other beams into itself. In summary, the intensity change of the primary reflection caused by the presence of at least one secondary reflection can be either positive (*Umweganregung*) or negative (*Aufhellung*) independent of the phase relationships between the different reflections. It depends only on the structure-factor moduli. Thus, in a three-beam case these effects are independent of the triplet phase and we denote them as phase independent. Moon & Shull (1964) pointed out that in the limit of low extinction and weak absorption the intensity change is independent of the diffraction geometry, *i.e.* the diffracted beams can be of either transmission (Laue) or reflection (Bragg) type or any mixture thereof.

On the other hand it was shown by dynamical-theory calculations (Hümmer & Billy, 1982) that in the limit of weak absorption ($\mu t < 0\cdot5$) the three-beam interference effect is also independent of the diffraction geometry. This criterion was always fulfilled. In our experiments both the interference effects and the phase-independent *Umweganregung* and *Aufhellung* effects are independent of the diffraction geometry, as can be seen in Figs. 5(*a*) and (*b*), where the couple of centrosymmetric three-beam cases have the same triplet phase. No significant differences of the profiles can be found.

The experimental results show that in general there is a superposition of the phase-independent and interference effects. The phase-independent effects may predominate over the interference effects if the ratio of the intensities of the primary reflection $I(\mathbf{h})$ and the secondary reflection $I(\mathbf{g})$ is too low or too high. In these cases it is very difficult to deduce any phase information from the ψ-scan profiles and to distinguish +90 and −90° profiles.

It should be pointed out that the discrimination of triplet phases near ±90° by the experiment allows the determination of the absolute configuration of a noncentrosymmetric structure or the determination of the absolute structure (Jones, 1984) because two enantiomorphic structures differ in the signs of the triplet phases. In this connection it should be mentioned that on the basis of a right-handed system of coordinates it is always possible to index all reflections without knowledge of the absolute structure. Here we do not agree with Shen & Collela (1986). In the case of benzil, for example, assuming atomic parameters consistent with the space group $P3_121$ would be in contradiction to the signs of the triplet phases determined from the experiment. Therefore, for our crystals $P3_221$ is the correct space group and the absolute configuration is given by the set of atomic coordinates consistent with this space group.

For L-asparagine the coordinates of Kartha & de Vries (1961) are confirmed.

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Crystallography, Geometry and Physics in Higher Dimensions. V. Polar and Mono-Incommensurate Point Groups in the Four-Dimensional Space $\mathbb{E}^4$

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Abstract

The crystallographic point groups of the four-dimensional Euclidean space $\mathbb{E}^4$ are a convenient means of studying some crystallized solids of physical space, for instance the groups of magnetic structures and the groups of mono-incommensurate structures, as is demonstrated by a simple example. The concept of polar crystallographic point groups defined here in $\mathbb{E}^4$, and also in $\mathbb{E}^n$ enables the list and the WPV notation {geometric symbol of Weigel, Phan & Veysseyre [*Acta Cryst.* (1987), **A43**, 294–304]} of these

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special structures to be stated in a more precise way. This paper is especially concerned with the mono-incommensurate structures while a discussion on magnetic structures will be published later.

Introduction

The crystallographic space and point groups of the four-dimensional space $\mathbb{E}^4$ have been listed in an abstract form (Bülow, Neubüser & Wondratscheck, 1971; Neubüser, Wondratschek & Bülow, 1971; Wondratschek, Bülow & Neubüser, 1971; Brown, Bülow, Neubüser, Wondratschek & Zassenhauss, 1978) and have been characterized by WPV geometrical symbols (Weigel, Phan & Veysseyre, 1984; Veysseyre, Phan & Weigel, 1985).

In this paper, we call a structure which has a one-dimensional modulation a 'mono-incommensurate structure' (MI structure for short) and we use the abbreviations PSO instead of point symmetry operation and PSG instead of point symmetry group.

We shall exemplify how one special type of crystallographic space and point groups of $\mathbb{E}^4$ can be used to describe the crystallized solids of physical space. This will be the groups of mono-incommensurate (MI) structures with de Wolff, Janssen & Janner (WJJ) symbols (de Wolff, Janssen & Janner 1981).

