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A Superspace Approach to the Structure and Morphology of Tetramethylammonium Tetrachlorozincate, $2C_4H_{12}N^+ . ZnCl_4^{2-}$

BY B. DAM AND A. JANNER

RIM Laboratory of Solid State Chemistry and Institute for Theoretical Physics, Faculty of Science, Catholic University of Nijmegen, Toernooiveld, NL-6525 ED Nijmegen, The Netherlands

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Abstract

It is shown that the modulated phases of tetramethylammonium tetrachlorozincate, $[(CH_3)_4N]_2ZnCl_4$, can be described by one superspace group: $Pcmn(00\gamma)(1s\bar{1})$. This group is consistent not only with the properties of the diffraction pattern of the commensurate and incommensurate phases (and in particular with the corresponding space-group assignments found in the literature) but also with the crystal morphology, the latter being studied here by growth sphere experiments. The description of the morphology in terms of main and satellite faces, analogous to the description of the diffraction pattern, reveals a simple order in the crystal morphology of the different phases. Whereas the main faces remain relatively unperturbed, the position and appearance of satellite faces are directly related to the modulation wave. In fact, the evolution of the modulation wave vector can be monitored from the position of the satellite faces with respect to the main faces. Morphological extinction conditions even show compatibility with the proposed superspace group. Though the bonding structure of the satellite faces is not quite understood yet, a preliminary explanation is given in terms of a stabilized step structure.

1. Introduction

In the past, identification of crystal faces $\{hkl\}$ on the basis of geometrical morphological laws served as an important tool in the determination of relative unit-cell parameters and the derivation of both point-group and possibly space-group symmetry.

After the introduction by de Wolff (1977) of the superspace description for one-dimensionally modulated structures, attempts have been made to characterize the morphology of these modulated crystals by extending the standard geometrical laws to include superspace-group symmetry. Indeed, from the morphology of Rb_2ZnBr_4 and Rb_2ZnCl_4, which at room temperature are displacively modulated β-K_2SO_4-type structures, extra so-called satellite faces related to the modulation wave vector could be determined (Janner, Rasing, Bennema & van der Linden, 1980; Rasing, 1982). In subsequent growth sphere experiments only for Rb_2ZnBr_4 were a few of the reported satellite faces found. However, it appeared to be possible to determine from the orientation of these satellite faces the relative length of the modulation wave with respect to the average unit-cell parameters (Dam & Janner, 1983).

Although this shows that the extended geometrical laws can be successfully applied to incommensurately modulated structures, the thermodynamic and structural reasons for their success is not clear. In this respect the microscopic nature of the satellite faces is still an open question; they can possibly be considered as *F* faces, *i.e.* as faces with a non-zero edge free energy (van der Eerden, 1979).

To study this problem in more detail the morphology of $[(CH_3)_4N]_2ZnCl_4$ (here denoted TMA-ZC) was investigated. Special attention was paid to the relation between the morphological importance (MI) of the satellite faces and the symmetry and periodicity of the modulation wave.

The basic structure of $[(CH_3)_4N]_2ZnCl_4$ is of the same type as that of Rb_2ZnBr_4 (Hogervorst, 1983) and has space-group symmetry *Pcmn*. The modulation vector $\mathbf{q} = \gamma\mathbf{c}^*$ has the same orientation as in Rb_2ZnBr_4 (along the c^* axis) but in TMA-ZC it can attain several values and five modulated phases have been found, as shown in Table 1 (Tanisaki & Mashiyama, 1980; Almairac, Ribet, Ribet & Bziouet, 1980).

TMA-ZC transforms below $T = 293$K from the para phase I (*Pcmn*) into phase II, which is incommensurate. Incommensurability arises because γ is temperature dependent within the same phase II, and therefore it cannot be expressed in terms of a given rational number, even if one does so at fixed temperature values (*e.g.* at about 290K one has $\gamma \sim 0{\cdot}42$).

The other four low-temperature phases are commensurate. Phase III shows a small ferroelectric effect (Sawada, Shiroishi, Yamamoto, Takashige & Matsuo, 1978) and is modulated with $\gamma = 2/5$, while in phases IV and VI $\gamma = 1/3$. The data known so far for phase V support the idea of $\gamma = 2$. Such a modulation, while keeping the same orthorhombic lattice, lowers the original space-group symmetry by changing the atomic positions within the same unit cell without,

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Table 1. *Description of the structural changes occurring in* $[(CH_3)_4N]_2ZnCl_4$ *below* 300 K

The wave vector **q** is taken along the pseudo-hexagonal **c** axis, the polarization being along the shortest axis **b**.

The various phases of $[(CH_3)_4N]_2ZnCl_4$					
VI	V	IV	III	II	I
$q=1/3c^*$	$q=2c^*$	$q=1/3c^*$	$q=2/5c^*$	$q\simeq 0{\cdot}42c^*$	para
$T<161$ K	$T>161$ K	$T>181$ K	$T>276{\cdot}5$ K	$T>279$ K	$T>293$ K
$P2_12_12_1$	$P2_1/c11$	$P112_1/n$	$Pc2_1n$	?	*Pcmn*
—	$\alpha=90{\cdot}02°$	$\gamma=90{\cdot}3°$	—	—	—

however, giving rise to additional satellite reflections. Note that only the room-temperature (average?) structure has been solved (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967).

