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Organic molecular compounds with modulated crystal structures

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Abstract. Even though the higher-dimensional superspace approach is an established method to describe aperiodic crystal structures, it is not yet fully considered and applied by a larger community of scientists. In this contribution the structural description of incommensurately and commensurately modulated molecular compounds is discussed and it is shown, that the higher-dimensional superspace approach is an elegant way for an exact structural description and an exact crystal-chemical analysis of such structures. While discussing several modulated molecular compounds, the idea behind the higher-dimensional superspace approach is shown. On the examples treated in the discussion it is explained, how to understand and how to interprete modulated molecular compounds. Also a short introduction is given to the higher-dimensional superspace approach itself, to the basic principles and to the applied nomenclature.

1. Introduction

The description of modulated structures applying the higher-dimensional superspace approach is now a well established method. Nevertheless, it is not yet fully accepted and applied by a larger community of scientists and it is sometimes believed to be something for "specialists". This might be due to the fact, that the superspace approach seems – at a first glance – somehow complicate and/or difficult to apply or – in the worst case – simply not necessary to be done for a proper crystal structure analysis. Another reason might be the lack of knowledge, with which software such structural work and analysis should be done.

It is not the idea of this contribution to give a complete discussion on the description of aperiodic crystal structures applying the higher-dimensional superspace approach. Nevertheless, for a better understanding of the following, a concise overview of the superspace approach is given in Sections 2.1 and 2.2 in more detail, to introduce the basic concept and the applied nomenclature. In Section 2.3 "*More literature*" some thorough accounts for a deeper study, including feature articles, reviews and textbooks dedicated to this topic, are proposed for the interested reader.

In Section 3 it is shown, that for incommensurately modulated crystal structures it is not only necessary but also appropriate and even profitable to describe aperiodic or better incommensurately modulated crystal structures within the higher-dimensional superspace approach. And (hopefully) it might be also shown, that to do so is not as complicate as it is feared. The effects of the modulation to a molecular crystal structure and also to the structure of the molecule are presented on some selected examples. It is also shown, how such structures can be understood and interpreted during refinement and in the crystal-chemical analysis.

2. The superspace approach

2.1 Periodic and aperiodic crystals

Crystalline matter is understood to be built up by a regular arrangement of its atomic constituents (like atoms, ions, molecules, ...) in space. This regular arrangement leads to a three-dimensional long-range order, which is reflected in sharp and discrete Bragg reflections in the diffraction pattern. The most common and most well know manifestation of long-range order is translational symmetry, *i.e.* periodicity. However, there are quite a few materials, in which three-dimensional periodicity is not present in the crystal structure [1]. Despite the lack of three-dimensional periodicity, these materials possess a (in principle) perfect three-dimensional long-range order in the spatial arrangement of their atomic constituents. They are called aperiodic crystals and are distinguished from the three-dimensional periodic ones – the *normal* crystals in the classical sense – by just this feature: their structures lack three-dimensional translational symmetry but nevertheless posses three-dimensional long-range order.

This is one of the main discoveries of the recent research of modern crystallography, that three-dimensional periodicity is not an essential condition for the existence of crystals [2]. Periodicity is not the only possible means to achieve long-range order. As a direct consequence, the classical textbook definition of a crystal demanding a "*regular repetition of the atomic constituents in the three-dimensional space*" is not valid any more. A more recent definition of a crystal by the IUCr ad interim Comission on Aperiodic Crystals is much less restrictive: here a crys-

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tal is defined as "*any solid having an essentially discrete diffraction diagram*" [1]. With this new definition crystals are not defined in direct space any more, but *via* their diffraction pattern in reciprocal space. This new definition is rather broad and general, but it has the advantage that it covers not only aperiodic crystals but also disordered ones and solid solutions which do not obey periodicity in a strict sense, too.

In general, three different kinds of aperiodic crystals are considered [3]. Modulated structures can be interpreted as a basic structure with three-dimensional space group symmetry, which is modulated by a periodic deformation (= modulation). The periodicity of the modulation (in the incommensurate case) does not belong to the periodicity of the basic structure. Composite or intergrowth crystal structures consist of two (or more) subsystems, whose basic structures are mutually incommensurate [4]. Each of the substructures has its own space-group symmetry. The space groups of the substructures can be uniquely derived from the overall superspace group. The single lattices are not sublattices of a common (three-dimensional) one and it is not possible to express one lattice by the other one with rational numbers. These compounds do not possess one common basic lattice. Nevertheless, the intergrowth is coherent, the intergrowth compounds have to be regarded as single thermodynamic phases. Quasicrystals are "*considered to be characterized by the absence of an average Bravais lattice and/or the observation of 'forbidden' crystallographic symmetry* (*e.g. decagonal*)" [5]. This means, that quasicrystals do not have a three-dimensional periodic basic structure, also the basic structure itself is incommensurate. Usually (but not necessarily) quasicrystals exhibit a non-crystallographic point symmetry in their diffraction pattern, *i.e.* a symmetry which is not compatible with the translational lattice symmetry, *e.g.* a 5-, 10- or 12-fold rotation axis. The present contribution is focussing on modulated structures of organic (molecular) compounds. Composite structures and quasicrystals will not be further discussed.

As crystal structures reflect the forces, which appear between the atomic constituents of solid matter, and as the understanding of the structures and the bonding between the atomic constituents is a fundamental condition for being able to explain, modify, or even predict their physical and chemical properties, the description of crystal structures has to be as precise and accurate as possible. Depending on the problem, it might not be appropriate to neglect the modulation or to mimic the modulation by a superstructure approximation (for an explanation, see later in the text in Section 3.3), but to exactly describe it within the $(3+d)$-dimensional superspace approach. The question arising is, which of the models describes the structure more efficient and which one yields a deeper physical and chemical insight of the material and its properties.

2.2 The higher-dimensional superspace

Aperiodic crystal structures can be understood and described within the higher-dimensional, *i.e.* $(3+d)$-dimensional superspace approach, which is now a well established method. The superspace can be understood as an extension of the three-dimensional space to $(3+d)$ dimensions. In this notation "$(3+d)$" the "3" at the first position represents the dimensions of the first subspace, *i.e.* the three-dimensional physical space, in which the atoms are positioned, or the three-dimensional reciprocal space of the diffraction patter, respectively. The "d" at the second position represents the additional dimensions of the second subspace, which is orthogonal to the first one. The first subspace is also called external or parallel space, V_E or $V^{\parallel}$, the second subspace also internal or perpendicular space, V_I or $V^{\perp}$. In other words, the superspace V is separated into two orthogonal subspaces

$$V = V_\mathrm{E} \oplus V_\mathrm{I}\,. \tag{1}$$

Please note, that in this context a $(3+1)$-dimensional superspace and a $(2+2)$-dimensional superspace are both four-dimensional spaces, but result in different interpretations.

Advantage of this approach is, that a three-dimensional aperiodic structure can be described and interpreted in superspace as a higher-dimensional periodic one. This means, that the concept of periodicity (translational symmetry), which is a well established and powerful tool in crystallography, can be retained.

2.2.1 Reciprocal space

A clear hint that a structure is an incommensurately modulated one, is given in the diffraction pattern. Two sets of peaks can be discriminated. One set is formed by the so-called main reflections, the other is formed by the so-called satellite reflections. The main reflections are in general stronger and span a three-dimensional lattice defined by the reciprocal lattice vectors $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, $\boldsymbol{c}^*$. The satellite reflections are weaker and do not represent lattice points with respect to $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, $\boldsymbol{c}^*$ or any other three-dimensional lattice, *i.e.* they can not be indexed with three small integer numbers. Two examples for such diffraction patterns of modulated structures are shown in Fig. 1. For incommensurate composite crystals and for quasicrystals the diffraction pattern is more complex.

To index in such cases all Bragg peaks (main reflections and satellite reflections) by small integer numbers, the three reciprocal lattice vectors $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, $\boldsymbol{c}^*$ are not sufficient any more, one or two or three additional vectors have to be introduced. In case of one additional vector $\boldsymbol{q}$, *i.e.* if four integers $hklm$ are required to index all peaks in a unique way according to Eq. (2) (Fig. 1a), the structure is one-dimensionally modulated, one extra dimension is needed for the description in superspace.

$$\begin{aligned}
\boldsymbol{S}_{(3+1)} &= h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^* + m\boldsymbol{q}\,,\\
\boldsymbol{S}_{(3+2)} &= h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^* + m\boldsymbol{q}_1 + n\boldsymbol{q}_2\,,\\
\boldsymbol{S}_{(3+3)} &= h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^* + m\boldsymbol{q}_1 + n\boldsymbol{q}_2 + p\boldsymbol{q}_3\,.
\end{aligned} \tag{2}$$

With two additional vectors $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$, *i.e.* five integers *hklmn* for indexation (Fig. 1b), the structure is two-dimensionally modulated, and with three additional vectors it is called three-dimensionally modulated.

