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Superspace-Group Description of Short-Period Commensurately Modulated Crystals

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Abstract

The symmetry of superstructures is described by an ordinary three-dimensional space group, based on a unit cell which is a multiple of the basic structure unit cell. Alternatively, superstructures can be looked upon as commensurately modulated structures. Then, the structure is described by its basic structure plus some distortion wave. In this paper the application to superstructures of superspace groups, originally devised to describe the symmetry of incommensurately modulated structures, is discussed. The Bravais classes of superspace groups for commensurately modulated structures are derived. A comparison is made between the superspace group and the ordinary three-dimensional space-group description for commensurately modulated structures. With the help of the structure of $Ag_{0.35}TiS_2$, the consequences for the interpretation of the diffraction pattern are discussed. Also, the nature and number of the independent parameters in the superspace-group approach are compared with the description of the structure by an ordinary space group.

1. Introduction

Modulated crystals are crystals with three-dimensional periodicity which have, in addition, some deviation from this periodicity. The distortion from the three-dimensional periodicity is itself periodic. However, the wavelength does not correspond to the basis vectors describing the translation symmetry of the undistorted structure.

The distortion wave can either be incommensurate or commensurate. In the latter case new, larger, basis vectors can be defined, which restore the three-dimensional translation symmetry. Incommensurate modulations are characterized by the fact that the wavelength of the distortion and the basis vectors of the undistorted structure do not have a common multiple. In that case the choice of a larger unit cell with three-dimensional periodicity is not possible.

The modulation wave is defined by modulation functions for the constituent atoms. Each independent atom of the basic structure has its own independent modulation function. Displacive modulation and occupational probability modulation are commonly encountered. In crystals with displacive modulation the positions $\mathbf{r}_{\mu L}$ of the atoms are given as the sum of their average position $\mathbf{r}^0_{\mu L}$ (having three-dimensional periodicity) and a periodic function which depends on the average position coordinates,

$$\mathbf{r}_{\mu L} = \mathbf{r}^0_{\mu L} + \mathbf{u}^\mu(\mathbf{q} \cdot \mathbf{r}^0_{\mu L}), \tag{1.1}$$

where $\mathbf{r}^0_{\mu L} = \mathbf{L} + \mathbf{x}^0_\mu$, with $\mathbf{L}$ a direct-lattice vector and $\mathbf{x}^0_\mu$ determines the average position of the μth atom in a unit cell. The modulation wave is characterized by its modulation wave vector $\mathbf{q}$. Here, the case of a one-dimensional modulation is considered. Generalization to more dimensions is easily performed (Janner, Janssen & de Wolff, 1983; van Smaalen, 1985). The modulation function $\mathbf{u}^\mu(\mathbf{q} \cdot \mathbf{r}^0_{\mu L})$ is periodic with a period of 1. An average occupation less than one is accounted for by an occupation probability $P_{\mu L}$ for each atomic site. In modulated structures the occupation probability is the sum of the average occupation probability P^0_μ and a modulation function $P_\mu(\mathbf{q} \cdot \mathbf{r}^0_{\mu L})$, which is also a periodic function with a period of 1:

$$P_{\mu L} = P^0_\mu + P_\mu(\mathbf{q} \cdot \mathbf{r}^0_{\mu L}). \tag{1.2}$$

For incommensurately modulated structures the argument of the modulation functions, $\mathbf{q} \cdot \mathbf{r}^0_{\mu L}$, assumes all values (modulo 1). {More precisely, $\mathbf{q} \cdot \mathbf{r}^0_{\mu L}$ (mod 1) is a dense set in the interval [0; 1] of the real numbers.} This means that any phase shift of the modulation functions gives a structure identical to the original one, but situated differently in space. In commensurately modulated structures the arguments (mod 1) of the modulation functions assume only a finite set (say N) of values. Equivalent three-dimensional structures are then obtained only for a shift of the argument by a multiple of $1/N$. Another phase shift produces a different structure. In this way there are infinitely many sets of N equivalent structures for one and the same set of modulation functions.