We shall analyse the structure of the compound γ-Na_2CO_3. The basic structure of the (MI) modulated phase γ-Na_2CO_3 (Bertaut, 1984; van Aalst, den Hollander, Peterse & de Wolff, 1976) is monoclinic and has the symmetry space groups $C2/m$. The four elements of its point group $2/m$ are defined by the following matrices through a correct basis:

$$1=\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}\qquad 2=\begin{pmatrix}-1&0&0\\0&1&0\\0&0&-1\end{pmatrix}$$

$$m=\begin{pmatrix}1&0&0\\0&-1&0\\0&0&0\end{pmatrix}\qquad \bar{1}=\begin{pmatrix}-1&0&0\\0&-1&0\\0&0&-1\end{pmatrix}.$$

The experimental diffraction pattern of the (MI) phase must be described by four Miller indices (three h, k, l for Bragg peaks, one for the satellites) in reciprocal space $\mathbb{E}^{3*}$. So the diffraction vector of each peak can be written as

$$\mathbf{H}=h\mathbf{a}^*+k\mathbf{b}^*+l\mathbf{c}^*+m\mathbf{q}^*$$

in $\mathbb{E}^{3*}$ with

$$\mathbf{q}^*=0{\cdot}182\mathbf{a}^*+0{\cdot}138\mathbf{c}^*$$

at 298 K.

The structure is really mono-incommensurate because all satellites are located along a unique line supported by the vector $\mathbf{q}^*$ though two irrational coefficients appear. Only one fourth (additional) vector $\mathbf{d}$ perpendicular to the space $\mathbb{E}^{3*}$ is necessary because there are four Miller indices. In the superspace $\mathbb{E}^{4*}$ the diffraction vector of each peak can be written as

$$\mathbf{H}=h\mathbf{a}^*+k\mathbf{b}+l\mathbf{c}^*+m(\mathbf{q}^*+\mathbf{d}).$$

The experimental diffraction pattern is just the projection of $\mathbf{H}$ along $\mathbf{d}$ into $\mathbb{E}^{3*}$. In fact, the (MI) phase is a crystal in the superspace $\mathbb{E}^4$ described by the dual cell

$$\mathbf{a}'=\mathbf{a}-0{\cdot}182\mathbf{d};\ \mathbf{b}'=\mathbf{b};\ \mathbf{c}'=\mathbf{c}-0{\cdot}318\mathbf{d};\ \mathbf{d}'=\mathbf{d}.$$

As the vectors **a** and **d** on the one hand and **c** and **d** on the other appear in linear combinations, the three vectors **a**, **c** and **d** must be transformed in the same way by any point symmetry operation (PSO) of the point group of the (MI) phase, *i.e.* by the four operators

$$1=\begin{pmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\qquad \bar{1}_{xzt}=\begin{pmatrix}-1&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}$$

$$m_y=\begin{pmatrix}1&0&0&0\\0&-1&0&0\\0&0&1&0\\0&0&0&1\end{pmatrix}\qquad \bar{1}_4=\begin{pmatrix}-1&0&0&0\\0&-1&0&0\\0&0&-1&0\\0&0&0&-1\end{pmatrix}.$$

We can remark that all matrices have the same form,

$$\begin{pmatrix}\varepsilon&&&\\&A_{1\times1}&&\\&&\varepsilon&\\&&&\varepsilon\end{pmatrix},$$

where $\varepsilon=+1$ for the first and third matrices, $\varepsilon=-1$ for the second and fourth matrices, and $A_{1\times1}$ is a 1×1 matrix, *i.e.* a scalar equal to +1 or −1.

Consequently, the point group in the superspace has WPV symbol $\bar{1}\perp m$ [right hyperprism based on an oblique parallelepiped (Weigel, Phan & Veysseyre, 1987)]. We have also shown that the space group is $S(1\text{-}2)\ \bar{1}\perp m_{d/2}$ (Veysseyre *et al.*, 1985) where $S(1\text{-}2)$ means that the faces (x, y) are centred and $m_{d/2}$ that the hyperplane $m(x\,z\,t)$ is a glide mirror $(d/2)$.

We can note that two PSOs (1 and m_y) have the same symbol in $\mathbb{E}^4$ as the corresponding elements of the point group of the basic structure; indeed, they are $(\mathrm{MI})^+$ PSOs (see § II).

In short, thanks to this example we have shown that the MI phases of the physical space are crystals of the superspace $\mathbb{E}^4$. In § II we shall systematically determine the (MI) point symmetry groups (PSGs) by way of (MI) PSOs that we have first defined; finally we shall assign WPV symbols to these groups.

However, the concept of polar crystallographic PSGs in $\mathbb{E}^4$ (and $\mathbb{E}^5, \mathbb{E}^6, \ldots$) that is defined here for the first time (§ I) makes the elaboration of the (MI) PSGs easier. We also give WPV symbols to the polar crystallographic PSGs which are isomorphic to the crystallographic PSGs in the lower-dimensional space.