In Fig. 1a a precession photograph of the $h1l$ layer of reciprocal space of quininium (R)-mandelate, $C_{20}H_{25}N_2O_2{}^+$

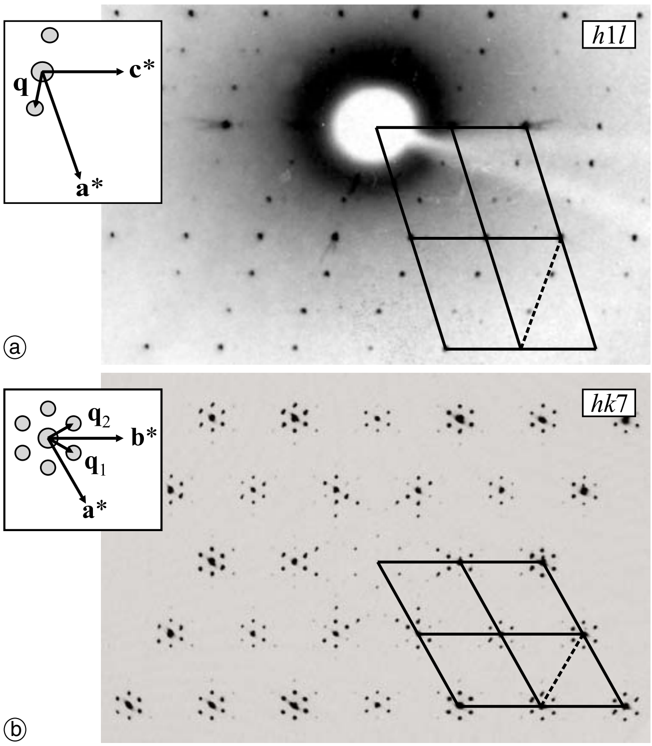

Fig. 1. (**a**) Precession photograph of the $h1l$ layer of reciprocal space of quininium (R)-mandelate at room temperature. All peaks can be indexed uniquely by four small integers $hklm$ applying the $(3+1)$-dimensional superspace approach with additional vector $\boldsymbol{q} = (\sigma_1, 0, \sigma_3)$. (**b**) Reconstruction of the $hk7$ layer of reciprocal space of Λ-Cobalt(III) sepulchrate trinitrate at $T = 115$ K. To index all peaks uniquely, five small integers $hklmn$ have to be applied within the $(3+2)$-dimensional superspace approach and two additional vectors $\boldsymbol{q}_1 = (\sigma, \sigma, 0)$ and $\boldsymbol{q}_2 = (-\sigma, 2\sigma, 0)$ (further explanation is given in the text).

$\cdot\ C_8H_7O_3{}^-$, at room temperature is shown (the photo was taken in-house with a sealed X-ray tube). This compound has monoclinic symmetry, the additional vector is $\boldsymbol{q} = (\sigma_1, 0, \sigma_3)$. Figure 1b exhibits the reconstruction of the $hk7$ layer of reciprocal space of Λ-Cobalt(III) sepulchrate trinitrate, $C_{12}H_{30}N_8Co^{3+} \cdot 3\ NO_3{}^-$, at $T = 115$ K (the data was collected with a CCD detector at the synchrotron). As the compound is hexagonal, the two additional vectors $\boldsymbol{q}_1 = (\sigma, \sigma, 0)$ and $\boldsymbol{q}_2 = (-\sigma, 2\sigma, 0)$ are related by symmetry.

From now on in this contribution all discussion shall be limited to the case of one-dimensionally modulated structures described in $(3+1)$-dimensional superspace.

The four vectors $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, $\boldsymbol{c}^*$ and $\boldsymbol{q}$ define the $(3+1)$-dimensional superspace. They are rationally independent, but not linearly independent vectors: the main reflections and the satellite reflections create a three-dimensional quasi-lattice of rank 4. With respect to the three reciprocal lattice vectors spanned by the main reflections (Fig. 1a) the fourth vector $\boldsymbol{q}$ can be expressed by

$$\boldsymbol{q} = \sigma_1 \boldsymbol{a}^* + \sigma_2 \boldsymbol{b}^* + \sigma_3 \boldsymbol{c}^* \,. \tag{3}$$

The vector $\boldsymbol{q}$ is called the "modulation wave vector", it represents direction and wavelength of the modulation wave through the crystal structure. If at least one of the components σ_i $(i = 1, 2, 3)$ has an irrational value (or is a function of temperature, pressure, ...), the structure is called "incommensurately modulated".

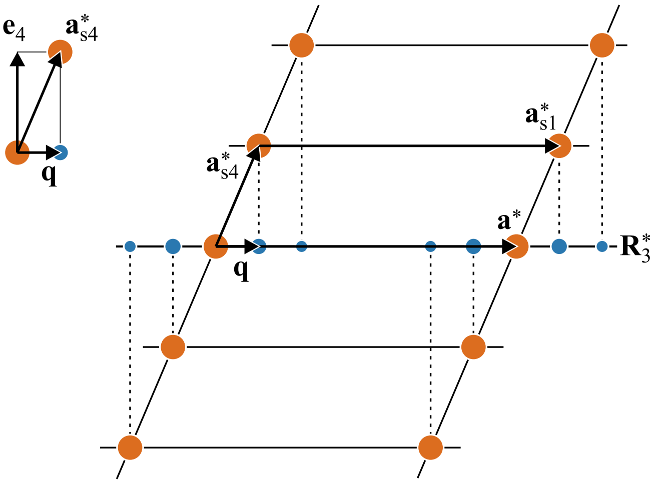

Fig. 2. Schematic drawing of the superspace approach in reciprocal space: the diffraction pattern of a modulated structure is represented by the horizontal line $\boldsymbol{R}_3^*$ along $\boldsymbol{a}^*$ with main reflections (orange) and satellite reflections (blue) up to second order, *i.e.* $m = \pm 2$ in Eq. (2). In this example, the modulation wave vector runs parallel $\boldsymbol{a}^*$ and can be written as $\boldsymbol{q} = (\sigma_1, 0, 0)$. The diffraction pattern along $\boldsymbol{R}_3^*$ is interpreted as a projection from higher-dimensional space, here $(3+1)$-dimensional, into three-dimensional space. The projected peaks are the satellite reflections (further explanation is given in the text).

To interprete the diffraction pattern with main reflections and additional satellite reflections, one can follow an idea of de Wolff [6] and understand it as a projection of higher-dimensional space into three-dimensional space. In Fig. 2 the three-dimensional diffraction pattern, represented by $\boldsymbol{R}_3^*$, consists of main reflections and of satellite reflections. The vector $\boldsymbol{e}_4$ is a unit vector of the four-dimensional Euclidean space orthogonal to $\boldsymbol{R}_3^*$. The reciprocal lattice vectors $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$ span the three-dimensional reciprocal lattice of main reflections, the vector $\boldsymbol{q}$ is the projection of the additional dimension into this three-dimensional reciprocal space. In the example of Fig. 2 it is the projection of $\boldsymbol{a}_{s4}^*$ into $\boldsymbol{R}_3^*$.

2.2.2 Direct space

How to interpret now the superspace approach for the description of an aperiodic crystal structure with respect to the atoms? How to describe an aperiodic crystal structure, *i.e.* the non-periodic arrangement of atoms in three-dimensional direct (physical) space, within the higher-dimensional superspace approach?

For classical three-dimensional periodic crystal structures the diffraction pattern in reciprocal space is understood as Fourier transform of the crystal structure in direct space. This holds also for aperiodic crystals structures. It is a general property of the Fourier transform, that the projection of a higher-dimensional lattice into three dimensions in reciprocal space corresponds to a three-dimensional section (or cut) of a higher-dimensional structure in direct space. Therefore, the three-dimensional (aperiodic) crystal structure will be interpreted as a three-dimensional section (or cut) of a higher-dimensional (periodic) structure. As a consequence, the atoms in higher-dimensional superspace are not discrete objects any more but have to be described by one-dimensional objects (for the case of a description in $(3+1)$-dimensional superspace) along the

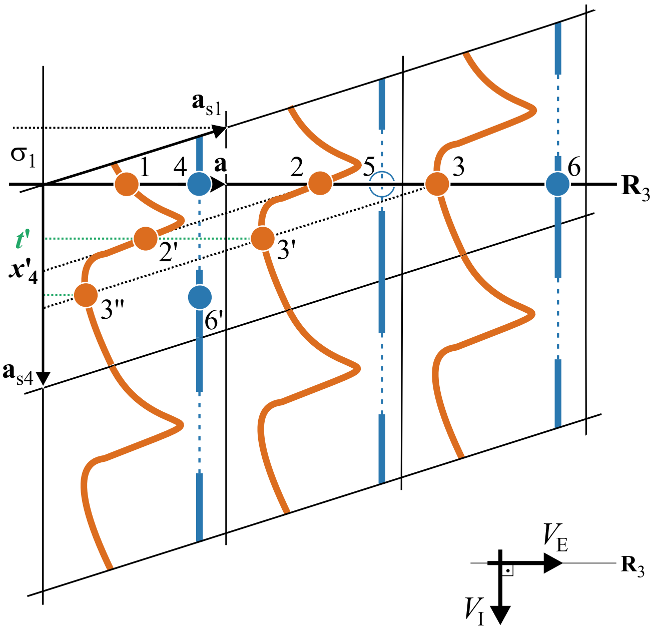

Fig. 3. Schematic drawing on the extension of an aperiodic crystal structure along $\boldsymbol{R}_3$ into superspace. Two atoms are drawn per unit cell, the orange one through positions 1, 2 and 3 shows a displacive modulation, the blue one through positions 4 and 6 an occupational one (further explanation is given in the text).

additional internal space V_I (Fig. 3). For $(3+2)$-dimensional superspace the atoms will be interpreted as two-dimensional objects and for $(3+3)$-dimensional superspace as three-dimensional objects, respectively.

Looking in Fig. 3 along the three-dimensional space $\boldsymbol{R}_3$ (the representation of the crystal structure in physical space V_E), the distance between the orange (light grey) atomic positions 1–2 of first and second unit cell is clearly larger than the one between 2–3 of second and third unit cell. Also the blue (dark grey) atomic position 5 in the second unit cell is not occupied, while positions 4 and 6 in the first and third unit cell are occupied: there is clearly no periodicity present in $\boldsymbol{R}_3$, neither with respect to atomic positions, nor with respect to the content of the unit cells. But looking now at the complete picture, the continuous orange line and the discontinuous blue line are both periodically distributed in the superspace lattice ($\boldsymbol{a}_{s1}$, $\boldsymbol{a}_{s4}$). So, the aperiodic structure along $\boldsymbol{R}_3$ becomes periodic in the higher-dimensional space, the aperiodic crystal structure in physical space is interpreted as a three-dimensional section (or cut) of those higher-dimensional periodic object. This means, within the superspace formalism a real, three-dimensional aperiodic structure is interpreted as a section (or cut) of a higher-dimensional periodic structure. The other way around, the three-dimensional section of a higher-dimensional periodic structure results in an aperiodic arrangement of the atoms. However, it has to be stressed again, even though the three-dimensional periodicity is lost, the atoms are not at all randomly distributed, the three-dimensional crystal structure is still perfectly long-range ordered along all three dimensions of physical space. The periodicity can be recovered in higher-dimensional space.