The symmetry of a commensurately modulated structure can always be described by an ordinary three-dimensional space group through the proper choice of a larger unit cell. For the modulation functions having N different values, a unit cell with a

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volume N times that of the unit cell of the basic structure will again have three-dimensional periodicity.

Incommensurately modulated structures do not have three-dimensional periodicity and, therefore, cannot be described by a three-dimensional space group. A description of their symmetry by so-called superspace groups was developed by Janner, Janssen & de Wolff (1983). Superspace groups are space groups based on $(3+d)$ basis translations. The first three refer to the periodicity of the undistorted structure. The d additional periodicities refer to the number of independent modulation waves in the crystal. That is, they are translations of the arguments of the modulation functions (1.1) and (1.2). In this paper only the case $d=1$ will be considered.

In the original derivation of the application of superspace groups to modulated structures (de Wolff, 1974; de Wolff, Janssen & Janner, 1981), the incommensurateness was considered to be an essential feature for this application to be possible. However, in their mathematical derivation of superspace groups, Janner & Janssen (1979) noted that incommensurateness of the modulation is not a necessary condition. This means that structures with a modulation wave vector which is a fraction of a reciprocal-lattice vector with a large denominator can be treated in the same way as truly incommensurately modulated structures. Structures in which the components of the modulation wave vector are simple fractions need a special treatment, because of the fact that one modulation function describes different modulated structures, owing to the possibility of different phase shifts.

The theory of superspace groups is now well established (Janner & Janssen, 1979; 1980*a*, *b*), and a tabulation of Bravais classes of superspace groups up to $d=3$ (Janner, Janssen & de Wolff, 1983) and of all superspace groups for $d=1$ (de Wolff, Janssen & Janner, 1981; Yamamoto, Janssen, Janner & de Wolff, 1985) is available. These tables contain only superspace groups for incommensurately modulated structures, *i.e.* at least one component of the modulation wave vector is unrestricted. If superspace groups are used to describe commensurately modulated structures, those superspace groups which have completely commensurate wave vectors are also of interest. It will appear that for these cases additional Bravais classes are needed. In § 2 these additional Bravais classes for $d=1$ will be derived.

As follows from the foregoing discussion, the symmetry of a commensurately modulated structure can be described either by a superspace group or by an ordinary three-dimensional space group. In § 3 a comparison of both descriptions will be made. As an example the modulated structures of $Ag_{0.35}TiS_2$ will be discussed. It will be shown that a better description of the X-ray diffraction pattern is obtained by the use of superspace groups. Also, it will be shown that the superspace-group approach can lead to more restrictions on the structural parameters than the three-dimensional space-group description.

2. Bravais classes of superspace groups for commensurate modulations ($d=1$)

The set of all $(3+d)$-dimensional superspace groups constitutes a subset of the $(3+d)$-dimensional space groups. For a one-dimensional ($d=1$) modulation with wave vector $\mathbf{q}$, the relation restricting a space group to be a superspace group is (de Wolff, Janssen & Janner, 1981)

$$R\mathbf{q}-\varepsilon\mathbf{q}=\mathbf{G} \tag{2.1}$$

where $\mathbf{G}$ is a reciprocal-lattice vector of the basic three-dimensional reciprocal lattice. R is the 3D part of the orthonormal transformation in the superspace group and ε is the fourth diagonal component. The superspace group is defined such that the angles of the fourth basis vector with the first three basis vectors are determined by the corresponding components of the modulation wave vector $\mathbf{q}$. Because R is a 3D orthonormal transformation and $(R\varepsilon)$ forms a $(3+1)$D orthonormal transformation, the value of ε is ± 1.

A lattice is associated with each space group. A Bravais class of space groups is a set of space groups which have an equivalent lattice (*International Tables for Crystallography*, 1983). This equivalence relation can be expressed in terms of the point group describing the symmetry of the lattice (holohedral point group). Two space groups belong to the same Bravais class if: (1) their holohedral point groups are related by a similarity transformation; (2) the orientation of the symmetry elements of the holohedral point group with respect to the lattice is the same. This latter condition is related directly to the occurrence of Bravais classes with a centred unit cell.

