots, 12$) and four rotative ones $\mathbf{R}_j(\mathbf{r})$, ($j = 1, 2, 3, 4$). The satellites due to this modulation are characterized by wave vectors $\mathbf{q}_\delta$ and $\mathbf{q}_{2\delta}$ with

$$\mathbf{q}_\delta = (1 - \delta)\mathbf{a}^*/3 \text{ and } \mathbf{q}_{2\delta} = \mathbf{a}^* - 2\mathbf{q}_\delta. \tag{21}$$

With respect to the basis $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ of Λ^* the vector $\mathbf{q}_\delta$ has components $\alpha = \frac{1}{3}(1 - \delta)$, $\beta = \gamma = 0$. The dimension of the internal space is $d = 1$. As coordinate system in superspace we choose the basis $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ and $\mathbf{e}$, where $\mathbf{e}$ is a vector in the internal space. Then a primitive basis for the lattice Σ in superspace is

$$(1, 0, 0, -\alpha), (0,1,0,0), (0,0,1,0) \text{ and } (0,0,0,1). \tag{22}$$

The Bravais class of this lattice is $P^P{}_{\bar{1}}^{\,m}{}_{1}^{\,m}{}_{1}^{\,m}$ [see Janner, Janssen & de Wolff (1979)]. The holohedry of this lattice is generated by the superspace point-group transformations $(m_x, \varepsilon = -1)$, $(m_y, \varepsilon = 1)$ and $(m_z, \varepsilon = 1)$, where $\varepsilon = R_I = \pm 1$.

Elements of the superspace group G have to fulfil the conditions (17), (18) and (19). The first one is satisfied if G_E is a subgroup of *Pnam*. For the invariance conditions (18) and (19) one uses the fact that the total displacement transforms according to the Σ_2 representation. The procedure of deriving directly from that information the superspace group has already been discussed in Janner & Janssen (1977). The point group of $\mathbf{q}_\delta$ has elements $1, m_y, m_z, 2_x$ with characters $1, -1, -1, 1$ respectively, in the Σ_2 representation. For these elements $\mathbf{K} = 0$; hence for $R = (m_y, 1)$ and $R = (m_z, 1)$, (18) and (19) reduce to

$$\mathbf{f}_j(\mathbf{q}) = -\mathbf{f}_j(\mathbf{q})\, e^{-i\mathbf{q}_I \mathbf{v}_I}$$

and (23)

$$\mathbf{R}_j(\mathbf{q}) = -\mathbf{R}_j(\mathbf{q})\, e^{-i\mathbf{q}_I \mathbf{v}_I},$$

where $\mathbf{q} = \mathbf{q}_\delta$. Accordingly, $\mathbf{q}_I = \mathbf{e}^*$ and (23) is satisfied for $\mathbf{v}_I = \frac{1}{2}\mathbf{e}$. This leads to the following set of non-primitive translations [taking (20) also into account]:

$$v(m_y, 1) = (\tfrac{1}{2}, \tfrac{1}{2}, 0, [1-\alpha]/2),$$

$$v(m_z, 1) = (0, 0, \tfrac{1}{2}, \tfrac{1}{2}). \qquad (24)$$

Finally, we consider $R_E = -1$, which implies $R_I = -1$. For this case also, $\mathbf{q} = \mathbf{q}_\delta$, and one gets $\mathbf{K} = 0$. Since the total displacement transforms according to a one-dimensional co-representation it follows that the $\mathbf{q}_\delta$ components of the modulation vector fields obey the relation

$$\mathbf{f}_j(\mathbf{q}) = -e^{i\varphi}\, \mathbf{f}_j(\mathbf{q})\, e^{-i\mathbf{q}_I \mathbf{v}_I}$$

and (25)

$$\mathbf{R}_j(\mathbf{q}) = -e^{i\varphi}\, \mathbf{R}_j(\mathbf{q})\, e^{-i\mathbf{q}_I \mathbf{v}_I}.$$

Hence there is an element $\mathbf{v}_I = \mathbf{v}_I(\bar{1},\bar{1})$ solving (25). Such a non-primitive translation is, however, equivalent to zero, and can be transformed away by a shift of the origin [taken along the x direction to keep (24) unchanged]. Consequently, the superspace group for K_2SeO_4 in the incommmensurate crystal phase is

$$P^P{}_{\bar{1}}^{\,n}{}_{s}^{\,a}{}_{s}^{\,m}. \qquad (26)$$

This group is generated by the translations (22) and by the following superspace-group elements:

$$\begin{aligned}
&\{(m_x, \bar{1})|v(m_x, \bar{1})\} : (x,y,z,t) \to (-x + \tfrac{1}{2}, y + \tfrac{1}{2}, z + \tfrac{1}{2}, -t - \tfrac{1}{2}\alpha),\\
&\{(m_y, 1)|v(m_y, 1)\} : (x,y,z,t) \to (x + \tfrac{1}{2}, -y + \tfrac{1}{2}, z, t + \tfrac{1}{2} - \tfrac{1}{2}\alpha), \qquad (27)\\
&\{(m_z, 1)|v(m_z, 1)\} : (x,y,z,t) \to (x, y, -z + \tfrac{1}{2}, t + \tfrac{1}{2}),
\end{aligned}$$

where a general point in the superspace is indicated by

$$(x,y,z,t) = x\mathbf{a} + y\mathbf{b} + z\mathbf{c} + t\mathbf{e}.$$

As de Wolff has pointed out, the systematic extinctions due to the superspace group $P^P{}_{\bar{1}}^{\,n}{}_{s}^{\,a}{}_{s}^{\,m}$ are only approximately observed. The assignment of the modulation to a Σ_2 representation (as assumed here) has therefore to be considered with some caution.