All these cases can be described in terms of a single periodic distortion wave (the modulation) of a basic crystal structure. The Fourier wave vectors **k** of its electron density distribution (which label the Bragg spots of the corresponding diffraction pattern and the crystal growth faces as well) are integral linear combinations of $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ and $\mathbf{q}=\gamma\mathbf{c}^*$. The first three vectors span the orthorhombic reciprocal lattice Λ^* of the undistorted basic structure (essentially that of phase I with space group *Pcmn*).

While the morphological consequences of the incommensurability for phase II, the undistorted phase I and the other two modulated phases III and IV are considered experimentally, the theoretical investigation given below also includes the two low-temperature phases V and VI.

The main result is that it is convenient to adopt the same description (structurally and morphologically) for all the different phases I to VI of TMA-ZC. This is possible on the basis of a $(3+1)$-dimensional superspace-group characterization. Indeed, phases II to VI can be viewed (within a very good approximation) as one-dimensional modulations of *orthorhombic* basic structures having the same undistorted space-group symmetry *Pcmn* as phase I.

All the structural information available at present is compatible with a single superspace-group assignment

$$Pcmn(00\gamma)(1s\bar{1}) = \text{No } 62.c9.4 \qquad (1)$$

characteristic for most of the incommensurate phases of compounds isostructural with K_2SO_4. The meaning of the superspace-group symbol will become clear below; the right-hand number is that adopted in a full classification list of $(3+1)$-dimensional superspace groups by de Wolff, Janssen & Janner (1981). Note that such a unique assignment is not in conflict with the change in space-group symmetry for these six phases. On the contrary, it supports the assignments made on the basis of diffraction data [not yet supported by detailed structure determinations] (Tanisaki & Mashiyama, 1980).

This result also fits with a more general analysis performed by Hogervorst (1985) on a large number of β-K_2SO_4-type crystal structures. He discusses the relevance of this same superspace group for most of the modulate phases of these compounds. Analogous ideas, but now formulated in terms of representations of the space group *Pcmn* and within the framework of Landau's theory for second-order phase transitions, have been expressed by Plesko, Kind & Arend (1980) and by Muralt, Arend, Altermatt & Chapuis (1984).

In this work we will first give a superspace analysis of the TMA-ZC structure. Then the classical geometrical morphological laws and their physical meaning are briefly discussed before extending them to include the superspace description of modulated crystals. These new laws and the proposed superspace group will then be tested on the morphology of TMA-ZC.

The main result of our morphological study of phases I to IV of TMA-ZC by growth sphere experiments reveals that the space group *Pcmn* of the average structure is reflected in the so-called main faces that are practically unaffected by the phase transitions. Only the so-called satellite faces are dependent on the crystal phase. Their position is directly related to the wave vector **q** and their appearance allows a superspace-group determination as discussed below. In addition, also from a morphological point of view, all the four investigated phases appear to share the same crystallographic symmetry in four dimensions indicated above.

2. The superspace description

The superspace is, in general, a $(3+d)$-dimensional Euclidean space, which has been introduced to recover the crystallographic symmetry of incommensurate modulated crystal phases. It is, however, a useful concept even if the modulation is commensurate and gives rise to a superstructure. To elucidate this, a few key concepts appearing in the superspace approach have to be presented and applied to TMA-ZC, the reader being referred to other papers for more details (Janner & Janssen, 1980; Janner, 1983).

As already said, Fourier wave vectors of TMA-ZC can be labelled by four integers (indices) h, k, l and m:

$$\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q} \in M^* \qquad (2)$$

with $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ orthorhombic and $\mathbf{q}=\gamma\mathbf{c}^*$.

In the *para phase* (I), $\gamma=0$, thus $m=0$ and the indices $\{hkl0\}=\{hkl\}$ describe the normal Bragg reflections (and the normal crystal growth faces denoted as main faces) submitted to the systematic extinction rules one finds in *International Tables for*

Crystallography (1983). For the space group *Pcmn*, the conditions for reflection are:

hkl: no conditions; $hk0$: $h+k$ even; $0kl$: l even. (3)

The atomic equivalent positions at x, y, z with

$$x=\mathbf{ra}^*, \quad y=\mathbf{rb}^* \quad \text{and} \quad z=\mathbf{rc}^* \tag{4}$$

are defined modulo integers n_1, n_2, n_3 as a consequence of the orthorhombic lattice translational symmetry $\mathbf{n}=n_1\mathbf{a}+n_2\mathbf{b}+n_3\mathbf{c}$ of the structure ($\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ span Λ^* and are reciprocal to $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$). Accordingly, as is well known, in the Fourier phase factor $\exp(2\pi i\mathbf{kr})$ the scalar product $\mathbf{kr}$ is expressible as an integral linear combination of these unit-cell coordinates x, y, z.

2.1. *The incommensurate phase*

In the incommensurate phase (II), $\gamma\sim 0{\cdot}42$ is considered irrational and thus $\mathbf{q}$ incommensurate with respect to Λ^*. Looking at (2), one sees that in order to keep the same property as above for the scalar product $\mathbf{kr}$ one needs *four coordinates*:

$$x=\mathbf{ra}^*, \quad y=\mathbf{rb}^*, \quad z=\mathbf{rc}^* \quad \text{and} \quad t=\mathbf{rq} \tag{5}$$

now defined four modulo integers n_1 to n_4. The additional coordinate t is of course not independent of x, y, z, but can be made so by considering the family of structures one gets through shift of the phase of the modulation wave, and representing the whole by plotting the t coordinate along a fourth axis $\mathbf{d}$ perpendicular to $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$ (and thus to $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$). It is convenient to choose $|\mathbf{d}|=\lambda$, the modulation wavelength (Fig. 1*a*). All the various three-dimensional modulated crystals then appear as sections for constant t of that pattern, which is called a *superspace embedding* of the modulated crystal. Note that as a result of such an embedding a four-dimensional lattice translational symmetry is obtained and a four-dimensional space-group symmetry is then the result.