For $(3+d)$-dimensional superspace groups an analogous definition exists (Janner, Janssen & de Wolff, 1983). However, the admitted similarity transformations are now only those which obey the condition given by (2.1).

The complete set of Bravais classes of $(3+1)$-dimensional superspace groups can be obtained by consideration of the 3D Bravais classes. For each point group with a set of operators $\{R\}$ and a corresponding set $\{\varepsilon\}$ of ε values, such that $\{(R\varepsilon)\}$ forms a group, (2.1) gives the restrictions on the modulation wave vector $\mathbf{q}$. Note that for the centred basis lattice only those vectors $\mathbf{G}$ are admitted which describe real reciprocal-lattice points. In general, it is possible that additional Bravais classes are generated by considering also the 3D centrosymmetric point groups which are a subgroup of the holohedral point group. There is only one such Bravais class reported in the

literature:

$$R\,{}^{P\bar{3}1m}_{\bar{1}\,1\,1}\,(\tfrac{1}{3}\tfrac{1}{3}\gamma),$$

no. 23 in Table 1 of de Wolff, Janssen & Janner (1981).

In the tables of de Wolff, Janssen & Janner (1981) all Bravais classes of the (3+1)-dimensional superspace groups for incommensurately modulated structures are given. That is, in those superspace groups at least one component of the modulation wave vector is unrestricted. Additional Bravais classes can occur when all components of the modulation wave vector become simple fractions. Of course, all components of the modulation wave vector then have particular commensurate values as determined by symmetry.

There are two ways in which such additional Bravais classes may arise. First, the Bravais class may contain the operation $(E\bar{1})$, where E is the identity operation. From (2.1), this gives as restriction for the modulation wave vector

$$2\mathbf{q} = \mathbf{G}. \qquad (2.2)$$

Therefore, if the components of the modulation wave vector are 0, $\frac{1}{2}$ or 1, the operator $(E\bar{1})$ may be present. In the incommensurate superspace groups this operator is never present. However, as can easily be derived, the effect of the operator $(E\bar{1})$ on the modulation functions (1.1) and (1.2) is the same as the effect of the identity, $(E1)$, in the superspace group. Therefore, this operator does not introduce additional symmetry of the structures, and I will not give the additional Bravais classes which arise by the introduction of $(E\bar{1})$. The above-mentioned case occurs when in a Bravais class of incommensurate (3+1)-dimensional space groups the components of the modulation wave vector all assume particular rational values.

It is also possible that the components of the wave vectors of a two- or higher dimensional incommensurate modulation all become commensurate, and result in a one-dimensional modulated structure. This is the second possibility for the occurrence of additional Bravais classes. The totally commensurate wave vector represents a special point in the unit cell. These Bravais classes are indeed new, and such superspace groups can be used to describe the symmetry of commensurately modulated structures, for which there is no appropriate superspace group amongst the incommensurate superspace groups.*

As an example we will derive the (3+1)D Bravais classes for *Immm* basic lattice symmetry and discuss this case also for commensurate structures. Let the modulation wave vector be given by its components (α, β, γ), $\mathbf{q} = \alpha\mathbf{a}^* + \beta\mathbf{b}^* + \gamma\mathbf{c}^*$. For each 3D operation and any of the values $\varepsilon = \pm 1$ the difference $(R\mathbf{q} - \varepsilon\mathbf{q})$ can be calculated. For each choice of ε values, restrictions on the components (α, β, γ) are then obtained with (2.1). Note that for the *I*-centred basic lattice the reciprocal lattice is face centred, so that the admitted **G** vectors are linear combinations of (110), (101) and (011). When it is realized that, for example, $(m_x\bar{1})(m_y1)(m_z1)$ is equivalent to $(m_x1)(m_y1)(m_z\bar{1})$ *etc.*, we are left with four different sets of ε values. The restrictions on $\mathbf{q}$ give the Bravais classes of superspace groups.

For $(m_x1)(m_y1)(m_z\bar{1})$ one obtains

$$P\,{}^{Immm}_{1\,1\,\bar{1}}$$

with $\mathbf{q} = (00\gamma)$, no. 12 in Table 1 of de Wolff, Janssen & Janner (1981).