There are several possibilities for a modulation of a crystal structure: The three most common types in chemical crystallography are the displacive modulation, the occupational modulation and/or the modulation of the anisotropic atomic displacement parameters (anisotropic ADPs). Displacive modulation means, that the position of the atoms, *i.e.* the fractional coordinates (xyz), varies along the internal space (such a modulation is represented by the continuous orange line in Fig. 3). With an occupational modulation the site occupancy of the atom (the discontinuous blue line in Fig. 3) is changing along V_I and with the modulation of the anisotropic ADPs the ADPs are changing, respectively. The "and/or" shall stress, that also combinations of the different types of modulation can appear. But in principle, every variable physical property can be modulated. There can be for example also some long-range charge ordering or within a magnetic structure a spin ordering, resulting in a charge density wave or in a spin density wave, respectively (which then might also affect the atomic positions and the ADPs).

Depending on the structure under investigation and depending on the modulation itself, these changes of the concerned atomic property (position, occupation, ...) can be approximated or described by different functions, which are all periodic along the internal space V_I. Such functions are called atomic modulation functions (AMFs). The continuous orange line in Fig. 3 for example might be described by a harmonic function

$$\begin{aligned} f_i(x_4) = \bar{x}_i &+ A_1^i \cos(2\pi\, 1x_4) + B_1^i \sin(2\pi\, 1x_4) \\ &+ A_2^i \cos(2\pi\, 2x_4) + B_2^i \sin(2\pi\, 2x_4) \\ &+ \dots, \end{aligned} \tag{4}$$

in which all $A_1^i, B_1^i,\ A_2^i, B_2^i,\ \dots$ have to be defined and then of course also refined to describe the modulation of the atom in a proper way. As the harmonic function is a continuous function, it is suitable to describe modulations with a smooth change of the atomic variable under consideration. In $(3+1)$-dimensional superspace it is possible to apply next to the harmonic functions also step like (block wave) or sawtooth functions [7, 8] as AMFs. The advantage of step like functions is, that they need in general less parameters to be refined than harmonic functions: a block wave function is defined by the two parameters width, Δx_4, and centre, x_4^o. The discontinuous blue line in Fig. 3 for example is better described by a step like function. Please note, that both functions (in Fig. 3 the orange and the blue lines) repeat periodically along $\boldsymbol{a}_{s4}$, the dimension in internal space V_I.

2.2.3 Symmetry in superspace

To be able to use symmetry considerations by applying the higher-dimensional superspace approach, the so-called higher-dimensional superspace groups (SSGs) have been set up. Those higher-dimensional superspace groups can be applied to the symmetry of modulated structures and of composite crystals. As quasicrystals show non-crystallographic pointgroup symmetry, they have to be treated with a different approach, which is, however, out of scope of this contribution.

To set up such a higher-dimensional superspace group from the experimental data of the structure under investigation – as in the case of the classical three-dimensional space groups – one first has to determine the point group symmetry from the symmetry of the diffraction pattern. In the next step then, the specific superspace group can be chosen on the basis of selection rules characterized by systematic absences in the diffracted intensities of main reflections AND of satellite reflections.

Again the discussion here shall be limited to the $(3+1)$-dimensional case. The $(3+1)$-dimensional superspace groups are four-dimensional space groups. As it is the case for the three-dimensional space groups, also the superspace groups represent groups of transformations, which are distance preserving. These transformations of the SSGs however are pairs of orthogonal transformations, one in external space V_E, one in internal space V_I. So a $(3+1)$-dimensional superspace group is a four-dimensional space group with the additional property, that it discriminates between the three-dimensional physical subspace V_E and the d-dimensional additional subspace V_I. Both subspaces V_E and V_I are left invariant, superspace symmetry operators are called to be $(3,\,1)$ reducible.

For the particular case of one-dimensionally modulated structures the set of $(3+1)$-dimensional superspace groups has been tabulated in the *International Tables for Crystallography, Volume C* [3]. Very recently complete lists of all $(3+1)$-, $(3+2)$- and $(3+3)$-dimensional superspace groups have been established and are accessible *via* an online data repository [9].

As an example the $(3+1)$-dimensional superspace group $P2/m\,(0\sigma_2 0)\,s0$ shall be briefly discussed (for further details the reader is refered to the literature listed in Section 2.3). The monoclinic lattice ($\boldsymbol{b}$-unique) is primitive, the modulation wave vector $\boldsymbol{q} = (0, \sigma_2, 0)$ is running parallel to the reciprocal lattice vector $\boldsymbol{b}^*$, which means, parallel to the twofold axis and perpendicular to the mirror plane. The twofold axis is associated with an intrinsic phase shift $^1/_2$, as indicated by the small letter s in the symbol (one can understand this as a "screw axis" with translational component along internal space). No intrinsic phase shift is associated with the mirror plane (as indicated by the 0 in the symbol). However, as the modulation wave vector $\boldsymbol{q}$ is perpendicular to the mirror plane, it is inverted by that mirror plane, the mirror plane is associated with a phase inversion $\bar{1}$ of the modulation wave along the fourth dimension. Therefore, as proposed by van Smaalen [10] one might write as an extended superspace group symbol: $P2/m\,(0\sigma_2 0)\,s\bar{1}$. The resulting symmetry operators for the four symmetry elements idendity, inversion, twofold rotation axis and mirror plane can be expressed as:

$$\begin{array}{rcrrrr} 1 & : & x_1 & x_2 & x_3 & x_4 \\ 2 & : & -x_1 & x_2 & -x_3 & x_4+\frac{1}{2} \\ \bar{1} & : & -x_1 & -x_2 & -x_3 & -x_4 \\ m & : & x_1 & -x_2 & x_3 & -x_4+\frac{1}{2} \end{array} \tag{5}$$

Please note, that the translational component $+^1/_2$ along the fourth dimension for the mirror plane is not an intrinsic shift, but an origin dependent one.

One can see on that example, that the $(3+1)$-dimensional superspace symmetry operator g_s consists on rotational and translational parts $[R_s\,|\,v_s]$, which can be expressed in the $(3,\,1)$ reducible form as $[(R, R_\mathrm{I})\,|\,(v, v_\mathrm{I})] = [(R\,|\,v),\,(R_\mathrm{I}\,|\,v_\mathrm{I})]$. For the $(3+1)$-dimensional case R_I is also denoted as ϵ and v_I as Δ. The part $(R\,|\,v)$ of the symmetry operation for the external space V_E belongs to the three dimensional space group of the basic structure, which is then associated with additional symmetry $(\epsilon\,|\,\Delta)$ in internal space V_I. In other words, the transformations of the space group of the basic structure give rise to a symmetry transformation for the modulated structure when combined with an appropriate phase shift Δ and a possible phase inversion ϵ. To keep the $(3,\,1)$ reducibility, the point group operation R must leave the orientation of the modulation wave vector $\boldsymbol{q}$ invariant. This is ensured by the relation

$$R\boldsymbol{q} = \epsilon\boldsymbol{q}\ , \tag{6}$$

modulo reciprocal lattice vector of the basic structure [3]. Then in the diffraction pattern the rotational operator R transforms main reflections only into main reflections and satellite reflections only into satellite reflections of same order m. As consequence of Eq. (6) the choice of the modulation wave vector $\boldsymbol{q}$ is related to the symmetry [10], the modulation wave vector components have to fulfil the relation (in case, that all rational components are zero).

$$(\sigma_1, \sigma_2, \sigma_3)\,R^{-1} - \epsilon^{-1}(\sigma_1, \sigma_2, \sigma_3) = (0, 0, 0)\,. \tag{7}$$

The superspace group symbol therefore gives in addition to the three-dimensional point group symmetry of the average structure also information on the possible centring of the higher-dimensional lattice, on the components of the modulation wave vector $\boldsymbol{q}$ and on the associated intrinsic shifts for each symmetry element (screw- or glide-components) along the additional dimension. The point group symmetry of the diffraction pattern is preserved by the higher-dimensional superspace group in both subspaces, the external space V_E and the internal space V_I.

In this context it is necessary to discuss the difference between the terms basic structure (which has been used already in Section 2.1) and average structure (which is used here). The basic structure is the undistorted crystal structure (sometimes also called reference structure). It is obtained by taking the modulated structure, removing all modulation parameters and keeping only the fractional coordinates (xyz) and the anisotropic ADPs U^{ij}. The average structure is the structure, which is averaged over all modulations and which is obtained by a refinement in three-dimensional space: only the main reflections are taken into account [11], the contribution of the satellite reflections is neglected. Both structures have three-dimensional space group symmetry. But please note also, that both structures, basic structure and average structure, are not real existing, they both have only hypothetical character. In case of strong modulation they also might not be chemically meaningful (for example with respect to interatomic distances and angles).