In the present context it is convenient to take as a basis in the four-dimensional space the orthorhombic basis set spanned by $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$, $\mathbf{d}$ even though it is not a basis for the four-dimensional lattice of symmetry translations in superspace. These lattice translations can be expressed in terms of the following set of equilvalent positions:

$$(x', y', z', t')=(x+n_1, y+n_2, z+n_3, t-\gamma n_3+n_4) \tag{6}$$

for any integer n_1, n_2, n_3, n_4. For M^* as in (2) a projection of a four-dimensional reciprocal lattice Σ^* spanned by $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ and $\mathbf{d}^*=\mathbf{q}+\mathbf{d}/\lambda^2$, the above coordinates are the components of vectors n_s of the corresponding direct lattice Σ (with origin at x, y, z, t).

In addition, one has the following set of equivalent positions associated with the point-group generators of the superspace group indicated in (1), the origin being at the inversion centre.

$$\begin{aligned}
g_s^1=(1,1): &\quad x, y, z, t\\
g_s^2=(c,1)_x: &\quad \tfrac{1}{2}-x, y, \tfrac{1}{2}+z, t-\tfrac{1}{2}\gamma\\
g_s^3=(m,s)_y: &\quad x, \tfrac{1}{2}-y, z, t+\tfrac{1}{2}\\
g_s^4=(n,\bar{1}s)_z: &\quad \tfrac{1}{2}+x, \tfrac{1}{2}+y, \tfrac{1}{2}-z, -t-\tfrac{1}{2}\gamma+\tfrac{1}{2}\\
g_s^5=(\bar{1},\bar{1}): &\quad -x, -y, -z, -t\\
g_s^6=(2_1,\bar{1})_x: &\quad \tfrac{1}{2}+x, -y, \tfrac{1}{2}-z, -t-\tfrac{1}{2}\gamma\\
g_s^7=(2_1,\bar{1}s)_y: &\quad -x, \tfrac{1}{2}+y, -z, -t+\tfrac{1}{2}\\
g_s^8=(2_1,s)_z: &\quad \tfrac{1}{2}-x, \tfrac{1}{2}-y, \tfrac{1}{2}+z, t-\tfrac{1}{2}\gamma+\tfrac{1}{2}.
\end{aligned} \tag{7}$$

For γ irrational any $t=$ constant section describes with arbitrary precision the same crystal structure in space, because the set of phases of the modulation wave occurring for a given atom in the undistorted structure is dense in the interval 0 to 2π.

2.2. *The commensurate phases*

In a good approximation all the phases II to VI have the same superspace-group symmetry given

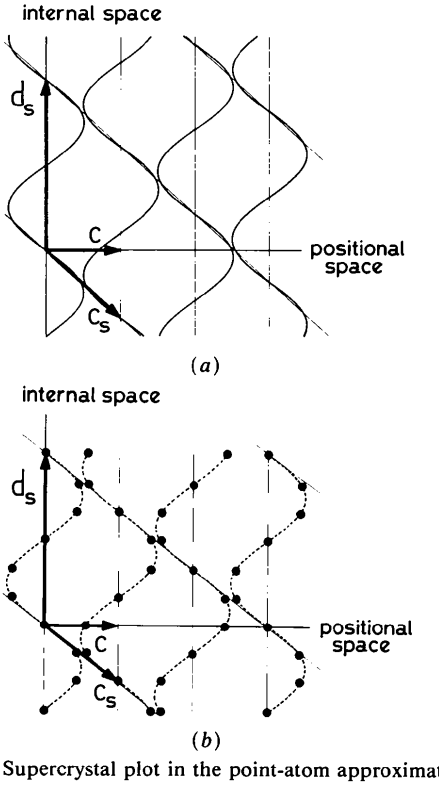

Fig. 1. (*a*) Supercrystal plot in the point-atom approximation for the incommensurate case. Each section perpendicular to the internal direction gives the same modulated structure, only differing in a choice of origin. The amplitude of the modulation wave is strongly exaggerated. (*b*) Corresponding supercrystal plot in the commensurate case ($\gamma=1/6$). Only sections at $t=0$, $\pm 1/6$, $\pm 2/6$, ... give modulated crystals with $P112_1/n$ space-group symmetry.

Table 2. *Conditions for superspace-group elements to induce 3D Euclidean symmetry in a given section t = constant, as a function of t and of the modulation wavelength $\lambda = c/\gamma$*

The integers m and n express translational symmetry, whereas the relative prime integers r and s occur in the commensurate modulated case only.

	Conditions for 3D Euclidean symmetry			
$\gamma = r/s$	$(c, 1)_x$ $2n/(1+2m)$	$(m, s)_y$ $(1+2n)/2m$	$(2_1, s)_z$ $(1+2n)/(1+2m)$	
$t' = t$	$(n, \bar{1}s)_z$ $(1+2n)/4-(1+2m)\gamma/4$	$(\bar{1}, \bar{1})$ $n/2-m\gamma/2$	$(2_1, \bar{1})_x$ $n/2-(1+2m)\gamma/4$	$(2_1, \bar{1}s)_y$ $(1+2n)/4-m\gamma/2$

above and can thus also be described in terms of the equivalent positions of (7).