Both the combinations $(m_x1)(m_y\bar{1})(m_z\bar{1})$ and $(m_x1)(m_y1)(m_z1)$ give as restrictions that (α, β, γ) should all be integers. The only new Bravais class of interest is given by $\mathbf{q} = (001)$, which corresponds to a loss of centring of the basic lattice. However, for this wave vector $(E\bar{1})$ is also a symmetry operation, and both point groups are in fact different subgroups of the holohedral point group $(m_x1)(m_y1)(m_z1)(E\bar{1})$. Another subgroup of this point group is (m_x1)-$(m_y1)(m_z\bar{1})$, which corresponds to the incommensurate superspace Bravais class

$$P\,{}^{Immm}_{1\,1\,\bar{1}}.$$

As pointed out earlier, the operator $(E\bar{1})$ is equivalent to the identity operator (for this particular wave vector), and all superspace-group symmetry can be described by the incommensurate Bravais class. No new Bravais class need be considered.

The last possibility is given by $(m_x\bar{1})(m_y\bar{1})(m_z\bar{1})$, which leads to the restrictions α, β, γ each $\pm 1/2$. The wave vector $\mathbf{q} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ is not contained in the tables of de Wolff, Janssen & Janner (1981). Now a new Bravais class does occur:

$$T\,{}^{Immm}_{\bar{1}\,\bar{1}\,\bar{1}}\,(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2}).$$

The prefix *T* is used here as an indication of a totally commensurate modulation.

A derivation of all Bravais classes of (3+1)D superspace groups was performed accordingly. This leads to seven Bravais classes for commensurately modulated structures, given in Table 1.

3. The relation between space-group symmetry and superspace-group symmetry

It is always possible to separate the modulation wave vector into a part for which the components have

* T. Janssen has pointed out to me that the Bravais classes of (3+1)-dimensional superspace groups, both incommensurate and commensurate, are isomorphous to the four-dimensional generalized magnetic point groups. See Janssen (1969).

Table 1. *Bravais classes of* $(3+1)D$ *superspace groups for totally commensurate modulated structures*

Column one: number of Bravais class; column two: symbol of Bravais class; column three: transformation to larger unit cell with $\mathbf{q}' = \mathbf{q}'_r = 0$; column four: conditions limiting possible reflections and conditions determining the value of m. To be present, a reflection HKL has to fulfil the given condition. Column five: the components of the commensurate modulation wave vector.

				$\alpha\ \beta\ \gamma$
Orthorhombic				
1	$T\ {}^{Immm}_{\bar{1}\,\bar{1}\,\bar{1}}$	$H=2h+m$ $K=2k+m$ $L=2l+m$	$H-m=2n$ $H-K=2n'$ $H-L=2n''$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
Tetragonal				
2	$T\ {}^{I4/mmm}_{\bar{1}\ \bar{1}\,\bar{1}1}$	$H=2h+m$ $K=2k+m$ $L=2l+m$	$H-m=2n$ $H-K=2n'$ $H-L=2n''$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
Cubic				
3*	$T\ {}^{Pm\bar{3}m}_{\bar{1}\,\bar{1}1}$	$H=2h+m$ $K=2k+m$ $L=2l+m$	$H-m=2n$ $H-K=2n'$ $H-L=2n''$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
4	$T\ {}^{Im\bar{3}m}_{\bar{1}\,\bar{1}1}$	$H=2h+m$ $K=2k+m$ $L=2l+m$	$H-m=2n$ $H-K=2n'$ $H-L=2n''$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$
5*	$T\ {}^{Im\bar{3}m}_{\bar{1}\,\bar{1}1}$	$H=2h+m$	$H-m=2n$	1 0 0
Hexagonal				
6	$T\ {}^{P6/mmm}_{\bar{1}\ 1\,\bar{1}1}$	$H=2h+k+m$ $K=-h+k$	$H-K-m=3n$	$\frac{1}{3}\frac{1}{3}0$
7	$T\ {}^{P6/mmm}_{\bar{1}\ 1\,\bar{1}1}$	$H=2h+k+m$ $K=-h+k$ $L=2l+m$	$H-K-m=3n$ $L-m=2n'$	$\frac{1}{3}\frac{1}{3}\frac{1}{2}$