If two atoms in a classical three-dimensional periodic structure are related by a symmetry operation g, the fractional coordinates of these two atoms for example are related *via*

$$\boldsymbol{r}' = g\boldsymbol{r} = (\boldsymbol{R}\,|\,\boldsymbol{v})\,\boldsymbol{r} = \boldsymbol{R}\boldsymbol{r} + \boldsymbol{v}\,. \tag{8}$$

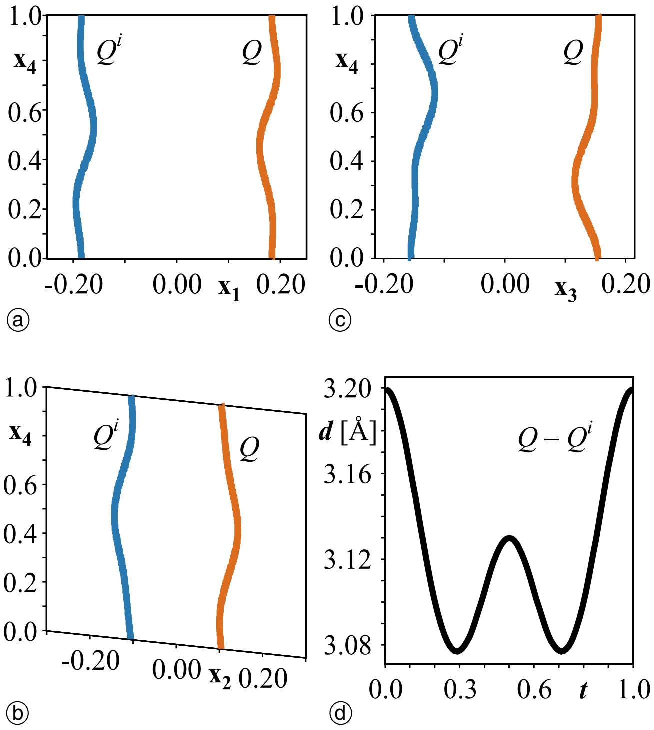

Fig. 4. (**a**)–(**c**) Schematic drawing of the displacive AMFs for the fractional coordinates $(x_1x_2x_3)$ along the internal space of an imaginary atom Q (orange line) with its symmetry equivalent atom Q^i (blue line) along x_4. The width of the maps is 3 Å, the symmetry code is i: $-x_1 - x_2 - x_3 - x_4$ (further information on lattice, symmetry and atomic parameters is given in the text). (**d**) t-Plot for the corresponding interatomic distance between the two symmetry equivalent atoms Q and Q^i, *i.e.* the variation of the distance between the two atoms as function of the phase of the modulation t.

In case of a modulated structure with displacive modulation in addition also the AMFs of the atoms are related by the symmetry operation. As it can also be seen in Eq. (4) for example, the AMFs are functions of the basic structure coordinates

$$x_{si} = \bar{x}_i + \boldsymbol{u}_i(\bar{x}_{s4}) \,. \tag{9}$$

The function $\boldsymbol{u}_i(\bar{x}_{s4})$ is the corresponding AMF. Then the transformation of this function of coordinates can be written as [10]

$$\boldsymbol{u}'(\bar{x}_{s4}) = \boldsymbol{R}\boldsymbol{u}([\boldsymbol{R}_s \,|\, \boldsymbol{v}_s]^{-1}\; \bar{x}_{s4}) \,, \tag{10}$$

an in case, that all rational components of the modulation wave vector are zero, as [10]

$$\boldsymbol{u}'(\bar{x}_{s4}) = \boldsymbol{R}\boldsymbol{u}[\epsilon^{-1}(\bar{x}_{s4} - v_{s4})] \,. \tag{11}$$

For an occupational modulation one can derive the expression [10]

$$\boldsymbol{p}'(\bar{x}_{s4}) = \boldsymbol{p}[\epsilon^{-1}(\bar{x}_{s4} - v_{s4})] \,. \tag{12}$$

For illustration, in Fig. 4a–c the AMFs for displacive modulation of an imaginary atom Q in a hypothetical structure is shown together with one of its symmetry equivalent atom Q^i. A monoclinic lattice was assumed with lattice parameters 6 Å, 5 Å, 7 Å, 90°, 92°, 90°. The above discussed superspace group $P2/m$ $(0\sigma_2 0)\, s\bar{1}$ is applied with the modulation wave vector component $\sigma_2 = 0.37$. The displacive modulation of atom Q is described with two harmonic waves (Eq. 4), the corresponding parameters are $\bar{x} = 0.18$, $A_1^x = 0.011$, $B_1^x = -0.007$, $A_2^x = -0.007$, $B_2^x = 0.003$, and $\bar{y} = 0.12$, $A_1^y = -0.019$, $B_1^y = -0.004$, $A_2^y = 0.004$, $B_2^y = -0.003$, and $\bar{z} = 0.14$, $A_1^z = 0.009$, $B_1^z = -0.014$, $A_2^z = 0.006$, $B_2^z = 0.005$.

2.2.4 Crystal-chemical analysis

For the crystal-chemical analysis of the aperiodic crystal structure, one has to consider, that in the superspace approach the crystal is understood as a three-dimensional section (or cut) of the higher-dimensional structure. And the spacial arrangement of the atoms in this section is aperiodic (but still long-ranged ordered). As consequence, one has not just one specific value for *e.g.* an interatomic distance between two atoms, but a range of values with a minimum, a maximum and an average value. This section (or cut) to be considered is a function of the phase of the modulation t, and not of the fractional coordinate x_4 in the superspace lattice. It is seen in Fig. 3, that *e.g.* the atomic positions 2 and 3, which are in the same cut of the higher-dimensional structure, have the same value for the parameter t, which holds also for the positions 2′ and 3′, respectively, but they have different values for x_4. In fact, as they are correlated by simple lattice translation, the positions 2 and 2′ and also 3 and 3′ (and 3″) have the same values for x_4, but are all in different sections (different values for t). The relation between t and x_4 is given by

$$t = x_4 - \boldsymbol{q}\boldsymbol{r} \,, \tag{13}$$

i.e. the relation between both depends on the position $\boldsymbol{r}$ of the atom and on the modulation wave vector $\boldsymbol{q}$. As consequence, for the crystal-chemical analysis only atoms with the same phase of the modulation, *i.e.* with the same value of t, have to be considered, as it is the case for the cut along $\boldsymbol{R}_3$. But now one can profit from the periodicity recovered in higher-dimensional superspace: it is possible to shift all atoms, *i.e.* the intersections of the atomic modulation funtions with $\boldsymbol{R}_3$ from this three-dimensional space line $\boldsymbol{R}_3$ into the first unit cell (applying the translational symmetry of the superspace $\boldsymbol{a}_{s1}$, $\boldsymbol{a}_{s2}$, $\boldsymbol{a}_{s3}$ and $\boldsymbol{a}_{s4}$).

It is seen again in Fig. 3, that the distance between the positions 2–3 corresponds to the distance between the positions 2′–3′. In other words, varying t for a certain geometric parameter, like an interatomic distance, from $t = 0$ to $t = 1$ does provide ALL values for this parameter occurring anywhere in the three-dimensional aperiodic crystal structure along $\boldsymbol{R}_3$. The graphical presentation of such analysis, *i.e.* the sketch of a parameter as function of t, is called a t-plot. Of course, not only interatomic distances but all other structural features such as angles, torsion angles, and also fractional coordinates, ADPs, site occupancies, valences, …, which change as function of the phase of the modulation t, are analysed in such way. And it is exactly this variation of those parameters with t that is the core of the discussion and crystal-chemical analysis for modulated crystal structures. The t-plot for the distance of the two symmetry equivalent atoms Q and Q^i of Fig. 4a–c is shown in Fig. 4d. The distance d_{Q-Q^i} varies as function of the phase of the modulation t between 3.067 Å and 3.189 Å, the average is about 3.113 Å. It can be also seen directly in Fig. 3, that the two distances 1–2 and 2–3 of neighbouring unit cells are not values next to each other with respect to t but are separated by the value of the corresponding modulation wave vector component (in the example of Fig. 3 it is σ_1). Therefore then also in the t-plot those values are separated by that value of the corresponding σ_i. The other way arround, neighbouring points in the t-plot are separated by several unit cells in $\boldsymbol{R}_3$.

2.2.5 Software

Most of the commercial and several non-commercial (depending on the purpose) diffractometer software and data reduction programs have implemented an option to index and integrate the diffraction peaks with up to six indices.

For structure solution several different approaches are possible *via* solving the (three-dimensional periodic) average structure or a superstructure approximation [12] with classical structure solution software (Patterson or direct methods) and then to add in the next step of structure refinement the modulation to the structural model. However, these are rather time consuming methods, which cause in case of large structures or strong modulation severe problems. A more elegant way is to solve the modulated structure directly and *ab initio* within the higher-dimensional superspace approach, *i.e.* to obtain information about fractional coordinates and also about the AMFs of the atoms directly during structure solution. This can be done with the charge flipping method applying the program Superflip [13].

For structure refinement of a modulated structure the first available software was Remos [14] for single crystal data and Premos (the powder version of Remos). Another very frequently used program package is Jana2006 [15]. The present release of Jana2006 allows refinement of non-modulated, modulated and composite structures against single-crystal and powder data, applying harmonic and/or block wave funtions for the AMFs, anharmonic ADPs or the TLS formalism. Also the option to refine magnetic structures applying higher-dimensional magnetic superspace groups is implemented [16].

With the program BayMEM discrete electron density maps applying the maximum entropy method (MEM) can be calculated in arbitrary dimensions [17]. This is a powerful tool in cases, where the AMFs can not by properly defined due to disorder or modulated anharmonic ADPs [18]. The MEM allows to gain model-independent information about the AMFs directly from the diffraction data.

Some more extended lists on software with further descriptions can be found in appendix A of [10] and in Section 4.3.5 of [19].

2.3 More literature

The development of the concept, a historical overview and further explanation concerning aperiodic crystal structures and the higher-dimensional superspace approach might be found in the following review articles (and references therein): Janssen and Janner [2], Janssen [20], van Smaalen [21] and Yamamoto [22] discuss incommensurability, aperiodic and quasiperiodic crystals, incommensurate crystal structures and how to describe them in the higher-dimensional superspace. Bertaut [23] is treating commensurate and incommensurate crystals, while Chapuis [24] considers modulated structures in the context of phase transitions. More recent reviews are those of Mironov *et al.* [25] about powder diffraction on modulated structures, of Maciá [26] about aperiodic order in science and technology (discussing *e.g.* also links between quasiperiodic crystals and hierarchical structures of biopolymers), of Bolotina [27] about the state of the art of X-ray diffraction analysis of modulated crystals and of Christensen [28] about how to think on and how to teach the concept of the higher-dimensional superspace approach to students.