The commensurability is expressed by the condition

$$\gamma = r/s \in Q, \tag{8}$$

with r, s relatively prime integers. For phases III and VI one has $\gamma = \frac{1}{3}$ and for phase IV $\gamma = \frac{2}{5}$. The three-dimensional Euclidean symmetry of the crystal structure (which is now a 3D space group) depends on r, s *and* the t value of the section t = constant. The condition for an element g_s of the superspace group G_s to induce a three-dimensional Euclidean symmetry in space is to leave such a section invariant.

Let us now discuss those conditions on r, s and t for the generators of the superspace group of TMA-ZC indicated in (7), each combined with the four-dimensional lattice translations of (6).

Consider first $g_s^2 = (c, 1)_x$. Combined with a lattice translation n_s it transforms the position x, y, z, t to

$$(x', y', z', t') = (\tfrac{1}{2} - x + n_1, y + n_2, \tfrac{1}{2} + z + n_3, t - \tfrac{1}{2}\gamma - n_3\gamma + n_4). \tag{9}$$

Accordingly the condition $t = t'$ requires

$$\gamma = r/s = 2n_4/(1+2n_3), \tag{10}$$

implying that $(c)_x$ is a symmetry element compatible with a modulated structure having $\gamma = \frac{2}{5}$ but not with one having $\gamma = \frac{1}{3}$.

In the same way, and now considering $g_s^3 = (m, s)_y$, one finds that $t = t'$ implies

$$\gamma = r/s = (1+2n_4)/2n_3, \tag{11}$$

so that m_y cannot be a symmetry element for a modulated structure with $\gamma = \frac{1}{3}$ or for one having $\gamma = \frac{2}{5}$.

The situation is different for the generator $g_s^4 = (n, \bar{1}s)_z$, again combined with lattice translations. The condition $t = t'$ now yields

$$-(1+2n_3)r + (2n_4+1)s = 4st. \tag{12}$$

For any integers r, s there is a solution (rational γ does not lead to restrictions) but only for discrete values of t. This simply reflects the fact that in a given (commensurate) modulated structure (superstructure) only a finite number of different phases of the modulation wave occur: which one occurs depends on the structure and on its space-group symmetry. Equation (12) implies, in particular, that in order to have $n_z = \{m_z|\frac{1}{2}, \frac{1}{2}, \frac{1}{2}\}$ as a symmetry element for the t = constant section the following conditions have to be satisfied:

$$\begin{aligned} &\text{for } \gamma = \tfrac{1}{3}: \quad t = \nu/6, \\ &\text{for } \gamma = \tfrac{2}{5}: \quad t = (2\nu+1)/20, \end{aligned} \tag{13}$$

for ν any integer (Fig. 1*b*).

This analysis can be completed by considering all other generators of the superspace group given in (7). The resulting conditions for the generators of *Pcmn* to be symmetry elements for the various modulated phases are indicated in Table 2 (see also Janssen, 1985). One sees, as already recognized in previous publications by other authors (Tanisaki & Mashiyama, 1980; Plesko, Kind & Arend, 1980; Muralt, Arend, Altermatt & Chapuis, 1984; Iizumi, Axe & Shirane, 1977), that the following space groups can occur for the **q** vectors involved:

$$\begin{aligned} &P2_12_12_1 \quad Pc2_1n \quad P(2_1/n)_z \\ &P(2_1/c)_x \quad Pc_x \quad \text{and} \quad P(2_1)_z, \end{aligned} \tag{14}$$

lower symmetries being of course possible but not expected.

The space groups assigned to phases III to VI by Tanisaki & Mashiyama (1980) are in full agreement with the present analysis. The corresponding values for γ and for equivalent sections at t are summarized in Table 3. In particular, for phase V the unusual value for the modulation $\gamma = 2$ is the smallest one for compatibility between the assigned space group and the common superspace group.

Note, however, that the non-orthorhombic phases still have (in the present approximation) a (pseudo-)orthorhombic lattice. The label pseudo indicates that the lattice symmetry is higher than that required by the (three-dimensional) space group. That lattice symmetry is, however, imposed by the superspace group.

The small deviations of β and α from 90° in phases IV and V, respectively, must be seen as symmetry breaking. The same possibly applies to the small ferroelectric effect observed in phase III. The 3D space-group assignment $Pc2_1n$ for this phase allows, in itself, ferroelectricity, *i.e.* a non-zero total electric moment within the fivefold supercell (with respect to the paraelectric phase I). The proposed superspace-group symmetry, however, implies in the incom-

Table 3. *Compatibility relations between 3D space-group and superspace-group symmetry in the commensurately modulated cases*

The space groups indicated are Euclidean symmetry groups for each of the sections t = constant indicated, whereas the superspace group leaves the set of equivalent sections labelled by an integer ν invariant.

	Space-group compatibility with $Pcmn(00\gamma)(1s\bar{1})$					
Phases	VI	V	IV	III	II	I
Space group	$P2_12_12_1$	$P2_1/c11$	$P112_1/n$	$Pc2_1n$	Incommensurate	$Pcmn$
γ	1/3	2	1/3	2/5	Irrational	0
t	$(1+2\nu)/12$	$\nu/2$	$\nu/6$	$(1+2\nu)/20$	Dense	Arbitrary

mensurate case a zero ferroelectric effect. For the commensurate case one needs more structural details in order to draw the same conclusion.

The high-temperature hexagonal K_2SO_4 structure lies beyond this discussion, as it is a *disordered* type *Pcmn* structure (Unruh, 1981).