* These Bravais classes have in addition the symmetry operation $(E\bar{1})$.

rational values as forced by symmetry and a part for which there are no symmetry restrictions on those components. The first part forms the vector $\mathbf{q}_r$, the second part forms the vector $\mathbf{q}_i$, such that (de Wolff, Janssen & Janner, 1981)

$$\mathbf{q} = \mathbf{q}_r + \mathbf{q}_i. \tag{3.1}$$

To analyse the diffraction pattern, or to calculate symmetry restrictions on the modulation function, it is convenient (de Wolff, Janssen & Janner, 1981) to describe a modulated structure in a larger unit cell, such that in this larger unit cell $\mathbf{q}_r = 0$. The advantage of the use of this larger unit cell is easily seen if one realizes that when $\mathbf{q}_r = 0$ the vector $\mathbf{G}$ is zero for all operations $(R\varepsilon)$ [equation (2.1)]. Only then do the $(3+1)$D orthonormal transformations assume their simplest form as a direct sum of a 3D operator R and a 1D operator $\varepsilon = \pm 1$. In this larger unit cell centring translations are present. Because the cell transformation was performed to get rid of the rational part $(\mathbf{q}_r)$ of the modulation wave vector, the centring translations have a non-zero fourth component and at least one of the first three components is different from zero.

For the Bravais classes of totally commensurate superspace groups, derived in § 2, $\mathbf{q}_i = 0$. Therefore, the larger unit cell is exactly the one used in the ordinary description by 3D space groups. The difference between the space-group description and the superspace-group description is expressed by the presence of centring translations in the latter case. Because the 3D part of the larger superspace unit cell is equal to the unit cell in ordinary space, this cell is convenient to make a comparison between superspace-group symmetry and space-group symmetry. In the case of a commensurate vector $\mathbf{q}_i$, with a short period (*e.g.* 2 or 3), the description by a larger unit cell with $\mathbf{q} = 0$ will also be convenient.

To obtain a general picture of the relation between the superspace group and the space group, consider a $(3+1)$D superspace-group operator,

$$(R\varepsilon\tau_1\ \ \tau_2\ \ \tau_3\ \ \tau_4). \tag{3.2}$$

The translations in superspace are given by $R =$ identity, $\varepsilon = +1$ and τ_i integers. The other operators have $R \neq$ identity and may have fractional values for the τ_i (glide planes *etc.*). The 3D space group is a subgroup of the superspace group. Therefore, all space-group operators are contained in the set of superspace-group operators. The condition for a superspace-group operator to be a space-group operator is (Yamamoto & Nakazawa, 1982; Yamamoto, 1984)

$$\mathbf{q} \cdot \boldsymbol{\tau}' = \tau_4, \tag{3.3}$$

with $\boldsymbol{\tau}' = (\tau_1, \tau_2, \tau_3)$. In the larger unit cell $\mathbf{q} = 0$, leading to the simpler condition

$$\tau_4 = 0. \tag{3.4}$$

Consideration of all superspace-group operations (including the centring translations) will then lead to the set of 3D operators and subsequently to the 3D space group.

3D space is a section of the supercrystal perpendicular to the internal coordinate axes (van Smaalen, 1985; de Wolff, Janssen & Janner, 1981). For commensurate modulations different sections refer to different 3D structures. This difference in structure is, in part, reflected in the 3D space group. Operators with $\varepsilon = +1$ have a τ_4 value independent of the choice of the origin along $\mathbf{a}_4$; they will be operators of the 3D space group or not, independent of the choice of origin, *i.e.* independent of the section chosen. For operators with $\varepsilon = -1$ the value of τ_4 depends on the choice of the origin along $\mathbf{a}_4$. Therefore, these operators can be part of the space group only for a finite set of 3D structures. The following picture is now obtained. For commensurately modulated structures the supercrystal corresponds to an infinite set of different 3D structures, all being described by one and the same superspace group. Which particular section represents the real 3D structure has to be determined in the structure determination. Expressed

in a different way, the phase of the modulation wave is a parameter which has to be determined in order to obtain the real 3D structure. For practically all sections, the same 3D space group is obtained, which corresponds to the operators with $\varepsilon = +1$. The phase of the modulation wave then corresponds to a free parameter in the 3D space-group description too. However, for a restricted set of sections the operators with $\varepsilon = -1$ are also present in the 3D space group. As a consequence, for these structures the 3D symmetry is higher than for the others. In this way, a knowledge of the 3D space-group symmetry can be used to determine the phase of the modulation wave.