A discussion on the superspace approach and on $(3 + 1)$-dimensional superspace groups is given in the *International Tables for Crystallography, Volume C* in chapter “Incommensurate and commensurate modulated structures” by Janssen *et al.* [3]. The diffraction of aperiodic crystals is treated in the *International Tables for Crystallography, Volume B* in chapter “Reciprocal-space images of aperiodic crystals” by Steurer and Haibach [29].

A special issue of Zeitschrift für Kristallographie (Issue 11, Vol. 219, 2004), editet by van Smaalen [30], is dedicated to *Incommensurate Crystallography of Modulated and Composite Crystals*, treating all different aspects of this field of research. This issue includes also an elementary introduction to superspace, some discussion of different experimental techniques and methods and the available software.

The interested reader is referred to three textbooks, introducing the principles of aperiodic crystals and the superspace approach from a “crystallographic point of view”: *Aperiodic Crystals – From Modulated Phases to Quasicrystals* by Janssen, Chapuis and de Boissieu [19] considers quasiperiodic crystals from a unified point of view, dealing with the characterization of the structure and study of the physical properties of aperiodic crystals within the higher-dimensional superspace approach. *Incommensurate crystallography* by van Smaalen [10] gives a profound and comprehensive account of the superspace theory to describe structure and symmetry of incommensurately modulated crystal structures and incommensurate composite crystals. *Crystallography of Quasicrystals – Concepts, Methods and Structures* by Steurer and Deloudi [31] deeply describes the field of quasicrystal structure analysis, covering metallic and photonic quasicrystals.

Finally, a non-mathematical introduction to the superspace description of modulated (molecular) structures as a kind of beginner’s guide or primer is given in [12]. In this publication – based on a real modulated crystal structure from a pharmaceutical crystallography service laboratory – a practical approach is presented and the reader is taken step by step through the approach how to tackle such problem and how to understand and interprete such structure.

3. Organic and organometallic compounds

Looking through the literature, at a first glance one might get the impression, that mainly inorganic compounds are affected by modulation. In the review of Cummins [32] about 65% and in the review of Yamamoto [22] even about 80% of the cited compounds are inorganic. A search in *B-IncStrDB – The Bilbao Inconmensurate Structures Database* on the *Bilbao Crystallographic Server* [33, 34] confirms this first impression.

But this is a somehow biased conclusion! There does exist also a rather large number of modulated organic and organometallic compounds. Also here a detailed and precise description of the modulated crystal structure is necessary to perform a crystal-chemical analysis for the interpretation of chemical stability and interactions of those compounds. For a better understanding of the nature of those modulated molecular crystals, both the chemical behaviour as well as the structural characteristics should be analysed and the corresponding origin of the modulation should be established. In case of a phase transition from a non-modulated to a modulated phase the knowledge of the geometry of the deviation from the underlying basic structure will help to understand the mechanism of the transition. This all can be achieved in a rather elegant way also for molecular organic and organometallic compounds by applying the higher-dimensional superspace approach (Section 2.2).

This approach, however, is not yet fully considered and applied by the corresponding community of researchers dealing with such (organic and organometallic) structures, even though also modulated molecular compounds are known since at least 60 years.

Some of the first examples questioning perfect three-dimensional periodicity in organic compounds might be the molecular complexes of 4:4′-dinitrodiphenyl with 4-chloro-, 4-bromo-, 4-iodo- and 4:4′-diiododiphenyl, published by James and Saunder in the years 1947 and 1948 [35, 36]. The structures are built by layers of dinitrodiphenyl molecules in a face-centred array creating tubular cavities, in which the halogenated diphenyl molecules are placed. While the halogenated diphenyl molecules lie approximately along the crystallographic ***c***-axis, the dinitrodiphenyl molecules are oriented approximately normal to it. The authors argue, that not a chemical bonding, but some dipole interaction generated by a mutual polarisation of the molecules might be responsible for the stability of the complexes. They conclude, that the regular spacing of the layers of the dinitrodiphenyl molecules is modified by some "periodic error" (!) along the crystallographic ***c***-axis. This periodic deformation is introduced by the length of the halogenated diphenyl molecules.

Another example appeared only a few years later. While studying the crystal structures of urea-hydrocarbon complexes, Smith reported in 1952 extra spots in the diffraction pattern with fractional "*l*" indices [37], indicating not a random but an ordered arrangement of the hydrocarbon molecules in the channels created by the urea molecules. Those structures are now known as urea inclusion compounds (host-guest structures) and have attracted until today quite some interest [38–45]. The urea molecules act as host and form a honeycomb structure which creates at room temperature parallel tunnels. The diameter of the tunnels is such, that alkane chains and derivations thereof can be inserted as guest molecules. In the host structure the urea molecules are connected to each other via hydrogen bonds forming a hexagonal structure with symmetry $P6_122$ (or pseudo-hexagonal, depending on the temperature). The guest molecules show a positional long range order forced by the steric constraints of the tunnels [43], but they are normally rotationally disordered along the tunnel axes at high temperature. Most of the urea inclusion compounds undergo a structural phase transition at low temperature (at about $T = 150$ K to 100 K), which results in a slight distortion of the host substructure and a decrease of symmetry to orthorhombic. Although the transition temperature varies with the different types of guest molecules, the type of structural distortion of the host structure seems quite similar to all compounds. As the phase transition induces multiple twinning, it is difficult to describe the low temperature structures [42], in which the order varies with different compounds. There are compounds showing a well ordered three-dimensional substructure, others show disorder even at very low temperatures [40]. The order mechanism between the tunnels is not yet fully understood. Because the host and guest substructures are incommensurate with respect to each other, the whole structure is better described while applying the superspace approach. It also has to be stressed, that the urea host structure is stabilized by the presence of the guest, urea itself without a present guest is crystallizing in a tetragonal structure.

One last "historical" example which will be mentioned here is the intermediate phase of thiourea, $SC(NH_2)_2$. It was reported in 1963, that the phase at low temperature between $T = 202$ K and $T = 169$ K exhibits satellite reflections in the diffraction pattern [46]. A first model of the modulated structure was proposed in 1971 [47] and then another one in 1980 applying the then already known higher-dimensional approach [48]. In 1988 the modulated structure of thiourea was re-interpreted [49] while describing the displacive modulation of the molecule in a "rigid-molecule refinement" (see Section 3.2). Two superspace groups were tested, the acentric $P2_1ma(0\sigma_20)\,\bar{1}\bar{1}0$ and the centrosymmetric $Pnma(0\sigma_20)\,s\bar{1}0$. However, for the latter one a large number of reflections $0klm$ contradicts the reflection condition $k + l \neq 2n$ for the n-glide plane. In both models the lattices are orthorhombic primitiv, the modulation wave vector $\boldsymbol{q}$ runs along the crystallographic $\boldsymbol{b}^*$-axis, its component σ_2 varies with temperature. The modulation is described as a rotation and a translation of the molecules with respect to the orientation and position of the molecules in the commensurate low-temperature phase. In 1989 a model for this commensurate low-temperature phase (below $T = 169$ K) within the superspace group $Pnma(0\sigma_20)\,s\bar{1}0$ and $\sigma_2 = {}^1\!/_9$ was proposed applying diffraction data of satellite reflections up to third order [50]. For a better description of the anharmonicity of the modulation functions (again in terms of rigid molecules) harmonics up to third order were applied. The shapes of the AMFs denote a beginning soliton regime.

3.1 Modulated molecular crystal, what does it mean?

In this section two illustrative examples shall be discussed to give some more detailed ideas about modulated molecular crystal structures.

3.1.1 Biphenyl

The rather simple molecule of biphenyl, $C_{12}H_{10}$, is non-rigid and just consists of two phenyl rings bonded by a central C—C single bond. Two competing factors are important for the molecular conformation, the π-electron effect favouring coplanarity of the two planes defined by the phenyl rings and the steric hindrance of the *ortho*-hydrogen atoms favouring a torsion of the molecule along the long molecular axis, which is parallel to the central C—C single bond (Fig. 5a).

Due to the repulsion of the *ortho*-hydrogen atoms, the conformation of the molecule in the gas phase is non-planar, the torsion angle between the planes of the two phenyl rings along the central single C—C bond is $\phi = 42(2)^\circ$ [51–53].

In the crystal structure at room temperature the molecule is – in contrast to the gas phase and at least on average – planar ($\phi = 0^\circ$), presumably due to intermolecular forces. It was concluded, that it is not possible to pack together non-planar molecules with their lower symmetry and to get as much approximately equal intermolecular contacts as with planar molecules [52]. Indeed, planar molecules better pack in the "heringbone" arrangement, which is quite often found for aromatic molecules [54], while the non-planar molecules do not properly fit together.

At room temperature the space group is $P2_1/a$, $\boldsymbol{b}$-unique, with two molecules situated on inversion sites, the molecular symmetry being *mmm* [52, 55]. The intermolecular forces and the intramolecular forces, which compete in the non-rigid molecule, seem to be of the same order of magnitude [56]. To overcome somehow the steric repulsion, the *ortho*-hydrogen atoms are displaced in–plane increasing their distances: while in the regular model their distance H—H should be about $d_{\text{H—H}} = 1.8$ Å, it was found to be $d_{\text{H—H}} = 2.07$ Å without loosing planarity (Fig. 5b). As consequence, also the corresponding C—C—H angles are bended up to $\varphi = 126^\circ$ [55]. This conformation of the molecules was confirmed for the structure at $T = 110$ K [57]. In [52] even a H—H distance of $d_{\text{H—H}} = 2.2$ Å is reported. Another investigation at room temperature has confirmed the planarity of the molecules, but has shown, that the libration around the long molecular axis is with an amplitude of $\simeq 10^\circ$ rather large [58].