I. Polar crystallographic point groups

I.1. *Examples*

The essential concepts already occur in the spaces $\mathbb{E}^1$, $\mathbb{E}^2$ or $\mathbb{E}^3$ and can be illustrated by some examples.

The point symmetry groups of ferroelectric crystals and polar molecules are called 'polar groups'. We notice that there are one in the space $\mathbb{E}^1$: 1, two in the space $\mathbb{E}^2$: 1 and *m* (group of the chemisorbed water molecule) and ten in the space $\mathbb{E}^3$: 1, *m*, 2, 3, 4, 6, 2*mm* (group of the water molecule in $\mathbb{E}^3$), 3*m*, 4*mm* and 6*mm* (Fig. 1).

We shall generalize the well known results in the spaces $\mathbb{E}^2$ and $\mathbb{E}^3$ to the space $\mathbb{E}^n$ by stating first the definition of the polar crystallographic PSOs, and then the definition of the polar PSGs.

I.2. *Polar crystallographic point symmetry operations*

Definition. A PSO of $\mathbb{E}^n$ is called 'polar' if it leaves unchanged at least one vectorial half straight line of $\mathbb{E}^n$ (Weigel & Veysseyre, 1982). The list of polar and non-polar crystallographic PSOs is given in Table 1 for the spaces $\mathbb{E}^1$, $\mathbb{E}^2$, $\mathbb{E}^3$ and $\mathbb{E}^4$.

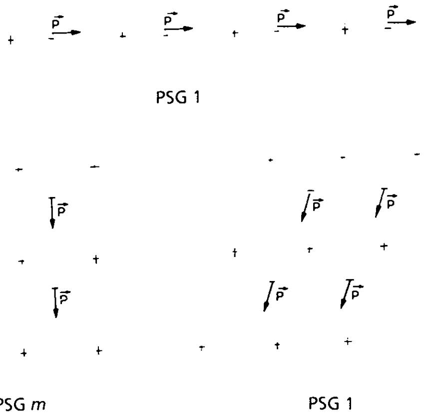
Remark. In the space $\mathbb{E}^1$, we prefer to call the symmetry with respect to a point 'reflection in a point-mirror'; hence its symbol *m* (Hermann, 1949).

Theorem. There are as many types of polar crystallographic PSOs in $\mathbb{E}^n$ as there are types of crystallographic PSOs in $\mathbb{E}^{n-1}$ and they have the same symbol.

As a matter of fact, let us write the space $\mathbb{E}^n$ as a direct sum of two supplementary and orthogonal subspaces,

$$\mathbb{E}^n = \mathbb{E}^{n-1} \oplus \mathbb{E}^1.$$

Among the crystallographic PSOs of $\mathbb{E}^n$ those which leave unchanged at least the subspace $\mathbb{E}^1$ are all the PSOs of $\mathbb{E}^{n-1}$, and therefore the proclaimed result is obtained. The number of types of polar and non-polar crystallographic PSOs is given in Table 2 for the spaces $\mathbb{E}^n$ where *n* varies from 1 to 6. The number of types of crystallographic PSOs has been previously found, for instance by Hermann (1949).



PSG 1

PSG *m*

PSG 1

Fig. 1. Point symmetry groups of ferroelectric crystals in $\mathbb{E}^1$ (top) and $\mathbb{E}^2$ (bottom).

Table 1. *Crystallographic point symmetry operations of the spaces* $\mathbb{E}^1$, $\mathbb{E}^2$, $\mathbb{E}^3$ *and* $\mathbb{E}^4$

	$\mathbb{E}^1$	$\mathbb{E}^2$	$\mathbb{E}^3$	$\mathbb{E}^4$	
PSO$^+$	$\boxed{1}$	$\boxed{1}$	$\boxed{1}$	$\boxed{1}$	$\bar{1}_4$, 55, 1010
		2	$\boxed{2}$	$\boxed{2}$	24, 26
		3	$\boxed{3}$	$\boxed{3}$	32, 33
		4	$\boxed{4}$	$\boxed{4}$	43, 44, 46, 88
		6	$\boxed{6}$	$\boxed{6}$	66, 63, 1212
PSO$^-$	*m*	$\boxed{m}$	$\boxed{m}$	$\boxed{m}$	
			$\bar{1}$	$\boxed{\bar{1}}$	
			$\bar{3}$	$\boxed{\bar{3}}$	
			$\bar{4}$	$\boxed{\bar{4}}$	
			$\bar{6}$	$\boxed{\bar{6}}$	

Symbols in squares refer to crystallographic polar PSOs.