6. Two-dimensional displacive modulation in a layered compound: $2H$-$TaSe_2$

The example considered here is a metallic layered compound with an incommensurate crystal phase between 90 and 122 K connected to the presence of a charge-density wave (CDW) which gives rise to a displacive modulation. The present analysis is based on the neutron scattering study of Moncton, Axe & DiSalvo (1977).

The basic structure of $2H$-$TaSe_2$ has the space-group symmetry $P6_3/mmc$. Adopting the hexagonal axes **a**, **b**, **c**, this space group is generated by the lattice Λ spanned by this basis and the elements:

$$\begin{aligned}
&\{6_z|\mathbf{v}_E(6_z)\} : (x,y,z) \to (x - y, x, z + \tfrac{1}{2}),\\
&\{m_x|\mathbf{v}_E(m_x)\} : (x,y,z) \to (-x, y - x, z + \tfrac{1}{2}), \qquad (28)\\
&\{m_z|\mathbf{v}_E(m_z)\} : (x,y,z) \to (x, y, -z + \tfrac{1}{2}).
\end{aligned}$$

There are two formula units per unit cell with atomic positions:

$$\begin{aligned}
&\text{Ta at } (b): \mathbf{r}_1 = (0, 0, -\tfrac{1}{4}), \mathbf{r}_2 = (0, 0, \tfrac{1}{4});\\
&\text{Se at } (f): \mathbf{r}_3 = (-\tfrac{1}{3}, -\tfrac{2}{3}, z - \tfrac{1}{2}), \mathbf{r}_4 = (\tfrac{1}{3}, \tfrac{2}{3}, -z), \qquad (29)\\
&\qquad\qquad \mathbf{r}_5 = (\tfrac{1}{3}, \tfrac{2}{3}, z), \mathbf{r}_6 = (\tfrac{1}{3}, \tfrac{2}{3}, -z + \tfrac{1}{2});
\end{aligned}$$

where $z \simeq 0{\cdot}18$. The modulation vectors $\mathbf{q}$ which characterize the displacive modulation are linear integral combinations of $\mathbf{q}_1$ and $\mathbf{q}_2$ with

$$\mathbf{q}_1 = (1 - \delta)\mathbf{a}^*/3 \quad \text{and} \quad \mathbf{q}_2 = -(1 - \delta)\mathbf{b}^*/3, \qquad (30)$$

where δ is a small, temperature dependent, real parameter. Accordingly, the Fourier spectrum of the incommensurate phase can be described in terms of integral linear combinations of five basis vectors, namely

$$\mathbf{a}_1^* = \mathbf{a}^*, \mathbf{a}_2^* = \mathbf{b}^*, \mathbf{a}_3^* = \mathbf{c}^*, \mathbf{a}_4^* = \mathbf{q}_1 \text{ and } \mathbf{a}_5^* = -\mathbf{q}_2. \qquad (31)$$

It follows that the matrix $\sigma(5)$ has the form

$$\sigma = \begin{pmatrix} \alpha & 0 & 0 \\ 0 & \alpha & 0 \end{pmatrix} \qquad (32)$$

with $\alpha = (1 - \delta)/3$. Hence the superspace is (3 + 2)-

dimensional, and the lattice Σ is generated by

$$a_1 = (1,0,0,-\alpha,0),\ a_2 = (0,1,0,0,-\alpha),\ a_3 = (0,0,1,0,0),$$
$$a_4 = (0,0,0,1,0) \quad \text{and} \quad a_5 = (0,0,0,0,1), \tag{33}$$

where we denote by (x,y,z,t,u) a general point (and a position vector) $x\mathbf{a} + y\mathbf{b} + z\mathbf{c} + t\mathbf{d} + u\mathbf{e}$ of the superspace with **a**, **b**, **c** basis of Λ as above in position space and **d**, **e** basis of a two-dimensional hexagonal lattice D in internal subspace.

The lattice Σ spanned by (33) belongs to the Bravais class $P^{P\,6/m\,m\,m}_{p\,6\,1\,m\,m}$ [see Janner, Janssen & de Wolff (1980)]. Its holohedry is generated by the following point-group elements:

$$R_1 = (6_z, 6_z) : (x,y,z,t,u) \to (x-y, x, z, t-u, t);$$
$$R_2 = (m_x, m_x) : (x,y,z,t,u) \to (-x, y-x, z, -t, u-t);$$
$$R_3 = (m_z, 1) : (x,y,z,t,u) \to (x, y, -z, t, u). \tag{34}$$