2.3. *Extinction rules*

The property that all phases I to VI of TMA-ZC share the same superspace-group symmetry implies the same conditions for occurrence of Fourier components, once a common four-indices labelling (h, k, l, m) as in (2) has been adopted. Then the group $Pcmn(00\gamma)(1s\bar{1})$ leads to the following conditions for reflection (de Wolff, Janssen & Janner, 1981):

$$\begin{aligned} &hklm\text{: no conditions;} \qquad hk00\text{: } h+k \text{ even;} \\ &h0lm\text{: } m \text{ even;} \qquad 0klm\text{: } l \text{ even.} \end{aligned} \tag{15}$$

The extinction rules for the space groups of the commensurate phases are normally expressed in terms of three indices (called here HKL), which refer to different bases, but have to be compatible with the above one as these space groups are subgroups of the same superspace group. For $\gamma = r/s$ with r, s relatively prime integers the reciprocal-lattice vectors $\mathbf{k}$ can be written as

$$\mathbf{k} = H\mathbf{A}^* + K\mathbf{B}^* + L\mathbf{C}^* \tag{16}$$

with $A^* = a^*$, $B^* = b^*$ and $C^* = c^*/s$. Accordingly we simply have

$$(h, k, l, m) = (h, k, sl + rm) = (H, K, L) \tag{17}$$

and one easily verifies that indeed the extinction rules for the various space groups given in (14) are compatible with (15).

Most remarkable is the fact that none of these space groups imply conditions for $H0L$ reflections. The $h0lm$, $m = 2n$ condition thus seems typical for the superspace group.

3. Modulated structures and morphology

3.1. *Classical geometrical laws and their physical interpretation*

According to the classical morphological laws of Bravais, Friedel, Donnay and Harker (BFDH), the larger the distance between equivalent lattice planes $\{hkl\}$, the larger the morphological importance (MI) of the crystal face parallel to these planes; this implies that h, k and l are small integers. It follows that $\{hkl\}$ faces related through point-group symmetry will all have the same MI. The non-primitive translational components of the space group manifest themselves by bisecting, trisecting *etc.* the distance between equivalent lattice planes, thus reducing the MI of such orientations. Evidently, both the definition of a three-dimensional (3D) space group and the applicability of the BFDH laws depend on the existence of lattice translational symmetry. In fact, lattice translational symmetry was derived from crystal morphology as it is implicit in the law of rational indices of Hauy (Friedel, 1911).

Thermodynamically, the equilibrium form of a crystal is determined by the minimalization of the surface free energy (Herring, 1951). Flat crystal faces of finite size can develop along planes that have a minimal edge free energy larger than zero. This energy γ generally decreases with increasing temperature and vanishes at the roughening temperature $T_R\{hkl\}$ (van der Eerden, Bennema & Cherepanova, 1978). Abstracting from the crystal growth parameters, one may say that in general MI$\{hkl\}$ increases with increasing γ and hence with increasing $(T_R\{hkl\} - T)$.

Structurally, a non-zero edge free energy is obtained when a 2D network of strong bonds can be constructed within the $\{hkl\}$ slice. The roughening temperature of such a bond network has been shown to be dependent on the strength and the geometry of the bond structure (Rijpkema, Knops, Bennema & van der Eerden, 1982). It must be noted that the distance between equivalent (or almost equivalent) bond structures is sometimes smaller than that of the equivalent lattice planes. Correspondingly, the MI of such orientations is lower than expected on the basis of BFDH [see Donnay & Donnay (1961) or Hartman (1968)].

In summary, it appears that the success of the geometrical laws of Bravais, Friedel, Donnay and Harker originates from a correspondence between the distance $d\{hkl\}$ and the strength of the 2D bond structure contained in the corresponding $\{hkl\}$ slice. In other words, the Fourier transform of electron densities usually resembles that of the bond densities.

3.2. *Extended morphological laws and their physical interpretation*

A direct generalization of the classical geometrical laws is possible if one considers crystal faces (and crystal planes) as wave fronts of Fourier density waves. For both commensurate and incommensurate modulations the BFDH laws then have to be applied to wave vectors $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$ lying normal to crystal faces $\{hklm\}$. Corresponding to the classical case we assume that the MI of such a face will increase with increasing $d\{hklm\}$ the distance between neighbouring wave fronts, assuming h, k, l and m to be small integers. Furthermore, superspace symmetry relating $\mathbf{k}$ and $\mathbf{k}'$ will result in the relation $\mathrm{MI}(\mathbf{k}) = \mathrm{MI}(\mathbf{k}')$, whereas systematic extinctions of the superspace group for $\mathbf{k}''$ will make $\mathrm{MI}(\mathbf{k}'') = 0$.

Note that $\mathbf{k}$ is defined in 3D space. Therefore, the condition *h, k, l and m* small does not follow directly from the requirement that $d\{hklm\}$ has to be large, but it is required for the corresponding lattice hyperplanes in 4D space.

Indeed, the vector $\mathbf{k}$ is the projection of a reciprocal-lattice vector k_s, which is a Fourier wave vector of the crystal embedded in superspace. As the latter does have lattice periodicity, an extension of the classical morphological laws to superspace is expected to be in complete analogy with the 3D case. However, at present, the absence of a description of the bond structure in superspace prevents this. Hence a physical interpretation of these extended laws when applied to a modulated 3D crystal as a cross section of the 4D supercrystal is not yet possible.