Table 2. *Number of types of crystallographic point symmetry operations of the spaces* $\mathbb{E}^1$, $\mathbb{E}^2$, $\mathbb{E}^3$, $\mathbb{E}^4$, $\mathbb{E}^5$ *and* $\mathbb{E}^6$

	$\mathbb{E}^0$	$\mathbb{E}^1$	$\mathbb{E}^2$	$\mathbb{E}^3$	$\mathbb{E}^4$	$\mathbb{E}^5$	$\mathbb{E}^6$
Number of types of crystallographic PSOs	1	2	6	10	25	38	78
Number of types of polar crystallographic PSOs		1	2	6	10	25	38

Table 3. *Number of crystallographic point symmetry groups in the spaces* $\mathbb{E}^1$, $\mathbb{E}^2$, $\mathbb{E}^3$, $\mathbb{E}^4$ *and* $\mathbb{E}^5$

	$\mathbb{E}^0$	$\mathbb{E}^1$	$\mathbb{E}^2$	$\mathbb{E}^3$	$\mathbb{E}^4$	$\mathbb{E}^5$
Number of crystallographic PSGs	1	2	10	32	227	
Number of polar crystallographic PSGs		1	2	10	32	227

I.3. *Polar crystallographic point symmetry groups of* $\mathbb{E}^n$

Definition. A crystallographic PSG of $\mathbb{E}^n$ is polar if all its elements (*i.e.* its PSOs) leave unchanged the same vectorial half straight line (*s*).

Theorem. The number of polar crystallographic PSGs of $\mathbb{E}^n$ is equal to the number of crystallographic PSGs of $\mathbb{E}^{n-1}$.

This number is given in Table 3 for *n* varying from 1 to 5.

The relation $\mathbb{E}^n = \mathbb{E}^{n-1} \oplus \mathbb{E}^1$ allows the theorem to be proved.

The WPV symbol of a polar crystallographic PSG of $\mathbb{E}^n$ is identical (except for the commas) to the symbol of the crystallographic PSG which has given rise to it.

In Tables 1 and 2 of Weigel *et al.* (1987) the 32 polar crystallographic PSGs of $\mathbb{E}^4$ were characterized by a point '.'; we verify that these 32 polar crystallographic PSGs have the same symbols as the Hermann–Mauguin symbols of the 32 crystallographic PSGs of physical space (except for the commas).

II. Point group of (MI) phases of physical space $\mathbb{E}^3$ $(x\,y\,z)$ in the superspace $\mathbb{E}^4$

II.1. *Definitions*

A crystal structure of $\mathbb{E}^3$ is called 'incommensurate' if, among all symmetry operations which leave unchanged this structure, there exist n translations defined by n linearly independent vectors, n being equal to at least four, such that: three describe the average crystal structure (non-modulated), called the basic structure, in the physical space $\mathbb{E}^3$; and the others, incommensurate with the former ones, can be interpreted as internal degrees of freedom. Let d be their number.

This structure does not have three-dimensional periodicity because it is not a crystal in the physical space $\mathbb{E}^3$ but it is described by a symmetry space group based on $(3+d)$ basis translations in a $(3+d)$-dimensional superspace where this phase is a crystal.

If d equals one, this phase is called 'mono-incommensurate' or MI for short and we are concerned with a crystal in a superspace $\mathbb{E}^4$.

As pointed out earlier, the experimental diffraction pattern of a (MI) phase must be described by four integers (h, k, l, m or Miller indices), each diffraction vector being defined in the reciprocal space $\mathbb{E}^{3*}$ by

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}^*$$

with

$$\mathbf{q}^* = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*.$$

The components (α, β, γ) of the vector $\mathbf{q}^*$ are not all integers or simple fractions, *i.e.* some of them are irrational. As the satellites are just defined by one vector $\mathbf{q}^*$, it is really a (MI) phase. As a matter of fact, different cases can occur according to the number of irrational components; we shall explain them in the next section.

II.2. *The mono-incommensurate PSOs of the superspace* $\mathbb{E}^4$

The (MI) PSOs of $\mathbb{E}^4$ are the elements of the PSG of a (MI) phase of a crystal in a superspace $\mathbb{E}^4$.

They are described with respect to an orthonormal basis by 4×4 matrices which have the form (de Wolff, 1974)

$$\left(\begin{array}{c|cc} Q & \multicolumn{2}{c}{0} \\ \hline \multirow{2}{*}{0} & \varepsilon & 0 \\ & 0 & \varepsilon \end{array}\right),$$

where Q is a 2×2 matrix describing a PSO of the plane $\mathbb{E}^2$ and ε equals 1 or -1. The (MI) PSOs can be classified by taking into consideration either the value of ε or the number of irrational components of the vector $\mathbf{q}^*$, and therefore the matrix Q.