To determine the point group and the non-primitive translations one uses the fact that the modulation function belongs to the Σ_1 representation of $P6_3/mmc$. Denoting by 3_z^{-1} the 120° clockwise rotation around $\mathbf{c}^*$ and by $T(3_z^{-1})$ the corresponding operator on the displacement field $\mathbf{f} = (\mathbf{f}_1, \mathbf{f}_2, \ldots, \mathbf{f}_6)$, one has

$$\mathbf{f}(\mathbf{q}_2) = T(3_z^{-1})\,\mathbf{f}(\mathbf{q}_1)\,e^{-i\varphi_1}$$

and (35)

$$\mathbf{f}(\mathbf{q}_3) = T(3_z^{-1})\,\mathbf{f}(\mathbf{q}_2)\,e^{-i\varphi_2},$$

where $\mathbf{q}_3 = -\mathbf{q}_1 - \mathbf{q}_2$. Here φ_1 and φ_2 are the relative phases of the modulation wave $\mathbf{q}_2$ with respect to that of $\mathbf{q}_1$ and correspondingly of $\mathbf{q}_3$ with respect to $\mathbf{q}_2$. The element $R = (R_E, R_I) = (3_z^{-1}, 3^{-1})$ belongs to the point group if there is a non-primitive translation $\mathbf{v}_I = \mathbf{v}_I(3_z^{-1}, 3^{-1})$ such that

$$T(3_z^{-1})\,\mathbf{f}(\mathbf{q}_j) = \mathbf{f}(3_z^{-1}\,\mathbf{q}_j)\,e^{i\varphi_j} = \mathbf{f}(3_z^{-1}\mathbf{q}_j)\exp(iR_I\,\mathbf{q}_{jI}.\mathbf{v}_I) \tag{36}$$

for $j = 1, 2$, where $R_I = 3^{-1}$ and $\mathbf{q}_{1I} = \mathbf{b}_1^*$, $\mathbf{q}_{2I} = -\mathbf{b}_2^*$; $\mathbf{b}_1^*$, $\mathbf{b}_2^*$ is the basis of D^* reciprocal to $\mathbf{b}_1 = \mathbf{d}$ and $\mathbf{b}_2 = \mathbf{e}$ in the internal space. Equation (36) is solved by

$$\mathbf{v}_I(3_z^{-1}, 3^{-1}) = -\frac{\varphi_1 + \varphi_2}{2\pi}\,\mathbf{b}_1 - \frac{\varphi_1}{2\pi}\,\mathbf{b}_2. \tag{37}$$

As next generator of the point group we take $R_E = m_y$, $R_I = m_y$, where $\mathbf{v}_E(m_y, m_y) = 0$. The Σ_1 transformation property implies

$$T(m_y)\,\mathbf{f}(\mathbf{q}_1) = \mathbf{f}(\mathbf{q}_1) \quad \text{as} \quad m_y\,\mathbf{q}_1 = \mathbf{q}_1;$$

furthermore,

$$T(m_y)\,\mathbf{f}(\mathbf{q}_2) = T(m_y\,3_z^{-1})\,\mathbf{f}(\mathbf{q}_1)\,e^{-i\varphi_1}$$
$$= T(3_z^{-2})\,\mathbf{f}(\mathbf{q}_1)\,e^{-i\varphi_1} = \mathbf{f}(\mathbf{q}_3)\,e^{+i\varphi_2}. \tag{38}$$

The (m_y, m_y) symmetry condition implies for $\mathbf{v}_I = \mathbf{v}_I(m_y, m_y)$

$$\mathbf{f}(\mathbf{q}_1) = \mathbf{f}(\mathbf{q}_1)\exp(i\mathbf{b}_1^*\,\mathbf{v}_I)$$

and (39)

$$\mathbf{f}(\mathbf{q}_3)\,e^{+i\varphi_2} = \mathbf{f}(\mathbf{q}_3)\exp[-i(\mathbf{b}_1^* - \mathbf{b}_2^*)\,\mathbf{v}_I]$$

and this equation is solved by

$$\mathbf{v}_I(m_y, m_y) = \varphi_2\mathbf{b}_2/2\pi. \tag{40}$$

As third generator we consider $R_E = m_z$, $R_I = 1$. This is a symmetry element with $v(m_z, 1) = 0$ since for the Σ_1 representation one has

$$T(m_z)\,\mathbf{f}(\mathbf{q}_j) = \mathbf{f}(\mathbf{q}_j), \qquad j = 1, 2, 3 \tag{41}$$

because $m_z\mathbf{q}_j = \mathbf{q}_j$.

All these internal components of non-primitive translations can be transformed away by a shift $\mathbf{s}_I$ of the origin in internal space. One verifies that

$$\mathbf{v}_I'(R) = \mathbf{v}_I(R) + (1 - R_I)\,\mathbf{s}_I = 0 \tag{42}$$

for $\mathbf{s}_I = (1/6\pi)\{(2\varphi_1 + \varphi_2)\,\mathbf{b}_1 + (\varphi_1 - \varphi_2)\,\mathbf{b}_2\}$ and R given by $(3_z^{-1}, 3^{-1})$, (m_y, m_y) and $(m_z, 1)$. By this choice of origin the modulation waves $\mathbf{q}_1$, $\mathbf{q}_2$, $\mathbf{q}_3$ all have the same phase ($\varphi_1 = \varphi_2 = 0$).

The element $R_E = -1$ (which implies $R_I = -1$) involves a one-dimensional co-representation, with basis $e(q_1)$ which can be chosen such that

$$T(\bar{1})\,e(q_1) = e(-q_1) = e^*(q_1) = -e(q_1). \tag{43}$$

If we write

$$\mathbf{f}(q_1) = e^{i\psi}\,e(q_1), \tag{44}$$

the conditions for central inversion symmetry become

$$-\mathbf{b}_1^*\,\mathbf{v}_I \equiv \mathbf{b}_2^*\,\mathbf{v}_I \equiv (\mathbf{b}_1^* - \mathbf{b}_2^*)\,\mathbf{v}_I \equiv 2\psi \pmod{2\pi}. \tag{45}$$

These relations allow a solution provided that

$$6\psi \equiv 0 \pmod{2\pi} \tag{46}$$

and in that case $\mathbf{v}_I = (\psi/\pi)\,(-\mathbf{b}_1 + \mathbf{b}_2)$. This non-primitive translation is also equivalent to zero.