In [59] the planar conformation of the molecule was interpreted as the result of dynamic disorder with $\langle\phi\rangle_{\text{time}} = 0^\circ$ and an actual molecular equilibrium geometry of $\phi = 27^\circ$ (but please note, that also in this description the crystal packing with its intermolecular forces has a flattening effect on the individual molecules).

At low temperatures two modulated crystalline phases with non-planar molecules ($\phi \neq 0^\circ$) [56, 60, 61] in the crystal structure are found. The inversion symmetry of the molecular structure and the inversion symmetry of the crystal structure are destroyed. The torsion angle of $\phi \neq 0^\circ$ between the planes of the phenyl rings as essential structural modification of the low-temperature phases in biphenyl is common with other polyphenyl structures. In biphenyl the phase transitions take place upon cooling at $T_{c1} = 40$ K and at $T_{c2} = 16$ K (at $T_{c1} = 38$ K and $T_{c2} = 21$ K for the deuterated compound) [56, 62, 63]. The torsion angle between the two phenyl rings in the molecules varies as function of the phase of the modulation t. In the intermediate phase between the two phase transitions, the modulation wave vector is reported as about $\boldsymbol{q} = 0.05\boldsymbol{a}^* + 0.46\boldsymbol{b}^*$. Please note however, that a modulation wave vector $(\sigma_1, \sigma_2, 0)$ is not compatible with a $\boldsymbol{b}$-unique setting. No further information regarding symmetry is given in [56]. In the low temperature phase the modulation wave vector is about $\boldsymbol{q} = 0.46\boldsymbol{b}^*$ [56]. As the modulation wave vector components (and also the intensities of the satellite reflections) vary with temperature in both phases, both phases have to be regarded as incommensurately modulated structures.

For the low temperature phase the (3 + 1)-dimensional superspace group is $Pa(0\sigma_2 0)\,\bar{1}$, as derived from systematic absences in the diffraction pattern. Also the centrosymmetric superspace symmetry $P2_1/a(0\sigma_2 0)\,0\bar{1}$ was tested and rejected by statistical arguments [61]. In the resulting refined modulated structure the phenyl rings have been considered as rigid bodies, *i.e.* all atoms of the ring must be in phase. The final structural model can be described by the following three main features [61, 64]: a torsion with an amplitude of 5.5° for each phenyl ring, *i.e.*, the maximum deformation angle being $\phi = 11^\circ$, a rotation around the normal to the mean molecular plane, with an amplitude of $\omega = 1^\circ$ and a translation along the long molecular axis with an amplitude of $d = 0.035$ Å (Fig. 6). The rotation ω was found to be 90° out of phase with the torsion while the translation d is in phase with the torsion.

The different molecular and crystal structures of biphenyl, $C_{12}H_{10}$, with a twisted molecule in the gas phase and a flattened molecule in the crystal structure at room tem-

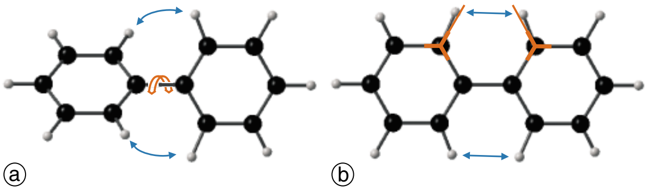

Fig. 5. The molecular structures of biphenyl in (**a**) the gas phase and (**b**) the crystal structure at room temperature. Due to steric strain by the *ortho*-hydrogen atoms (indicated by the blue arrows), the molecule is twisted in the gas phase and bended in the crystal structure at room temperature with respect to a regular planar reference structure.

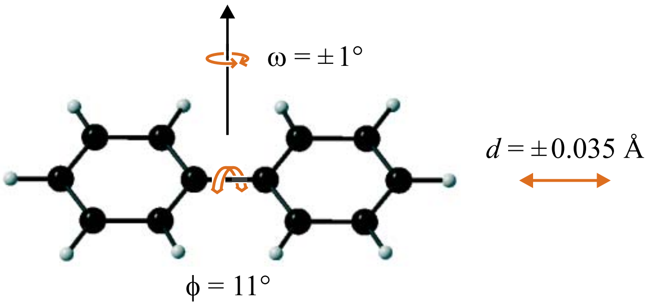

Fig. 6. Schematic drawing summarizing the effect of the modulation to the individual molecules, which are twisted, rotated and shifted. As the actual values for ϕ, ω and d vary with the phase of the modulation t, only the maximum values are indicated.

perature, nicely demonstrate the competition between crystal packing (intermolecular force) and molecular conformation (intramolecular force) in molecular crystals. In addition, the torsion in the molecules around the long molecular axis is the essential feature of the modulation of the crystal structure in the low temperature phases. The temperature dependence of the torsion angle can be explained by mutual frustrations of the intra- and intermolecular contributions to the lattice energy.

3.1.2 2-Phenylbenzimidazole

Next to biphenyl and also next to 4,4′-dichlorobiphenyl sulphone, $(ClC_6H_4)_2SO_2$ [65], which shall be just mentioned here without detailed discussion, the compound 2-phenylbenzimidazole, $C_{13}H_{10}N_2$, is another clear and comprehensible example for an incommensurately modulated molecular crystal structure [66]. The molecule consists of two planar moieties, a phenyl ring and a benzimidazole group, which are linked *via* a C—C single bond (Fig. 7a). The applied superspace group is $C2/c(0\sigma_2 0)\,s\bar{1}$ with $\sigma_2 = 0.368$. This means, that the lattice is monoclinic $\boldsymbol{b}$-unique with additional $(3+1)$-dimensional centring $(^1/_2\ ^1/_2\ 0\ 0)$ and a modulation wave vector parallel to the crystallographic $\boldsymbol{b}^*$-axis. The twofold rotation axis is associated with an intrinsic shift of $^1/_2$ along the fourth dimension, the *c*-glide plane with a phase inversion of the modulation wave. Again, the variation of the intramolecular torsion angle between the two flat moieties of the molecule can be understood as the main feature of the modulation. This variation is caused by the crystal packing, which forces the molecular conformation to be close to planar while the *ortho*-hydrogen atoms favour a twisted molecule.

The structure has two independent molecules A and B in the asymmetric unit, which are connected by intermolecular N—H$\cdots$N contacts. The *t*-plots (see Section 2.2) for the torsion angles is given in Fig. 7b for both molecules. It can be seen, that the variation of molecule A, *i.e.* the modulation of the torsion angle as function of the phase of the modulation *t*, is slightly larger then that of molecule B.

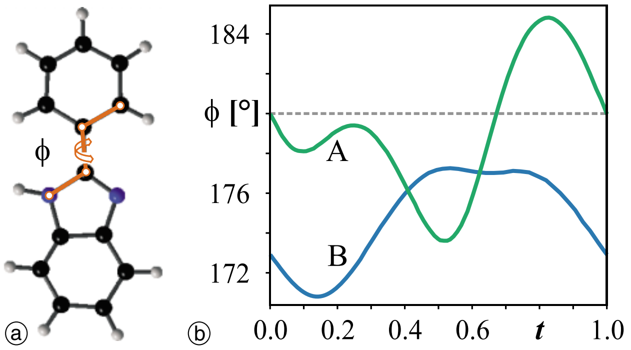

Fig. 7. (**a**) The molecular structure of 2-phenylbenzimidazole, consisting of a planar phenyl ring (top) and a planar benzimidazole group (bottom). (**b**) *t*-Plot of the torsion angle between the two planar moieties as indicated in (a) for molecule A (green) with an amplitude of ±5° and molecule B (blue) with an amplitude of ±3° (redrawn from [66]). The broken grey line indicates the value $\phi = 180°$ corresponding to a flat molecule.

3.2 Modulated molecules

In the crystal structure the molecules are coupled by intermolecular forces, they interact with their neighbours *via* van der Waals and hydrogen bonds. Their molecular conformations are defined by intramolecular forces. As shown in the previous section, this can cause some conflict. Generally, the mutual frustrations of conflicting intramolecular and intermolecular forces are believed to be one possible reason for the modulation of the crystal structures of molecular compounds [67, 68]. As seen in the above mentioned "historical" examples of the 4:4′-dinitrodiphenyl complexes [35, 36] and in the urea inclusion compounds [37], also a conflict in the packing of the molecules due to "non-compatible" sizes of the involved molecules can result in a modulation of the crystal structure. Depending on the rigidity of the molecules then also the molecular conformation might be modulated. In case of a structural flexibility of the molecules, the frustrations caused by the packing might be compensated by modulating the molecular conformation.

Intramolecular forces are the covalent bonds between the atoms, defining interatomic distances and angles and therefore the geometry of molecular units in the molecule, *e.g.* the regular shape of a flat phenyl ring with equal distances between the six carbon atoms and angles of about 120°. In this respect the intramolecular forces are creating some kind of rigid bodies. Intermolecular forces are mainly van der Waals and hydrogen bonds. They determine the packing of the molecules in the crystal structure, *i.e.* the spacial arrangement and therefore also the conformation of the single molecules. Assuming now a molecule built up by several rigid molecular units, the intermolecular forces stabilize the arrangement of these units with respect to each other. This was already seen in the example of biphenyl (Section 2.1): the two planar phenyl rings were treated as rigid-bodies, while the orientation between them had some degree of freedom, represented by the torsion angle ϕ along the central C—C bond connecting these two rigid-units.