II.2.1. By definition, a (MI) PSO is a

$$(\mathrm{MI})^+ \text{ PSO if } \varepsilon = 1$$

$$(\mathrm{MI})^- \text{ PSO if } \varepsilon = -1.$$

It is easy to list these different types of (MI) PSOs. There are six $(\mathrm{MI})^+$ PSOs which are isomorphic to all crystallographic PSOs of the plane $\mathbb{E}^2$, *i.e.* to all polar crystallographic PSOs of the physical space $\mathbb{E}^3$, and they have the same symbol:

$$1,\ 2_{xy},\ 3^{\pm1}_{xy},\ 4^{\pm1}_{zt},\ 6^{\pm1}_{xy},\ m_x.$$

There are six $(\mathrm{MI})^-$ PSOs:

$$2_{zt},\ \bar{1}_4,\ 2_{zt}3^{\pm1}_{xy},\ 2_{zt}4^{\pm1}_{xy},\ 2_{zt}6^{\pm1}_{xy},\ \bar{1}_{xzt}.$$

Later, we shall explain that the first five PSOs are the five black or magnetic PSOs of the superspace $\mathbb{E}^4$.

II.2.2. We now study the different possibilities according to the number of irrational components of the vector $\mathbf{q}^*$.

(i) First, we suppose that just *one* coefficient, γ for instance, is irrational, *i.e.*

$$\mathbf{q}^* = \gamma\mathbf{c}^*.$$

Then this (MI) phase is a crystal in the superspace $\mathbb{E}^4$ defined by

$$\mathbf{a}' = \mathbf{a};\ \mathbf{b}' = \mathbf{b};\ \mathbf{c}' = \mathbf{c} - \gamma\mathbf{d};\ \mathbf{d}' = \mathbf{d}.$$

The vector $\mathbf{d}$ is orthogonal to the space $(\mathbf{a}', \mathbf{b}', \mathbf{c}')$. The vectors $\mathbf{c}'$ and $\mathbf{d}$ which appear in linear combination must be transformed in the same way by each PSO of the PSG of this structure. So the corresponding matrices have the general form

$$\left(\begin{array}{c|cc} A & \multicolumn{2}{c}{0} \\ \hline \multirow{2}{*}{0} & \varepsilon & 0 \\ & 0 & \varepsilon \end{array}\right)$$

where $\varepsilon = \pm1$ and A is a 2×2 matrix.

Therefore, we find:

eight 'general' PSOs,

$$2_{xy}, 3^{\pm1}_{xy}, 4^{\pm1}_{xy}, 6^{\pm1}_{xy}, 2_{zt}, 2_{zt}3^{\pm1}_{xy}, 2_{zt}4^{\pm1}_{xy}, 2_{zt}6^{\pm1}_{xy};$$

two 'particular' PSOs,

$$m_x \text{ (or } m_y\text{) if } A = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \text{ and } \varepsilon = +1;$$

$$\bar{1}_{xzt} \text{ (or } \bar{1}_{yzt}\text{) if } A = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \text{ and } \varepsilon = -1;$$

and two 'very particular' PSOs,

$$1 \text{ if } A = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \text{ and } \varepsilon = 1$$

$$\bar{1}_4 \text{ if } A = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \text{ and } \varepsilon = -1.$$

(ii) Then we suppose that *two* coefficients, α and γ for instance, are irrational, *i.e.*

$$\mathbf{q}^* = \alpha\mathbf{a}^* + \gamma\mathbf{c}^*.$$

This is the example given in the *Introduction.* As previously, we define the vectors

$$\mathbf{a}' = \mathbf{a} - \alpha\mathbf{d};\ \mathbf{b}' = \mathbf{b};\ \mathbf{c}' = \mathbf{c} - \gamma\mathbf{d};\ \mathbf{d}' = \mathbf{d}.$$

In this case the matrices which describe all PSOs have the following general form, because the vectors **a** and **d** in the first part, **c** and **d** in the other part, must be described in the same way:

$$\begin{pmatrix} \varepsilon & 0 & 0 & 0 \\ 0 & A & 0 & 0 \\ 0 & 0 & \varepsilon & 0 \\ 0 & 0 & 0 & \varepsilon \end{pmatrix}$$

with $\varepsilon = \pm 1$; A is a scalar, and therefore it equals 1 or -1. Only the two particular PSOs and the two very particular PSOs can appear.