In conclusion, on the basis of the data reported by Moncton, Axe & DiSalvo (1977), two superspace groups may occur as the symmetry of the incommensurate phase of $2H$-$TaSe_2$. Either

$$G_1 = P^{P\,\bar{6}\,2\,c}_{p\,3\,m\,m} \tag{47}$$

generated by the translations (33) and by the elements

$$\{(3_z, 3)|0\} : (x,y,z,t,u) \to (-y, x-y, z, -u, t-u),$$
$$\{(m_y, m_y)|0\} : (x,y,z,t,u) \to (x, x-y, z, t, t-u), \tag{48}$$
$$\{(m_z, 1)|a_3/2\} : (x,y,z,t,u) \to (x, y, -z + \tfrac{1}{2}, t, u),$$

or, if condition (46) is satisfied

$$G_2 = P^{P\,6_3/m\,m\,c}_{p\,6\,1\,m\,m} \tag{49}$$

which is generated by (33), (48) and

$$\{(\bar{1},\bar{1})|0\}:(x,y,z,t,u)\rightarrow(-x,-y,-z,-t,-u). \quad (50)$$

7. Occupation-wave modulation

We consider a crystal described in terms of a density function $\rho(\mathbf{r})$ of the form

$$\rho(\mathbf{r})=\sum_{\nu=1}^{m} p_\nu(\mathbf{r})\,\rho_\nu(\mathbf{r}) \quad (51)$$

where $\rho_\nu(\mathbf{r})$ is a density function with space-group symmetry G_ν [*i.e.* $\rho_\nu(\mathbf{r})$ describes a commensurate crystal] and where $p_\nu(\mathbf{r})$ is some (space-dependent) probability function. This happens, for example, in crystals where atoms occupy different positions in the unit cell according to some probability distribution.

We speak of *occupation waves* if the probabilities $p_\nu(\mathbf{r})$ are expressible as

$$p_\nu(\mathbf{r})=\sum_{\mathbf{q}}\hat{p}_\nu(\mathbf{q})\,e^{i\mathbf{q}\mathbf{r}} \quad (52)$$

with $\mathbf{q}=\sum_l z_l\,\mathbf{q}_l$ involving a finite number of vectors $\mathbf{q}_l$ only. We assume that the translation lattices Λ_ν of the space groups G_ν are mutually commensurable and, for simplicity, we consider the case that they coincide. The more general case of different lattices is easily dealt with, and the incommensurable case is discussed in part II.

The Fourier transform of $\rho(\mathbf{r})$ can be obtained by convolution from that of $p(\mathbf{r})$ and $\rho_\nu(\mathbf{r})$

$$\hat{\rho}(\mathbf{k})=\sum_{\nu=1}^{m}\sum_{\mathbf{K}\in\Lambda_\nu^*}\hat{p}_\nu(\mathbf{k}-\mathbf{K})\,\hat{\rho}_\nu(\mathbf{K}), \quad (53)$$

where $\mathbf{k}-\mathbf{K}=\sum_j z_j\,\mathbf{q}_j$. We denote by $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$ a basis of $\Lambda^*=\Lambda_1^*=\ldots=\Lambda_m^*$, and we consider the case where the occupation waves are incommensurate with Λ, *i.e.* the vectors $\mathbf{q}_j$ are incommensurate with Λ^*. Putting

$$\mathbf{a}_{3+j}^*=\mathbf{q}_j,\qquad j=1,2,\ldots,d, \quad (54)$$

we see that $\rho(\mathbf{r})$ satisfies the definition for a crystal given in §3, and the associated supercrystal $\tilde{\rho}(\mathbf{r},\mathbf{t})$ can be constructed making use of (9). The symmetry condition for $\tilde{\rho}$ by (g_E,g_I) given in (10) can be expressed as an invariance condition for the crystal configurations described by the $\rho_\nu(\mathbf{r})$ and for the corresponding probability function $p_\nu(\mathbf{r})$. In particular, in the case of a point-atom distribution as above, one gets the following set of invariance conditions for $g=\{R|v\}=(\{R_E|\mathbf{v}_E\},\{R_I|\mathbf{v}_I\})$:

$$R_E(\mathbf{n}+\mathbf{r}_{\nu j})+\mathbf{v}_E=\mathbf{n}'+\mathbf{r}_{\nu' j'} \quad (55)$$

and

$$\hat{p}_\nu(\mathbf{q})=\hat{p}_{\nu'}(\mathbf{q}')\exp(iRq.v+i\mathbf{K}\mathbf{r}_{\nu' j'}, \quad (56)$$

where $q=(\mathbf{q},\mathbf{q}_I)$, $\mathbf{q}'=R_E\,\mathbf{q}+\mathbf{K}$ and $\mathbf{q}_I'=R_I\,\mathbf{q}_I$, just as in (18). Actually (56) is the scalar version of that equation.

8. Occupation waves in $NaNO_2$

The compound $NaNO_2$ shows a number of phase transitions characterized by the appearance of occupation-wave modulation. Our analysis is based on the *Habilitationsschrift* by Böhm (1977). We have left out of our considerations the model proposed by Kucharczyk, Pietrasko & Lukaszewicz (1978) in which displacive modulation occurs in addition to the occupation waves.