In the late 1980's a small series of papers was published by Petricek, Gao, Coppens and others, treating the formalism and theory behind the *structure analysis of modulated molecular crystals*. In those papers the authors introduced the "rigid-body refinement" for the translational and rotational modulation of molecules or some parts of it. This series of papers shall be shortly discussed here.

In some first publications [64, 69] the "rigid-body approach" known from the treatment of thermal motion [70] was extended and applied to the displacive modulation of molecular crystal structures assuming a molecule or a part of it to be displaced as a rigid-unit. It is argued, that due to stiffness of the intramolecular linkages between the atoms – for example due to covalent bonds – translational and rotational displacement does not affect only individual atoms but the complete molecule or at least some of its segments. As reference for the phase of the molecular displacement the molecule's centre of mass is proposed, allowing the refinement of different displacements for different molecules. As all other parameters like fractional coordinates or anisotropic ADPs are freely refined, the geometry of each molecule can be – despite the rigid-body displacement – fully adjusted.

In a second publication this rigid-molecule model was applied in a re-investigation of thiourea, $SC(NH_2)_2$ [49]. In thiourea three types of $N—H\cdots S$ contacts do exist, which are classified as hydrogen bonds. Interesting is the fact, that a variation of these contacts as function of the phase of the modulation t is reported. The shortest of these hydrogen bonds shows only a small variation and was therefore identified as the main force for restraining the translational and rotational displacements of the molecule (for more details see the discussion on the "historical" examples above). Another publication in this series presents then an investigation on the lattice energy of the modulated phase of thiourea [71], confirming the first results and concluding, that the extensive hydrogen-bonding network in the crystal has to be considered as driving force for the modulation. The modulated phase being the intermediate phase between the paraelectric and the ferroelectric phase is now understood as a gradual transition from the first to the latter.

The next publications in this series [72, 73] are dedicated to theoretical considerations on scattering and superspace groups, extending the formalism to the general $(3 + d)$-dimensional case ($d \geq 1$) and on symmetry restrictions applied to the amplitudes of the modulation functions for the case, that the atoms or rigid-bodies are located at special positions in the modulated crystal structure. As a direct application for the case $d \geq 1$ the modulated structure of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) in five-dimensional space is discussed [74]. Also here the molecules have been assumed to behave as rigid-bodies. This assumption was then confirmed during the structure refinement process.

The approach of dividing a larger non-rigid molecule into several rigid-units and to refine a common modulation for all atoms in such group has the advantage of reducing the number of parameters to be refined and of course also of keeping a certain geometry of the molecule. This might help in the case of a limited number of reflections (especially only a small number of observed satellite reflections) or when the data quality is not as high as prefered. In the rigid-body approach the fractional coordinates and anisotropic ADPs of the atoms can be refined individually or can be also treated as "molecular parameters".

3.2.1 Yet another example

This idea of describing the molecule *via* several rigid segments was applied to the modulated crystal structure of (6*R*,7a*S*)-6-(*tert*-butyl-dimethylsilanyloxy)-1-hydroxy-2-phenyl-5,6,7,7a-tetrahydropyrrolizin-3-one, $C_{19}H_{27}NO_3Si$ [12], reducing the number of refined parameters from 1396 for the individual refinement of the atomic modulation functions for all non-H atoms to 775 for the refinement of modulation functions of several molecular segments *via* rigid-bodies. The molecule and the definition of the rigid segments is introduced in Fig. 8. However, this refinement did not converge properly due to some correlations between molecular parameters. As in this special case the quality of the data was high and a sufficient large number of observed satellite reflections (up to fourth order) was present in the data set, in the final step all atoms were treated individually also for the modulation functions, but still keeping a very high data-to-parameter ratio. Therefore this crystal structure can nicely serve as a test example to verify the validity of the rigid-body approach. Both models with individual atoms and rigid units gave agreement parameters in the same order of magnitude [12]. The ones for individual atoms are slightly lower, but also the number of parameters is clearly larger.

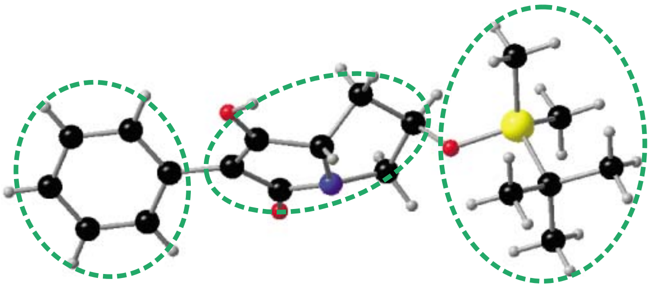

Fig. 8. The molecular structure of (6*R*,7a*S*)-6-(*tert*-butyl-dimethylsilanyloxy)-1-hydroxy-2-phenyl-5,6,7,7a-tetrahydropyrrolizin-3-one, $C_{19}H_{27}NO_3Si$ [12]. The molecule can be divided into the three rigid units phenyl ring (left), pyrrolizinone moiety (middle) and *tert*-butyl-dimethylsilanyloxy group (right).

As indicated by the diffraction pattern, the structure at $T = 100$ K is incommensurately modulated. The superspace group is $P2_1(\sigma_1 0 \sigma_3)\,\bar{1}$ (monoclinic, ***b***-unique) and the components of the modulation wave vector $\boldsymbol{q}$ are $\sigma_1 = 0.1422(2)$ and $\sigma_3 = 0.3839(8)$ [12]. The modulation wave vector runs perpendicular to the monoclinic axis, therefore the 2_1-screw axis is associated with a phase inversion of the modulation wave. It was noticed, that the intensities of the first-order satellite reflections are of the same order of magnitude as the intensities of the main reflections. Furthermore, satellite reflections up to fourth order can be observed. Both features indicate a very strong modulation in the structure suggesting displacive atomic modulation functions with large amplitudes together with a significant modulation of the anisotropic ADPs.

To describe the modulation, in the final model continuous atomic modulation functions for displacive modulation (with higher harmonics up to fourth order) and modulation of the anisotropic ADPs (with higher harmonics up to second order) are applied to all non-hydrogen atoms. The hydrogen atoms are coupled *via* a riding model to their corresponding carbon atoms. As an example demonstrating the strong modulation, Fourier maps in superspace are presented for the Si atom in Fig. 9.

To analyse the structure, the molecule can be divided into several units, as was shown in Fig. 8. Those units can be interpreted as rigid bodies, because the interatomic distances and angles in those molecular parts are not affected by modulation. As an example in Fig. 10a the bond lengths d and angles ϑ around the Si atom in the *tert*-butyl-dimethylsilanyloxy unit are shown. As can be seen, the deviation from the average value of the bond lengths as function of the phase of the modulation t is smaller

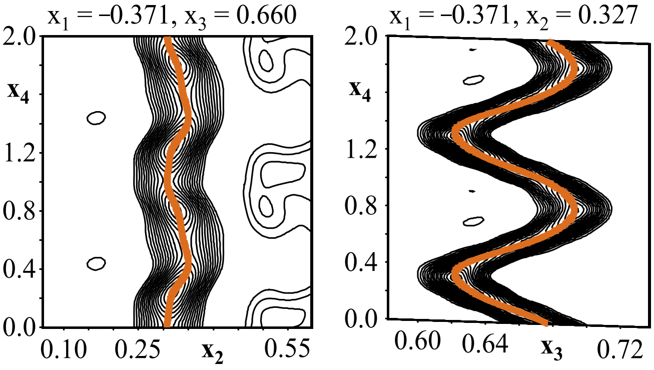

Fig. 9. The atomic modulation functions of the Si atom (orange lines) superposed on the electron density for the two sections (x_2, x_4) and (x_3, x_4) of (3 + 1)-dimensional superspace (for sake of clarity two periods are drawn along x_4). The horizontal width of each section corresponds to 3.5 Å, showing the different amplitudes of the atomic modulation funcions along the different directions in physical space (x_2 and x_3, respectively) and especially the large amplitude of the AMF along x_3 of about ±0.9 Å (redrawn from [12]).

than $\Delta d = \pm 0.045$ Å, the deviation of the angles smaller than $\Delta\vartheta = \pm 0.7°$, even though the amplitude for the displacement of the Si atom along x_3 is of about ±0.9 Å (see also Table 3 in [12]).

The five-membered ring of the pyrrolizinone moiety linked to the *tert*-butyl-dimethylsilanyloxy group shows an envelope structure, which also is supporting the rigid body approach. It can be seen that the one carbon atom is on average $d_{\text{ave}} = 0.625(1)$ Å out of the plane defined by the other four atoms, and that this distance is only slightly affected by the modulation (Fig. 10b). The maximum deviation from this average value is $\Delta d = \pm 0.03$ Å with the minimum absolute value $d_{\min} = 0.594$ Å and the maximum absolute value $d_{\max} = 0.651$ Å.

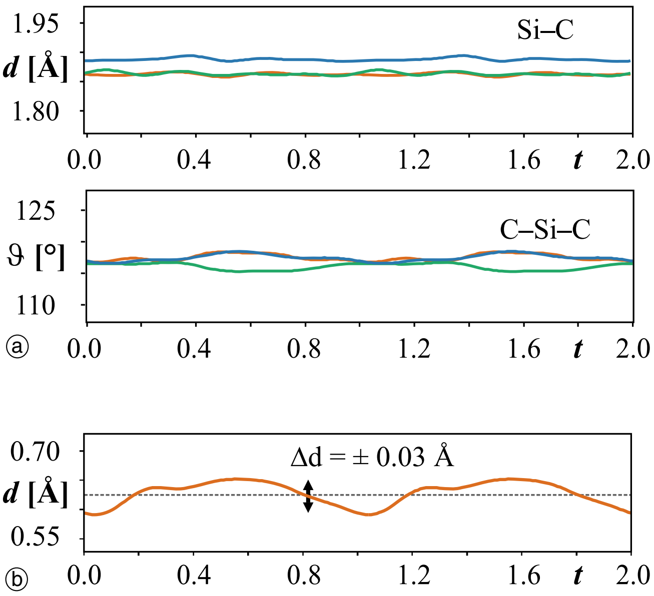

Fig. 10. *t*-Plots to support the assumption of rigid bodies. As can be seen, the displayed parameters are only slightly affected by the modulation (for sake of clarity two periods are drawn along the phase of the modulation *t*). (**a**) *t*-Plots of selected interatomic distances and angles around the atom Si atom in the *tert*-butyl-dimethylsilanyloxy unit. (**b**) *t*-Plot of the distance *d* of the carbon atom out of the plane defined by the other four atoms to demonstrate also the rigidity of the envelope structure in the non-planar pyrrolizinone moiety.