(iii) Finally, we suppose that the *three* coefficients α, β and γ are irrational. The superspace $\mathbb{E}^4$ is defined by the vectors

$$\mathbf{a}' = \mathbf{a} - \alpha\mathbf{d};\ \mathbf{b}' = \mathbf{b} - \beta\mathbf{d};\ \mathbf{c}' = \mathbf{c} - \gamma\mathbf{d};\ \mathbf{d}' = \mathbf{d},$$

and the vectors **a** and **d** in the first part, **b** and **d**, **c** and **d** in the other part, must be described in the same way. So the matrices must have the form

$$\begin{pmatrix} \varepsilon & & & \\ & \varepsilon & & \\ & & \varepsilon & \\ & & & \varepsilon \end{pmatrix} \text{ with } \varepsilon = \pm 1$$

and only the 'very particular' PSOs can appear. They are fully degenerate (Weigel, Veysseyre, Phan, Effantin & Billiet, 1984).

The other cases of incommensurability are described:

(i) in $\mathbb{E}^5$ if

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m_1\mathbf{q}_1^* + m_2\mathbf{q}_2^*$$

(two different lines of satellites occur in the experimental diffraction pattern; it is a two-incommensurate structure);

(ii) or in $\mathbb{E}^6$ if

$$\mathbf{H} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m_1\mathbf{q}_1^* + m_2\mathbf{q}_2^* + m_3\mathbf{q}_3^*$$

(three different lines of satellites occur in the experimental diffraction pattern; it is a three-incommensurate structure).

II.3. (*MI*) *point symmetry group of* $\mathbb{E}^4$

A (MI) point symmetry group, (MI) PSG for short, is a PSG in which all elements are (MI) PSOs.

All possible modulated (MI) structures are described by 31 (MI) PSGs (de Wolff, 1974), but two of them correspond to the same crystallographic PSG of $\mathbb{E}^4$. One is defined by the matrix

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

and its WPV symbol is 2; the other is defined by

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

and its WPV symbol is $2^{\blacktriangledown}$ (the sign $\blacktriangledown$ is explained below). Therefore 30 among the 227 PSGs of $\mathbb{E}^4$ generate all (MI) PSGs. Table 4 lists the (MI) PSGs of $\mathbb{E}^4$.

We call a PSG which contains only $(\mathrm{MI})^+$ PSOs a $(\mathrm{MI})^+$ PSG. For instance, the PSG *m*, *m*, 2 is a $(\mathrm{MI})^+$ PSG.

If a (MI) PSG contains at least one $(\mathrm{MI})^-$ PSG it is called a $(\mathrm{MI})^-$ PSG. We can mention the (MI) PSG $2^{\blacktriangledown}\perp 3$, *m* as an example. The $(\mathrm{MI})^-$ PSOs which appear in the WPV symbol of a $(\mathrm{MI})^-$ PSG are indicated by the sign $\blacktriangledown$; they belong to the set of possible generators of this $(\mathrm{MI})^-$ PSG. In a $(\mathrm{MI})^-$ PSG, the $(\mathrm{MI})^+$ PSOs form a subgroup of index two which is its $(\mathrm{MI})^+$ PSG.

Remarks.

(i) Just as the $(\mathrm{MI})^+$ PSOs and $(\mathrm{MI})^-$ PSOs must not be confused with PSO^+s and PSO^-s so the $(\mathrm{MI})^+$ PSGs and $(\mathrm{MI})^-$ PSGs must not be confused with PSG^+s and PSG^-s defined by Weigel, Phan & Veysseyre (1984). We recall that the determinant of the matrix associated with a PSO^+ equals $+1$ and that associated with a PSO^- equals -1; a PSG^+ contains only PSO^+s while a PSG^- contains at least one PSO^-.

(ii) The PSG 2 of $\mathbb{E}^4$ gives rise to a $(\mathrm{MI})^+$ PSG 2 and a $(\mathrm{MI})^-$ PSG $2^{\blacktriangledown}$.

Properties of the (*MI*) *PSGs of* $\mathbb{E}^4$. Among the 31 (MI) PSGs of $\mathbb{E}^4$, the ten polar PSGs of $\mathbb{E}^4$ correspond to $\varepsilon = +1$. Their symbols are identical to those of the ten crystallographic PSGs of $\mathbb{E}^3$, except for the commas. They are the only $(\mathrm{MI})^+$ PSGs of $\mathbb{E}^4$. Another polar crystallographic PSG, $2^{\blacktriangledown}/m$, of $\mathbb{E}^4$ is also a (MI) PSG but it is a $(\mathrm{MI})^-$ PSG. There are 21 $(\mathrm{MI})^-$ PSGs.