$NaNO_2$ has four phases: ferroelectric (F: $T<T_1=435{\cdot}8$ K), sinusoidal ferroelectric (SF: $T_1<T<T_2\simeq 436$ K), antiferroelectric (AF: $T_2<T<T_3\simeq 437$ K) and paraelectric (P: $T_3<T$). The transition temperatures depend on the thermal treatment of the crystal. The phases SF and AF are incommensurate. The structure of all four phases can be described in terms of the two crystal configurations $\nu=1,2$, both having space-group symmetry $G_1=G_2=Im2m$. There is one formula unit per unit cell with Na and N ions at Wyckoff position (a) and O ions at position (c).

$$\begin{aligned}&\text{Na},\ j=1,\quad \mathbf{r}_{11}=(0,y_1,0),\\ &\text{N},\ j=2,\quad \mathbf{r}_{12}=(0,y_2,0),\\ &\text{O},\ j=3,4,\quad \mathbf{r}_{13}=(0,y_3,z_3)\text{ and }\mathbf{r}_{14}=(0,y_3,-z_3).\end{aligned} \quad (57)$$

The corresponding positions for the $\nu=2$ configuration are obtained by an m_y mirror transformation. At $T=435{\cdot}5$ K, one has $y_1=0{\cdot}541$, $y_2=0{\cdot}078$, $y_3=-0{\cdot}034$ and $z_3=0{\cdot}196$.

In the P phase the probability function p_ν is space independent and given by $p_1=p_2=\frac{1}{2}$. The corresponding crystal symmetry is the (three-dimensional) space group $Immm$. In the F phase, also, the probability is space independent with occupation of one configuration only. Accordingly, the space group is $Im2m$. In the SF and AF phases satellite reflections appear characterized by a wave vector

$$\mathbf{q}=2\alpha\mathbf{a}^*=(2\alpha,0,0)_*. \quad (58)$$

The structure of these two phases has been analyzed by Böhm (1977) in terms of occupation waves with Fourier components

$$\begin{aligned}&\hat{p}_1(0)=\hat{p}_2(0)=\tfrac{1}{2}\text{ in the }AF\text{ phase},\\ &\hat{p}_1(0)=\tfrac{1}{2}+\varepsilon(T),\hat{p}_2(0)=\tfrac{1}{2}-\varepsilon(T)\text{ in the }SF\text{ phase},\\ &\hat{p}_1(2\alpha\mathbf{a}^*)=-\hat{p}_2(2\alpha\mathbf{a}^*)=\delta\text{ in both phases},\end{aligned} \quad (59)$$

with $\varepsilon(T)\simeq 0{\cdot}08$ and $|\delta|\simeq 0{\cdot}105$ at $435{\cdot}5$ K.

The lattice A^* reciprocal to $222I$ is generated by

$$\mathbf{a}_1^* = (0,1,1)_*,\ \mathbf{a}_2^* = (1,0,1)_* \text{ and } \mathbf{a}_3^* = (1,1,0)_*. \quad (60)$$

Since $\mathbf{a}_4^* = (2\alpha,0,0)_*$ the matrix σ of (5) is

$$\sigma = (-\alpha,\alpha,\alpha). \quad (61)$$

The superspace is (3 + 1)-dimensional spanned by the orthorhombic (centered) basis **a**, **b**, **c** as above and a vector **d** in the internal space. The superspace groups of both phases have lattice symmetry Σ generated by

$$a_1 = (\bar{\tfrac{1}{2}},\tfrac{1}{2},\tfrac{1}{2},\alpha),\ a_2 = (\tfrac{1}{2},\bar{\tfrac{1}{2}},\tfrac{1}{2},\bar{\alpha}),$$
$$a_3 = (\tfrac{1}{2},\tfrac{1}{2},\bar{\tfrac{1}{2}},\bar{\alpha}),\ a_4 = (0,0,0,1), \quad (62)$$

where (x,y,z,t) denotes $x\mathbf{a} + y\mathbf{b} + z\mathbf{c} + t\mathbf{d}$. From Janner, Janssen & de Wolff (1979) it follows that the Bravais class of Σ is

$$P^I{}_{\bar{1}\,1\,1}^{m\,m\,m} \quad (63)$$

with holohedry generated by $(m_x,\bar{1})$, $(m_y,1)$ and $(m_z,1)$.

In order to find the other generators of the superspace groups one considers (55) and (56) for each element of the holohedry. One verifies that these elements satisfy (55). The check of the corresponding other equation can be done as follows:

For $(m_x,\bar{1})$ one has: $v' = v$, $\mathbf{q}' = -\mathbf{q}$, $\mathbf{v}_E = 0$ and $\mathbf{K} = 0$, thus (56) becomes

$$\hat{p}_v(\mathbf{q}) = \hat{p}_v^*(\mathbf{q}) \exp(-i\mathbf{q}_I.\mathbf{v}_I). \quad (64)$$

For $\mathbf{q} = 0$, the relation is satisfied. For $\mathbf{q} = 2\alpha\mathbf{a}^*$, the phase of $\hat{p}_v(\mathbf{q})$ is arbitrary because of the incommensurability and by choosing $\hat{p}_v(\mathbf{q})$ real, one gets the solution $\mathbf{v}_I(m_x,\bar{1}) = 0$.

For $(m_z,1)$, one has $v' = v$, $\mathbf{q}' = \mathbf{q}$, $\mathbf{v}_E = 0$ and $\mathbf{K} = 0$; and (56) is satisfied with $\mathbf{v}_I(m_z,1) = 0$.