We will illustrate the importance of the superspace-group description by the example of $Ag_{0.35}TiS_2$. At room temperature, $Ag_{0.35}TiS_2$ crystallizes (Gerards, Roede, Haange, Boukamp & Wiegers, 1984/1985) in space group $P\bar{3}m1$, belonging to the Bravais class $P6/mmm$. On lowering the temperature, new reflections occur in the diffraction pattern at positions $m\mathbf{q}$, with $\mathbf{q} = \frac{1}{3}\mathbf{a}^* + \frac{1}{3}\mathbf{b}^* + \frac{1}{2}\mathbf{c}^*$ and m an integer, meaning that a commensurately modulated structure has developed with a modulation wave vector $\mathbf{q} = (\frac{111}{332})$.

The symmetry of the reciprocal lattice remains $6/mmm$. The (3+1)D Bravais class is therefore

$$T\begin{matrix}P6/mmm\\ \bar{1}\ 1\ \bar{1}\ 1\end{matrix}(\tfrac{1}{3}\tfrac{1}{3}\tfrac{1}{2}),$$

no. 7 in Table 1. The superspace group compatible with the observed diffraction pattern and the average structure is

$$T\begin{matrix}P\bar{3}m1\\ \bar{1}\ \bar{1}\ 1\ 1\end{matrix}(\tfrac{1}{3}\tfrac{1}{3}\tfrac{1}{2})$$

(van Smaalen, Bronsema & Wiegers, 1987).

3D periodicity is restored by the choice of a larger, $\sqrt{3}a \times \sqrt{3}a \times 2c$, unit cell (Fig. 1). The 3D Bravais class of the modulated structure is again $P6/mmm$. The space group of the superstructure was reported to be $P\bar{3}1c$ (Gerards *et al.*, 1984/1985). Note the different orientation of the mirror planes with respect to the translation vectors in $3m1$ and $31m$ symmetry (Fig. 1).

Careful analysis of the diffraction pattern shows that the extinction condition corresponding to the c glide is only approximately fulfilled. Therefore, the true space group is $P\bar{3}$ or $P3$. The assignment of the (3+1)D superspace group is independent of the presence of the extinction condition representing the 3D c glide. In fact, 3D symmetries $P3$ and $P\bar{3}1c$ correspond to the different sections of the supercrystal mentioned previously.

The larger unit cell with $\mathbf{q}_r = \mathbf{q} = 0$ is exactly that of the 3D space group of the modulated structure. Because in this larger unit cell $\mathbf{q} = 0$, the position of each reflection is given by only three indices HKL. In the superspace group each reflection has a fourth index, m, determining the order of the satellite. The relations defining the value of m for each reflection HKL are given in the fourth column of Table 1. Note that in the incommensurate case (with $\mathbf{q}_i \neq 0$) these relations are extinction conditions limiting possible reflections. For Bravais class no. 7 these relations are (n, n' integers)

$$\begin{aligned} m &= H - K + 3n \\ m &= L + 2n'. \end{aligned} \tag{3.5}$$

Now the approximate presence of the c glide can be understood, because the nearly extinct reflections HHL with L odd are third-order satellites and are therefore expected to be weak. In fact, Gerards *et al.* (1984/1985) have already noted that all HKL reflections with $H - K = 3n$ and L odd are very weak or absent. These reflections are precisely the third-order satellites.