Anyhow, a fruitful approach to this problem is to distinguish between main $\{hkl0\}$ and satellite $\{hklm\}$ faces, though now defined in 3D space, just as one does for the diffraction pattern in terms of main and satellite reflections. Lattice planes are discussed for the commensurate modulation case (superstructure) while treating incommensurability as a limiting case. At phase transitions characterized by a change of $\mathbf{q}$ it is evident that $d\{hklm\}$ changes only when $m \neq 0$. Indeed, it is easily seen that some orientations of superstructures have this property (Fig. 2). For example, in s-fold superstructures along $\mathbf{c}$, $\{h'k'l'\}^s$ faces, where h', k' and l' are the indices of the s-fold superstructure, can be identified as main $\{hkl0\}$ faces

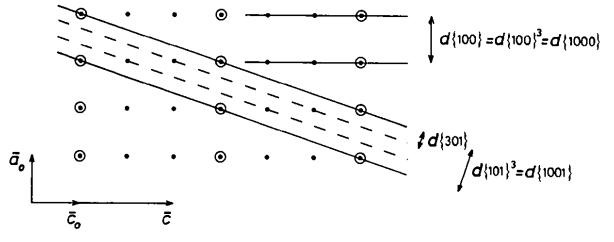

Fig. 2. The changes occurring in lattice planes after a modulation triples the c axis.

Table 4. *Comparitive morphology of* $[(CH_3)_4N]_2ZnCl_4$, *as far as main faces are concerned*

For commensurate superstructures the present faces are described in the classical three-index notation $\{HKL\}$. For the incommensurate case the use of the four-index notation with $\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$ and $\mathbf{q}$ as basis vectors is inevitable. This notation can in fact be used to describe the morphology in all phases (column 1).

The main faces of $[(CH_3)_4N]_2ZnCl_4$

Phases	IV	III	II	I
$\{hklm\}$	$q = 1/3c^*$	$q = 2/5c^*$	$q \simeq 0.42c^*$	Para
{2000}	{200}	{200}	{2000}	{200}
{2010}	{203}	{205}	{2010}	{201}
{1010}	{103}	{105}	{1010}	{101}
{1020}	{106}	{1,0,10}	{1020}	{102}
{0020}	{006}	{0,0,10}	{0020}	{002}
{1100}	{110}	{110}	{1100}	{110}
{1110}	{113}	{115}	{1110}	{111}
{0200}	{020}	{020}	{0200}	{020}
{0120}	{016}	{0,1,$\bar{10}$}	{0120}	{012}

if $l' = zs$ (z integer and h, k, l indices of the basic structure). The action of a modulation wave $\mathbf{q} = \gamma\mathbf{c}^*$ upon these orientations will only affect the periodicity of the 2D bond structure parallel to this orientation; *i.e.* the $\{hkl0\}$ bond structure unit is made up from modulated $\{hkl\}$ units. The distance between the lattice planes is left unperturbed. As long as the structural changes involved by the modulation wave are small, its effect on the MI of $\{hkl0\}$ planes will be small; *i.e.* $\mathrm{MI}\{hkl\} \sim \mathrm{MI}\{hkl0\}$.

On the other hand, a satellite slice $\{hklm\}$ of a crystal in its modulated phase will contain 's' (if $\gamma = r/s$) lattice planes, which have become inequivalent through the action of the modulation. Clearly, the increased distance between equivalent lattice planes opens the possibility for the formation of new bond structures and hence an enhancing of the MI of these orientations. On the other hand, it may happen that in each of these lattice planes a stable 2D bond structure is already present. Then, one has the case described by Donnay & Donnay (1961), which shows the difference between the crystal described in terms of bonds or in terms of electron densities. The MI of such an orientation will only slightly change when going into that modulated phase; the strongest of the 's' inequivalent bond structures present will determine the MI. The existence of pseudo-translations cannot be determined from the geometry of the diffraction pattern only, as it is typically a property of the bond structure. Because these faces behave like main faces it will be better to describe them as main/satellite faces. This hybrid characterization of some of the faces of a modulated crystal is also justified from the purely geometrical point of view of the crystal form in superspace, for those 2D intersections between satellite and main 3D faces of the supercrystal that lie in the physical space (Janner, 1983).

In the case of an incommensurate modulation an $\{hklm\}$ slice contains an infinite number of now inequivalent lattice planes. The reticular density of lattice points of each of these planes is, however, zero. This shows that for a modulated incommensurate 3D crystal one can only speak in a formal sense of $d\{hklm\}$ as the distance between equivalent lattice planes. Hence, we will call $d\{hklm\}$ the thickness of a crystal slice, *i.e.* the distance between planes of constant phase.

The need for the distinction between main and satellite faces will be illustrated by the description of the morphology of TMA-ZC. This will give us also some clues to the more detailed structural aspects of satellite faces.

4. The phase-dependent morphology of $[(CH_3)_4N]_2ZnCl_4$

4.1. *Sphere experiments on crystal form and crystal symmetry*

Single crystals of TMA-ZC were grown at 303 K from acidified aqueous solutions of $[(CH_3)_4N]Cl$ and $ZnCl_2$ in a 2:1 molar ratio. Clear transparent crystals were obtained that did not show any aging effects. After grinding and polishing them into spheres, the crystals were grown for about one day in slightly supersaturated solutions at temperatures between 298 and 274 K.