For $(m_y,1)$, one has $\mathbf{q}' = \mathbf{q}$, $\mathbf{v}_E = 0$, $\mathbf{K} = 0$ but $v \neq v'$. Hence (56) becomes

$$\hat{p}_1(0) = \hat{p}_2(0) \quad (65)$$

and

$$\hat{p}_1(2\alpha\mathbf{a}^*) = \hat{p}_2(2\alpha\mathbf{a}^*)\exp(i\mathbf{d}^*.\mathbf{V}_I)$$
$$= -\hat{p}_1(2\alpha\mathbf{a}^*)\exp(i\mathbf{d}^*.\mathbf{v}_I).$$

Only in the AF phase is there a solution: $\mathbf{v}_I(m_y,1) = \frac{1}{2}\mathbf{d}$. Therefore, the superspace groups for the incommensurate phases SF and AF are

$$G_{AF} = P^I{}_{\bar{1}\,s\,1}^{m\,m\,m} \text{ and } G_{SF} = P^I{}_{\bar{1}\,1\,1}^{m\,2\,m}. \quad (66)$$

The group G_{SF} is generated by the translations (62) and by the following superspace-group elements:

$$\{(m_x,\bar{1})|0\}:(x,y,z,t) \to (-x,y,z,-t);$$
$$\{(m_z,1)|0\}:(x,y,z,t) \to (x,y,-z,t). \quad (67)$$

In addition to all these generators the group G_{AF} has also

$$\{(m_y,1)|\tfrac{1}{2}\mathbf{d}\}:(x,y,z,t) \to (x,-y,z,t+\tfrac{1}{2}). \quad (68)$$

Notice that in the AF phase the 4-vector $(h,0,l,m)_*$ (which is $h\mathbf{a}^* + l\mathbf{c}^* + m\mathbf{q}$, h, l, m integers) is left invariant by $(m_y,1)$. Hence the non-primitive translation $\mathbf{v}_I(m_y,1) = \frac{1}{2}\mathbf{d}$ implies the extinction rule

$$I(h,0,l,m) = 0 \text{ for } m \text{ odd}. \quad (69)$$

Since only first-order satellites occur, this means that the plane $(h,0,l)_*$ of main reflections is free of satellites, as has been observed.

9. Magnetic superspace groups

As shown by Overhauser (1962, 1968), the ground state of an electron gas in a crystal does not necessarily have a uniform spin and charge distribution, but may show charge-density waves (CDW) and/or spin-density waves (SDW). We have already seen that CDW's may lead to an incommensurate crystal phase. The same can occur in magnetic crystals through SDW's. Actually, incommensurability was discovered first in magnetic systems, and the canonical example of an incommensurate magnetic crystal, that of chromium, will be considered further to illustrate the present approach. A magnetic crystal can be described by a (scalar) charge density $\rho(\mathbf{r})$ and by a spin density $\mathbf{S}(\mathbf{r})$ [see *e.g.* Arrot (1966)], which transforms like an axial vector field, changing sign under time inversion. In the magnetic group approach [see Opechowski & Guccione (1965)] for describing the symmetry of magnetic crystals one considers as allowed transformations pairs (g,ε) of a Euclidean transformation $g = \{R|\mathbf{v}\} \in E(3)$ and an element of the time-inversion group θ; $\varepsilon = 1$ denotes the unit element and $\varepsilon = -1$ the time inversion. The corresponding transformation law of $\mathbf{S}(\mathbf{r})$ is given by

$$(g,\varepsilon)\,\mathbf{S}(\mathbf{r}) = \varepsilon(\det R)\,R\mathbf{S}(g^{-1}\mathbf{r}), \quad (70)$$

whereas for $\rho(\mathbf{r})$ one simply has

$$(g,\varepsilon)\,\rho(\mathbf{r}) = \rho(g^{-1}\mathbf{r}). \quad (71)$$

The *magnetic symmetry group*, M, of the crystal is the group of all pairs (g,ε) leaving the charge and the spin density of the crystal invariant. This group is a three-dimensional *magnetic space group* in the commensurate case [see Opechowski & Guccione (1965) for more details]. In the incommensurate case, this is no longer true. If the corresponding charge density still has a three-dimensional space-group symmetry, then one can take into account the magnetic incommensurability by allowing additional transformations in the spin space only; one then gets so-called *spin space groups* [see Litvin & Opechowski (1974)], magnetic space groups being a particular case of spin space groups. The situation is different when the charge density itself is that of an incommensurate crystal phase. Such a case is the normal one when incom-

mensurate SDW's interact with localized magnetic moments at atomic positions. The superspace-group approach can be generalized to incommensurate magnetic crystals also.