II.4. (*MI*) *crystal systems*

A crystal system is called (MI) if all PSGs of this system are (MI) PSGs. There are seven (MI) crystal systems in $\mathbb{E}^4$ which are the systems numbered 1, 2, 3, 4, 7, 8 and 9 in the classification of Brown *et al.* (1978). They are the only systems which contain (MI) PSGs.

(i) The two PSGs, 1 and $\bar{1}_4$ (Weigel *et al.*, 1987) of the hexaclinic crystal system (no. 1) contain only

Table 4. *The (MI) PSGs of the space* $\mathbb{E}^4$

The first three columns indicate the respective numbers of the family, the system and the PSG and the last column the WPV symbols of these PSGs. The sign ▼ characterizes the $(\mathrm{MI})^-$ PSOs which appear in the WPV symbols.

Family	System	PSG	WPV symbols
I	01	01	1
		02	$\bar{1}_4^{\blacktriangledown}$
II	02	01	m
		02	$\bar{1}^{\blacktriangledown}$
		03	$\bar{1}^{\blacktriangledown} \perp m$
III	03	01	$\left\{\begin{array}{l}2\\2^{\blacktriangledown}\end{array}\right.$
		02	$2 \perp 2^{\blacktriangledown}$
IV	04	01	$m, m, 2$
		02	$2^{\blacktriangledown}/m$
		03	$2, \bar{1}^{\blacktriangledown}, \bar{1}^{\blacktriangledown}$
		04	$2^{\blacktriangledown} \perp 2, m, m$
VI	07	01	$(24)^{\blacktriangledown}$
		02	4
		03	$2^{\blacktriangledown} \perp 4$
		04	$(24)^{\blacktriangledown}, m, \bar{1}^{\blacktriangledown}$
		05	$4, \bar{1}^{\blacktriangledown}, \bar{1}^{\blacktriangledown}$
		06	$4, m, m$
		07	$2^{\blacktriangledown} \perp 4, m, m$
VII	08	01	3
		02	$(26)^{\blacktriangledown}$
		03	$3, m$
		04	$3, \bar{1}^{\blacktriangledown}$
		05	$(26)^{\blacktriangledown}, m, \bar{1}^{\blacktriangledown}$
VII	09	01	6
		02	$2^{\blacktriangledown} \perp 3$
		03	$2^{\blacktriangledown} \perp 6$
		04	$6, m, m$
		05	$6, \bar{1}^{\blacktriangledown}, \bar{1}^{\blacktriangledown}$
		06	$2^{\blacktriangledown} \perp 3, m$
		07	$2^{\blacktriangledown} \perp 6, m, m$

one or two very particular (MI) PSOs *i.e.* 1 or $\bar{1}_4$. Therefore, they describe the (MI) phases for which the three coefficients are irrational.

(ii) The three PSGs m, $\bar{1}$ and $\bar{1} \perp m$ (Weigel *et al.*, 1987) of the crystal system no. 2 (right hyperprism based on an oblique parallelepiped) do not contain general PSOs but contain at least one particular (MI) PSO: m or $\bar{1}$; they describe the modulated (MI) phases such as γ-Na_2CO_3 for which two of the three coefficients α, β and γ are irrational (see *Introduction*).

(iii) The PSGs of the five remaining systems contain at least one general (MI) PSO. They are the following systems:

system no. 3: di orthogonal parallelograms
system no. 4: orthogonal parallelogram rectangle
system no. 5: orthogonal parallelogram square
system no. 8: orthogonal parallelogram hexagon $R(2, 3, 4)$
system no. 9: orthogonal parallelogram hexagon.

We will illustrate these notions by two examples.

(i) The first concerns the compound K_2SeO_4. Its basic structure is orthorhombic and its main symmetry groups are $2_1/n\ 2_1/a\ 2_1/m$ (space group) and $2/m\,m\,m$ (point group of order 8) (van Smaalen, Bronsema & Mahy, 1986). The modulation vector is given by $\mathbf{q}^* = \alpha\mathbf{a}$. Thus it belongs to the system no. 4 (orthogonal parallelogram rectangle). In the superspace $\mathbb{E}^4$ the symmetry of this structure is described by the $(\mathrm{MI})^-$ PSG $2^{\blacktriangledown} \perp 2$, $m\ m$ of order 8. With the previous notations, the 2×2 matrix Q successively describes one of the four PSOs of the PSG $2\ m\ m$. As each matrix Q can be associated with $\varepsilon = 1$ or $\varepsilon = -1$, the order of the $(\mathrm{MI})^-$ PSG is twice as high as that of the PSG $2\ m\ m$.