Their morphology, as measured by goniometry (at room temperature), can be indexed very easily using $\{hklm\}$ indices, taking the room-temperature lattice parameters $a = 15{\cdot}541$, $b = 8{\cdot}998$ and $c = 12{\cdot}276$ Å (Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967) as a basis, while **q** changes from phase to phase. Thus, the law of rational indices applied to *e.g.* $\{h0lm\}$ faces retricts the angle φ between [001] and $[h0l]$ to possible ratios:

$$\tan\varphi = ha^*/(l+m\gamma)c^*. \qquad (18)$$

In Table 4 the presence of main $\{hkl0\}$ faces is indicated for the various phases. The classification of {0020} as a main face might seem a bit ambiguous, as it can be seen as a {0001} satellite face as well. Geometrically it is an example of those main/satellite faces discussed above. From the point of view of bond structure, it is seen that all slices are equivalent, if one views the modulation wave as a homogeneous plane wave polarized along **b**. On the other hand, the presence of this orientation in the para phase shows its main-face character.

Clearly, the appearance of the main faces is not affected by the phase transitions. Throughout the whole temperature range considered here, the configurational point-group symmetry of these faces remains *mmm*. Deviations from orthorhombicity could not be observed. The $\{hklm\}$ indexing shows its convenience by the fact that it can be used not only in the incommensurate phase, where it is the only possible notation in terms of integers, but describes the morphology in the other modulated phases as well. Moreover, one and the same $\{hkl0\}$ symbol can be used to describe the main faces observed so far in any of the modulated phases, using only the integers 0, 1 and 2.

Table 5. *The satellite morphology of* $[(CH_3)_4N]_2ZnCl_4$

The comprehensive notation of column 1 is valid for all phases again. The presence of a particular satellite is indicated by giving its three- or four-index symbol in the column of the phase in question.

	Satellite faces of TMA-ZC			
Phases	IV	III	II	I
$\{hklm\}$	$q = 1/3c^*$	$q = 2/5c^*$	$q = 0{\cdot}42c^*$	para
$\{10\bar{1}2\}$	{101}	{101}	$\{10\bar{1}2\}$	—
{1002}	{102}	—	—	—
{1101}	{111}	{112}	{1101}	—
$\{111\bar{1}\}$	{112}	{113}	$\{111\bar{1}\}$	—
{0101}	{011}	{012}	{0101}	—
{0102}	{012}	—	—	—

A similar simplicity is seen in the description of the satellite faces given in Table 5. Again, the configurational symmetry observed was *mmm* (Fig. 3), which indicates that the external (or three-dimensional) part of the four-dimensional point group is *mmm*, despite the fact that the point group of phase IV is $2/m$. Now, for the same reasons as in the diffraction pattern satellite faces $\{hklm\}$ change in orientation with respect to the main faces at each change of **q**. In Fig. 4 the morphologically derived changes in δ [where $\mathbf{q} = (1/3+\delta)\mathbf{c}^*$] have been plotted as a function of temperature. Each point represents the average δ value for a specific crystal as computed from the positions of all satellite faces found on that crystal. Owing to surface roughness the spread in δ is crystal dependent and varies between ±0·005 and ±0·01. Qualitatively, the figure compares well with that based on diffraction data as given by Almairac, Ribet, Ribet & Bziouet (1980) and

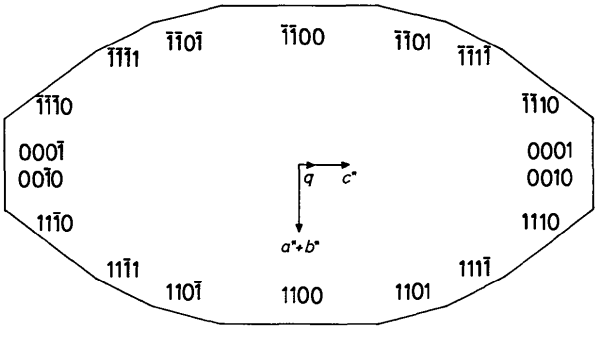

Fig. 3. Faces normal to wave vectors $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^* + m\mathbf{q}$ present in the $[1\bar{1}0]$ zone when $\mathbf{q} = 1/3\mathbf{c}^*$. A change in the modulation vector **q** results in a change of the orientation of the satellite faces only. The morphological importance of satellites is exaggerated in this figure.

Marion, Almairac, Lefebvre & Ribet (1981). Also in their measurements the incommensurate–commensurate phase transition appears to be rather smooth. The transition temperature deviates somewhat though, but this sample dependence is not abnormal.

Generally, apart from the value of the index m, satellite faces can be distinguished from main faces by the fact that the intensity of reflected light observed at the goniometer is rather weak. Only on crystals grown in phase IV were satellite faces observed as macroscopically visible facets, whereas, especially in the incommensurate phase, satellite faces are very difficult to observe. This indicates a relationship between MI and the modulation amplitude: generally it is observed that the amplitude of the modulation wave increases at lower temperatures (Hogervorst, 1983). In Table 6 the relative MI (crudely indicated by + and ++) of main and satellite faces of the [010] zone in phase III is compared with their $d\{hklm\}$. Evidently, the MI of satellite faces is less than what one would expect on the basis of their $d\{hklm\}$, which again stresses the importance of distinguishing between main and satellite faces.