The *magnetic superspace group*, M, is the magnetic symmetry group of the supercrystal charge and spin density. It is this group that we consider as the correct characterization of the symmetry of an incommensurate magnetic crystal. The symmetry condition for an element $(\{R|v\}, \varepsilon) = (\{R_E|\mathbf{v}_E\}, \{R_I \pm \mathbf{v}_I\}, \varepsilon)$ of M expressed in terms of the Fourier components is given by (11) and by

$$\varepsilon(\det R_E)\, R_E\, \mathbf{S}(\mathbf{k}) = \mathbf{S}(\mathbf{k}')\, e^{iRk\,.\,v} \tag{72}$$

with $k = (\mathbf{k}, \mathbf{k}_I)$ and $Rk = (\mathbf{k}', \mathbf{k}_I')$. The theory of magnetic superspace groups can also be formulated in terms of spin arrangements as defined in Opechowski & Guccione (1965) and Litvin & Opechowski (1974) if localized magnetic moments are considered defined at the atomic positions of the crystal. In that case $\mathbf{k}' = R_E\mathbf{k} + \mathbf{K}$, $\mathbf{k}_I' = R_I\mathbf{k}$ and an additional phase factor $\exp(i\mathbf{K}\mathbf{r}_{j'})$ appears as in (19). Let us not go into details. The aim of this section was not to give a full theory, but only to introduce the concepts needed for approaching on a concrete example the interplay between crystal structure and magnetic symmetry in an incommensurate phase. In what follows we shall adopt the standard notation: $(g,1) = g$ and $(g,\bar{1}) = g'$.

10. Magnetic superspace-group symmetry of Cr

Our analysis is based on those of Tsunoda, Mori, Kunitomi, Teraoka & Kanamori (1974), Eagen & Werner (1975) and Pynn, Press & Shapiro (1976). For less-recent references the reader is referred to the review paper of Arrot (1966). Cr is paramagnetic with b.c.c. structure above $T_N = 312$ K. Below this temperature the metal shows incommensurate SDW's. Between 312 and 122 K (phase AF_1) the basic structure is orthorhombic (space group *Immm*) and the magnetic structure is nearly antiferromagnetic. In the single-domain case, the fundamental SDW wave vector $\mathbf{Q}$ and the (transverse) polarization are directed along the cubic axes. At 122 K there is a phase transition to the AF_2 phase which has tetragonal basic structure (space group $I4/mmm$) and a nearly antiferromagnetic structure with a longitudinal incommensurate SDW. In both AF_1 and AF_2 phases a longitudinal displacive modulation is observed with wave vector $2\mathbf{Q}$. In all phases there is one atom per unit cell (of the basic structure), chosen at the origin. As reference system we take the orthogonal $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ of the body-centered lattice A. Then a primitive basis of it is

$$\mathbf{a}_1 = (\bar{\tfrac{1}{2}},\tfrac{1}{2},\tfrac{1}{2}),\ \mathbf{a}_2 = (\tfrac{1}{2},\bar{\tfrac{1}{2}},\tfrac{1}{2}) \text{ and } \mathbf{a}_3 = (\tfrac{1}{2},\tfrac{1}{2},\bar{\tfrac{1}{2}}) \tag{73}$$

and its reciprocal basis is

$$\mathbf{a}_1^* = (0,1,1)_*,\ \mathbf{a}_2^* = (1,0,1)_* \text{ and } \mathbf{a}_3^* = (1,1,0)_*. \tag{74}$$

If the z axis is the unique tetragonal axis, one has $\mathbf{q} = 2\mathbf{Q} = 2(0,0,1-\varepsilon)_*$ with $\varepsilon \simeq 0{\cdot}05$. In the AF_1 phase we take the spin polarization along the x axis ($S_y = S_z = 0$).

To consider the non-magnetic superspace group one disregards the spins and determines the group leaving the charge density invariant (*i.e.* the symmetry group of the crystal with displacive modulation) along the same lines as in the previous examples. The Fourier spectrum of $\rho(\mathbf{r})$ is described by an integral linear combination of four basis vectors $\mathbf{a}_1^*$, $\mathbf{a}_2^*$, $\mathbf{a}_3^*$ as above, and $\mathbf{a}_4^* = (0,0,2\varepsilon)_*$. Hence the matrix σ_c (where the subscript c recalls that it is expressed on a centered basis) is given by

$$\sigma_c = (0,0,2\varepsilon). \tag{75}$$

The superspace is four-dimensional and spanned by $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ in V_E and by $\mathbf{d}$ (in V_I). The lattice Σ has as basis:

$$a_1 = (\bar{\tfrac{1}{2}},\tfrac{1}{2},\tfrac{1}{2},\bar{\varepsilon}),\ a_2 = (\tfrac{1}{2},\bar{\tfrac{1}{2}},\tfrac{1}{2},\bar{\varepsilon}),\ a_3 = (\tfrac{1}{2},\tfrac{1}{2},\bar{\tfrac{1}{2}},\varepsilon),\ a_4 = (0,0,0,1), \tag{76}$$

and the reciprocal basis is:

$$a_1^* = (0,1,1,0)_*,\ a_2^* = (1,0,1,0)_*,\ a_3^* = (1,1,0,0)_*,\quad a_4^* = (0,0,2\varepsilon,1)_*. \tag{77}$$

In the AF_1 phase the Bravais class of Σ is $P^I{}_{1\ 1\ \bar{1}}^{m\ m\ m}$ with holohedry generated by $(R_E, R_I) = (m_x, 1)$, $(m_y, \bar{1})$ and $(m_z, \bar{1})$. In the AF_2 phase the Bravais class is $P^I{}_{1\ \bar{1}\ 1}^{4/m\ m\ m}$ with holohedry generated by $(4_z, \bar{1})$, $(m_z, 1)$ and $(m_x, 1)$. Using (18) with $j = j' = 1$, $\mathbf{r}_j = 0$ and $\mathbf{f}_1(\mathbf{q})$ parallel to the z axis, one verifies easily that the generators of the holohedry leave the modulation invariant with $v = 0$. Hence one gets the superspace groups

$$G_{AF_1} = P^I{}_{1\ 1\ \bar{1}}^{m\ m\ m} \text{ and } G_{AF_2} = P^I{}_{1\ \bar{1}\ 1}^{4/m\ m\ m}. \tag{78}$$