(ii) The second example is related to the compound $NbTe_4$ which corresponds to the quadratic basic structure with the symmetry groups $P4/m\,c\,c$ (space group) and $4/m\,m\,m$ (point group of order 16). In this case the modulation vector is

$$\mathbf{q}^* = \tfrac{1}{2}\mathbf{a}^* + \tfrac{1}{2}\mathbf{b}^* + \gamma\mathbf{c}^*$$

and we remark that one only component of the vector $\mathbf{q}^*$ is irrational. So it belongs to the system no. 8 (orthogonal parallelogram square). In the superspace $\mathbb{E}^4$, the symmetry of this (MI) structure is described by the $(\mathrm{MI})^-$ PSG $2 \perp 4$, m, m of order 16. In this example, the 2×2 matrix Q successively describes one of the eight PSOs of the crystallographic PSG $4m\,m$ of $\mathbb{E}^2$.

Thanks to these two examples, we notice that the crystal system and the PSG of the modulated structure in the superspace $\mathbb{E}^4$ are implied by the crystal system and the PSG of the basic structure in the space $\mathbb{E}^3$. So, if the basic structure of the modulated phase is hexagon (primitive or rhombic) the point group belongs to one of the two crystal systems 8 or 9. These two systems constitute the crystal family no. VII with holohedry $2 \perp 6$, m, m (Brown *et al.*, 1978; Weigel *et al.*, 1987).

In a following publication, we shall discuss in detail these two examples and in particular we shall establish the relations between the WJJ symbols and the WPV symbols of the space groups of these (MI) phases.

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Modified Multislice Theory for Calculating the Energy-Filtered Inelastic Images in REM and HREM

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Abstract

Inelastic plasmon diffuse scattering (PDS) is treated as an effective position-dependent potential perturbing the incident electron wavelength in a solid surface, resulting in an extra phase grating term in the slice transmission function. This potential is derived for the geometry of reflection electron microscopy (REM) and high-resolution electron microscopy (HREM). The energy-filtered inelastic images can be calculated following the routine image simulation procedures by using different slice transmission functions for the elastic and inelastic waves, by considering the 'transitions' of the elastic scattered electrons to the inelastic scattered electrons. It is predicted that the inelastic scattering could modify the electron intensity distribution at a surface. It is possible to take high-resolution energy-filtered inelastic images of crystals, the resolution of which is about the same as that taken from the elastic scattered electrons.

1. Introduction

Multislice theory has been successfully applied in image simulation for high-resolution electron microscopy (HREM). Recently, this theory has been modified for calculating the image contrast and electron resonance processes at a crystal surface in the geometry of reflection electron microscopy (REM) or reflection high-energy electron diffraction (RHEED). Contrast variations of an atomic surface step under different focusing conditions were interpreted (Peng & Cowley, 1987). Surface-layer resonance properties under resonance conditions were simulated; the generating processes of reflection waves at an atomic flat surface and a surface with a step up or down were investigated and compared with REM observations (Wang, Lu & Cowley, 1987; Wang, 1988). All these calculations, however, were based on elastic scattering theory. In the REM case, most of the incident electrons have lost the energy of the surface plasmon during the scattering (Wang & Cowley, 1988), and the calculated results from the elastic theory cannot represent the real interaction behavior of the electrons with surfaces. A new theory which includes the effects of electron inelastic scattering in the dynamical calculations is required for quantitative analysis of REM and RHEED data. This situation also happens in HREM if a sample is thicker than the inelastic mean free path of the electrons.

Recently Wang & Lu (1988) have suggested a new method, from which the plasmon diffuse scattering (PDS) can be included in the calculation of the multislice theory. The energy loss of the electrons due to plasmon excitations was characterized by an effective potential modifying the kinetic energy of the incident electrons, and resulting in a perturbation to the electron wavelength. The phase grating function of each slice is the product of an elastic with an inelastic function arising from the plasmon losses. Thus multiple excitations of plasmons were automatically involved in the calculations.

In this paper, as a continuation of our previous work (Wang & Lu, 1988), (1) the relativistic dielectric response theory will be employed to calculate the electron energy loss rate and its associated perturbation effect on the slice transmission function (STF); (2) the quantum-mechanical basis of this method will be addressed; (3) a modified multislice theory for

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