The advantage of the superspace-group description for commensurately modulated structures is best illustrated by considering the number of independent parameters needed to describe the structure. The space-group description has the positions of the atoms as independent parameters. Consideration of only the translation symmetry gives for the superstructure N times the number of parameters of the average structure, when an N-fold supercell is needed. In the superspace-group description the parameters are those of the average structure plus the amplitudes of a finite number of harmonics of the modulation functions. It can easily be shown that the number of parameters is the same in both descriptions. However, the introduction of the rotational symmetry reduces the number of independent parameters. For a 3D symmetry not referring to a special section of the supercrystal (see previous paragraphs), the number of independent parameters in the 3D description will be larger than or equal to the number of independent parameters obtained with the superspace group. Only in the case of a 3D symmetry

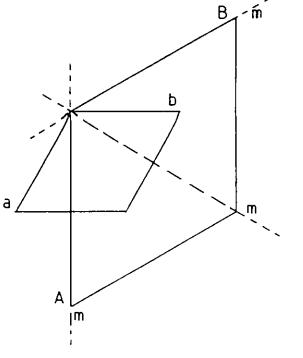

Fig. 1. Projection along **c** of the unit cell of $Ag_{0.35}TiS_2$. Shown are the unit cell (**a**, **b**) of the average structure and the $\sqrt{3}a \times \sqrt{3}a \times 2c$ supercell (**A**, **B**). Also indicated are the mirror planes present in this structure.

belonging to a particular section may the 3D space give rise to more restrictions. In the superspace-group description the phase of the modulation function is free and gives rise to a number of independent parameters in the modulation functions. The 3D symmetry corresponds to a particular phase. Consequently, knowledge of the 3D space group can be used to determine this phase. Taking this into account, the (3+1)D superspace-group description gives an equal or smaller number of independent parameters than the space-group description.

The example of $Ag_{0.35}TiS_2$ corresponds to such a unique section of superspace. The approximate 3D space group $P\bar{3}1c$ has the same number of independent parameters as the superspace group

$$T\begin{matrix}P\bar{3}m1\\ \bar{1}\bar{1}1\end{matrix}\left(\tfrac{1}{3}\tfrac{1}{3}\tfrac{1}{2}\right).$$

However, for an accurate description of the structure, taking into account also the nearly extinct reflections, the space group $P3$ should be used. Then many more parameters are needed to describe the structure in the three-dimensional space group than in the superspace group with a free phase of the modulation wave (van Smaalen, Bronsema & Wiegers, 1987). Another example is the case of $K_{0.5}V_5S_8$ (Bronsema, 1985), where the superspace group also gives a description with a smaller number of parameters.

Another advantage of the superspace-group description is that the new independent parameters represent in a natural way the order parameters in Landau theory (Perez-Mato, Madariaga & Tello, 1984). This holds also for commensurate modulations. It enables one to discriminate between more-important (first-order) and less-important (second-order and higher) parameters describing the modulation. In the space-group description of the modulated structure no relation exists between the independent parameters and the way the structure distorts. These effects are discussed in detail for the case of $Ag_{0.35}TiS_2$ in a following publication (van Smaalen, Bronsema & Wiegers, 1987).

4. Summary and concluding remarks

In this paper the consequences of the superspace-group description for commensurately modulated structures are discussed.

In § 2 the Bravais classes of (3+1)D superspace groups are derived which apply to commensurate modulations only. These Bravais classes are not given by de Wolff, Janssen & Janner (1981), who gave only Bravais classes of superspace groups for incommensurately modulated structures.

For incommensurately modulated structures, a superspace group for a given basic structure and a given modulation wave vector correspond to one set of ordinary 3D operators (the latter not forming a 3D space group, because of the incommensurateness). For commensurately modulated structures there are several 3D space groups possible for the 3D structure. The different space groups correspond to different phases of the modulation wave. It is shown that in many cases the superspace-group description leads to a reduction of the number of independent parameters compared with an ordinary space-group description.

The superspace-group approach leads to a better understanding of the diffraction pattern. Reflections which are very weak or absent can be indexed as higher-order satellites, which are expected to be weak. This observation, together with the superspace-group description of the structure, enables one to determine the parameters (higher-order harmonics) responsible for the intensity at these points.

It is argued that there is a close relation between the superspace-group approach and the order parameters in the Landau theory of phase transitions.

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