In deriving this result the phase of the modulation was chosen in such a way that

$$\mathbf{f}_1(-\mathbf{q}) = -\mathbf{f}_1(\mathbf{q}). \tag{79}$$

Considering now the spin distribution as well, one takes into account the condition on the magnetic superspace group to leave the charge density invariant by requiring that

$$M \subseteq G \times \theta,\ i = 1,2, \tag{80}$$

with $G = G_{AF_i}$ as above. For v, a translation of M, condition (72) becomes

$$\varepsilon\mathbf{S}(\mathbf{k}) = \mathbf{S}(\mathbf{k})\, e^{ikv}. \tag{81}$$

In the case of a single $\mathbf{Q}$-SDW we have

$$\mathbf{k} = (0,0,1-\varepsilon)_* = \tfrac{1}{2}(\mathbf{a}_1^* + \mathbf{a}_2^* - \mathbf{a}_3^* - \mathbf{a}_4^*)$$

implying

$$k = \tfrac{1}{2}(a_1^* + a_2^* - a_3^* - a_4^*)$$

and thus $ka_i = \pi$ for $i = 1, 2, 3, 4$. Therefore each of the basis vectors of Σ is to be combined with $\varepsilon = -1$. The same is true for the 3**Q**-SDW (Pynn, Press & Shapiro, 1976). Therefore the magnetic lattice translations of M are generated by

$$a_i' = (a_i, -1), i = 1, 2, 3, 4 \tag{82}$$

both in the AF_1 and in the AF_2 phase.

To determine the magnetic point group, notice that for both the 1**Q**- and the 3**Q**-SDW's and R from the point group of G_{AF_i} one has $\mathbf{k}' = R_E\mathbf{k}$ and $v(R) = 0$; this reduces (72) to

$$\varepsilon(\det R_E)\, R_E\, \mathbf{S}(\mathbf{k}) = \mathbf{S}(R_E\,\mathbf{k}). \tag{83}$$

In the AF_1 phase $\mathbf{S}(\mathbf{k})$ is parallel to the x axis and left invariant by $(m_x, 1)'$ and $(m_y, 1)'$. It is also left invariant by $(m_z, \bar{1})$ provided the phase relation

$$S_x(-\mathbf{k}) = S_x(\mathbf{k}) \tag{84}$$

is satisfied. This relation is plausible if one considers the phase relation of the corresponding CDW, but in the papers on which this analysis is based no direct experimental evidence for it is quoted. In any case, if (84) is satisfied, then the magnetic superspace group for the AF_1 phase is

$$M_{AF_1} = P^{I_p m' m' \underline{m}}_{\ b\ 1\ 1\ \bar{1}} \tag{85}$$

whose generators are a_1', a_2', a_3' (indicated by the subscript p), a_4' (indicated by the subscript b), $(m_x, 1)'$, $(m_y, 1)'$ and $(m_z, \bar{1})$.

In the AF_2 phase $\mathbf{S}(\mathbf{k})$ is parallel to the z axis and left invariant [according to (72)] by $(4_z, 1)$ and $(m_x, 1)'$. Again, if the phase relation (84) holds, then it is also left invariant by $(m_z, \bar{1})$. In this case the magnetic superspace group for the AF_2 phase is

$$M_{AF_2} = P^{I_p 4/\underline{m} m' m'}_{\ b 1\ \bar{1}\ 1\ 1}. \tag{86}$$

In the present derivation we started from a nonmagnetic basic structure, we determined the nonmagnetic superspace group first and derived the magnetic superspace group. One could have started from a magnetic basic structure, which is the antiferromagnetic approximation to the actual structure, considering then CDW's and SDW's modulations: the final result would have been the same.

Furthermore, the general theory requires that the basic magnetic space group M_E has to be a (proper or improper) subgroup of the magnetic space group of the basic structure. In the present case they coincide in both the AF_1 and the AF_2 phases. One has

$$M_{OAF_1} = M_{EAF_1} = I_p m' m' m$$
$$\text{and } M_{OAF_2} = M_{EAF_2} = I_p 4/mm'm', \tag{87}$$

and this is very satisfactory.

11. Concluding remarks

Crystals whose charge densities, ρ, have Fourier components with wave vectors expressible as linear combinations with integral coefficients of a finite number of fundamental reciprocal-space vectors admit a superspace group as symmetry. This group is uniquely determined (within its equivalence class) by the given charge density ρ.

The examples discussed here show that the extension from the Euclidean three-dimensional space to the Euclidean $(3 + d)$-dimensional superspace is meaningful and increases insight into the structural relations occurring in incommensurate crystal phases. This is particularly the case in the point-atom approximation and if one starts from a so-called basic structure. This basic structure has a three-dimensional space-group symmetry in all the cases considered here and represents a kind of unperturbed state of a system in which incommensurability can be ascribed to interactions considered as perturbation.

In part II are considered cases in which the natural basic structure is already an incommensurate one and requires a superspace-group description for its symmetry for the reasons explained in this paper.

The concept of basic structure is not always a well defined one, in particular for systems with a poor degree of localizability. The superspace-group symmetry, however, does not depend on the ambiguity in the basic structure concept. This is true in quite the same way as the properties of a total Hamiltonian are independent from the ambiguity of what is considered its unperturbed part. It has been shown that the generalization to the magnetic symmetry case is also meaningful and does not lead to great problems.

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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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