In the commensurate case the way in which main and satellite faces are indexed is of course not unique. In each case our first purpose has been to keep the h, k, l indices as low as possible. Even then, in phase IV the $\{1002\}$ can be indexed as $\{101\bar{1}\}$ as well (the same for $\{101\bar{2}\}$ and $\{1001\}$). This ambiguity is not present in the description of phase III. Hence, in a unified description of the satellite morphology, we prefer $\{1002\}$ and $\{101\bar{2}\}$. Above all they beautifully demonstrate the $\{h0lm\}$ condition typical for the proposed superspace group. Also, all other observed main and satellite faces are compatible with $Pcmn(00\gamma)(1s\bar{1})$ as symmetry group.

From this description of the morphology of TMA-ZC we learn that it depends on the modulation vector. The positions of satellite faces are coupled to the modulation vector and extinction conditions seem to govern their appearance. The configurational point-group symmetry mmm of both main and satellite faces of TMA-ZC appears to be determined by the 3D component of the superspace point group.

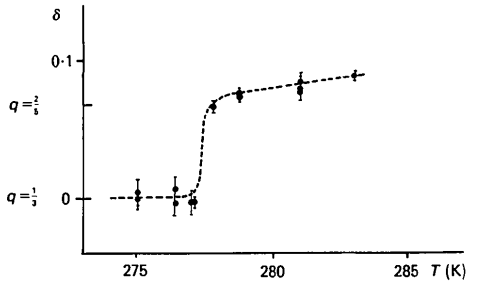

Fig. 4. Morphologically monitored evolution of the incommensurability δ, where $\mathbf{q}=(1/3+\delta)$, as a function of temperature. Instrumental error in δ is given by the spot size. Error bars indicate the spread due to surface inhomogeneities.

Table 6. *The relative MI of main and satellite faces in the* [010] *zone, as observed in phase* III

The faces are listed according to their $d\{hklm\}$. MI = + means that the facet is only visible as a reflection at the goniometer, whereas if MI = ++ the facet is grown out as a macroscopically visible facet.

$\{hkl\}$	$d\{hkl\}$	MI	$\{hklm\}$
{100}	15·5	++	{1000}
{101}	14·3	+	{101$\bar{2}$}
{102}	11·9	+	{1002}
{103}	9·6	++	{1010}
{203}	6.6	++	{2010}
{106}	5·7	+	{1020}

4.2. *The microscopic structure of the satellite faces*

It appeared to be relevant to distinguish between satellite and main faces. The main faces can be treated as being independent of the modulation wave and behave according to the classical morphological laws. The satellite faces are strongly related to the modulation wave. Especially as their position seems to vary continuously with $\mathbf{q}$, their microscopic structure is far from evident. Also with respect to $d\{hklm\}$, main and satellite faces cannot be treated on the same level. On the other hand, the satellite face morphology is not completely independent of the habit of main faces. Satellite faces are only found in zones defined by a strong F face and the $\mathbf{q}$ direction of the modulation. The relation with the main faces is even such that, for each $\{hklm\}$, $\{hkl0\}$ is present as a main F face (disregarding for the moment possible slice halving of $\{hkl0\}$ due to the external part of the superspace group).

As the structural changes at the phase transitions are very small, the formation of new bonds is unlikely. However, there is a change in periodicity and the newly formed $\{hkl0\}$ faces consist of modulated bond structures $\{hkl\}$. As a structural model for the satellite faces one could then think of an $\{hklm\}$ face as being constructed from monolayer stepped $\{hkl0\}$ faces. Normally stepped interfaces are not stable. Only some coupling between (the phase of) the modulation wave and the step structure could result in an energetically stable orientation. Further stabilization would be achieved when the steps repel each other (Landau, 1965).

If the stability of step positions depends only on the relative phase of the modulation wave, macroscopic step structures will be most stable when the steps form equi-phase lines. Hence $\{hklm\}$ and $\{hkl0\}$ have to be situated in a zone whose axis is normal to $\mathbf{q}$.

Indeed, for TMA-ZC with $\mathbf{q}=\gamma\mathbf{c}^*$ and $\gamma=r/s$, satellite faces are found in the [110], [100] and [010] zones. In every zone each $\{hklm\}$ can be built up from

$|m|r$ steps per s $\{hkl\}$ bond structures. The $m=2$ condition in zone [010] can now be understood from the geometry of the modulation wave with respect to the step structures in this zone. The $\binom{m}{s}=(m, s)_y$ superspace-group symmetry element implies that the modulation wave remains invariant after reflection in a mirror normal to **b** and a shift by π of the modulation wave. Hence, step structures will be most stable if they are invariant under the same operation and there will be at least two stable step positions per modulation period.

Though the stepped surface hypothesis explains some of the morphological features of TMA-ZC, it is clear that it is still a rather phenomenological description of the satellite faces. It would be interesting to see whether this description is compatible with the 4D electron density distributions of TMA-ZC.

Recently, *in situ* microscopy on TMA-ZC and K_2ZnCl_4 (a β-K_2SO_4 modulated structure with $\mathbf{q}=1/3\mathbf{c}^*$) has been started, using oblique illumination as described earlier (Dam, Polman & van Enckevort, 1984). The first results showed no difference between the surface morphology of main and satellite faces. In both cases circular steps around growth centres were observed. To gain more insight into the binding properties of modulated crystals a more detailed surface characterization is needed. A superspace embedding of the bond structure, analogous to that of the electron density, could help to recognize the relevant features, but such work has still to be done.

The present derivation of the space-group symmetry of sections of the crystal embedded in superspace follows a suggestion by T. Janssen, whose contribution is gratefully acknowledged. Further, we are indebted to J. W. van Kessel for technical assistance. Thanks are also due to the Stichting ZWO/SON and the Stichting FOM for partial support of the present investigation.

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