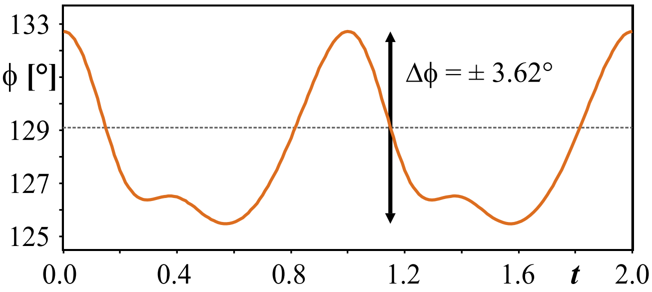

Fig. 11. *t*-Plot of a dihedral angle between the *tert*-butyl-dimethylsilanyloxy group and the pyrrolizinone moiety showing the modulation of the molecular conformation as function of the phase of the modulation *t* (for sake of clarity two periods are drawn along *t*).

The modulation therefore mainly affects the orientation – expressed by dihedral angles – between the three rigid segments, changing the conformation of the molecule as a whole, but not of the molecular units themselves. As example the *t*-plot of a dihedral angle between the *tert*-butyl-dimethylsilanyloxy group and the pyrrolizinone moiety is shown in Fig. 11. The deviation of the dihedral angle is larger than $\Delta\phi = \pm 3.6°$ (see also Table 4 and Fig. 21 in [12]).

3.3 Superstructures

The higher-dimensional superspace approach can also be applied to commensurately modulated structures [75, 76]. The only condition to do so is to devide the data set of measured reflections into a subset of main reflections and a subset of superstructure reflections [21]. The latter ones are the satellite reflections.

Therefore, a *n*-fold superstructure (*n* being a small integer number), can be described by the two different models: First, by the classical three-dimensional superstructure with several independent formula units in the asymmetric unit; the diffracted intensities are all treated in the same way, indexed by three integers *hkl*. Second, by a commensurately modulated structure in (3 + 1)-dimensional superspace with one formula unit per asymmetric unit; the diffracted intensities are classified into main reflections and satellite reflections, indexed by four integers *hklm*. This discrimination of reflections can be justified by the fact, that the superstructure reflections are – in general – somehow weaker in intensity then the main reflections of the underlying basic structure.

Both models describe the structure with the same efficiency: the same number of parameters has to be refined, the statistical results are of the same order of magnitude (as they are supposed to be – it is the same structure described with two different models) [77]. In the first model several independent molecules have to be described, each one with its own fractional coordinates and anisotropic ADPs for the individual atoms. In the second model, one molecule exists in the asymmetric unit to which a modulation is superposed. The intermolecular atomic distances, angles, dihedral and torsion angles of both models are consistent. Depending on the structure under investigation, the model described in superspace might need less parameters than the superstructure in three-dimensional space

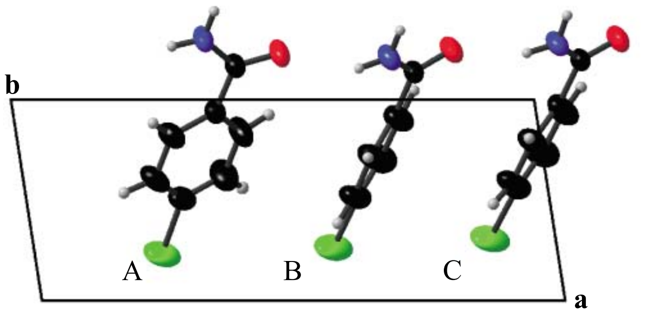

Fig. 12. The three molecules A, B and C in the asymmetric unit of the threefold superstructure of *p*-chlorobenzamide at room temperature, viewed along the crystallographic ***c***-axis.

[76]. This is due to the fact, that the superspace model can profit from some hidden intrinsic symmetry in the structure.

A first example is the room temperature structure of *p*-chlorobenzamide, C_7H_6ClNO [78]. It is a non-planar non-rigid mono-molecular organic compound, which is commensurately modulated. The structure was described in a classical approach as a threefold superstructure (Fig. 12), but it can also be understood as a commensurately modulated crystal structure described in $(3+1)$-dimensional superspace. The three molecules show not only a different orientation with respect to the lattice, but also different torsion angles between the plane defined by the phenyl ring and the one defined by the amide group: $\phi_A = 19.0(2)^\circ$, $\phi_B = 33.9(2)^\circ$, $\phi_C = 28.6(2)^\circ$ (the average value is $\phi_{ave} = 27.2^\circ$). The diffraction pattern is characterized by a clear difference in intensity between main reflections and satellite reflections [78]. The $(3+1)$-dimensional superspace symmetry is $P\bar{1}(\sigma_1\sigma_2\sigma_3)\,\bar{1}$ with the commensurate modulation wave vector $\boldsymbol{q} = (^1/_3, 0, 0)$, *i.e.* all three components can be expressed by rational numbers. The space group of the threefold superstructure is $P\bar{1}$. The structure undergoes a phase transition at high temperature. During the phase transition the superstructure or satellite reflections vanish in the diffraction pattern. The resulting non-modulated high temperature phase has one molecule in the asymmetric unit ($\phi = 27.3(3)^\circ$) in space group symmetry $P\bar{1}$ [78]. The high temperature structure resembles the basic structure of the modulated model at room temperature. The phase transition can therefore be understood as a loss of the modulation at high temperature. The description in superspace has the clear advantage, that a unique relation can be established between the (modulated) room temperature phase and the (non-modulated) high-temperature phase. The same structural model serves as reference structure for the commensurately modulated phase at room-temperature and as structural model for the high-temperature phase [78]. This means, that the superspace approach delivers a unique image for the phase relation between both phases.

Another example for a commensurately modulated structure described within the higher-dimensional superspace approach is the low-temperature ζ-phase of bis(propylammonium) tetrachloromanganate(II), $[NH_3(C_3H_7)]_2MnCl_4$ [79]. It is explicitly stated by the authors, that it would have been possible to describe the structure with a conventional superstructure. But as the satellite reflections are rather weak, this could have caused some problems during refinement of that superstructure. Also in this case the description in superspace allows to better compare the ζ-phase with the neighbouring ε-phase, stable at higher temperature. This ϵ-phase is an incommensurately modulated phase [80]. The modulation in this structure is caused by a hindered freezing of the dynamical disorder of the propylammonium ions caused by an interlayer of terminal methyl groups and by an ordering of the associated hydrogen bonds.

3.3.1 Structures with large Z'

A lot of crystal structures are built up by more than one independent molecule (or formula unit) in the asymmetric unit. An investigation by Brock in 1996 through the structures stored in the *Cambridge Structural Database* [81] resulted in about 8% of all entries to present compounds with two or more such molecules [54]. It was assumed, that this result is biased down due to the fact that such structures are difficult to solve and difficult to refine and that this number of 8% is supposed to be somewhat larger. The parameter specifying the number of molecules in the assymetric unit is called Z' [54]. It can be calculated by the number of formula units in the unit cell Z divided by the number of independent general positions. It is worth mentioning, that in general bond lengths and angles of the independent molecules are quite similar and that the molecules are somehow related to each other *via pseudo*-symmetry. The molecules differ by small but significant deviations from each other.

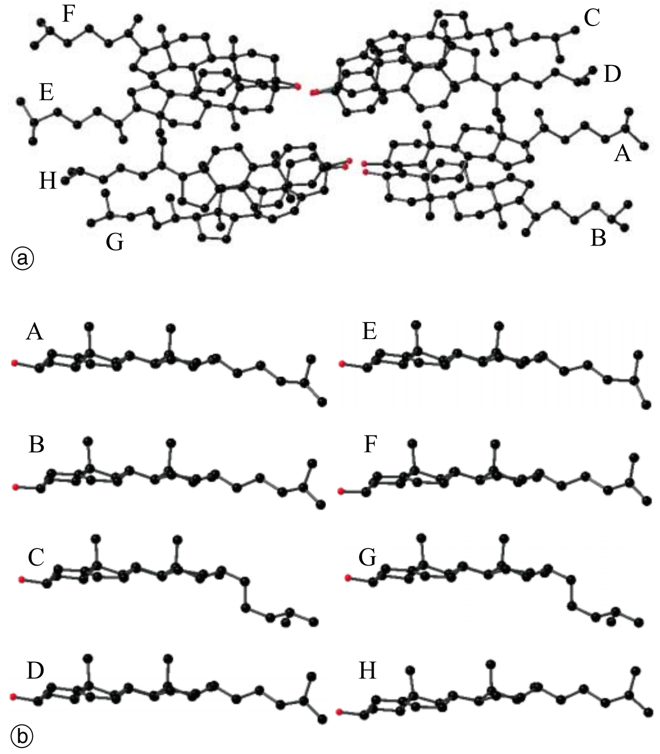

Fig. 13. The eight crystallographically independent molecules in the room temperature phase of cholesterol (without hydrogen atoms). In (**a**) the asymmetric unit is shown along the crystallographic ***c***-axis, in (**b**) the molecules are displayed parallel to their mean plane. The molecular pairs which are *pseudo*symmetrically related by a 2_1-screw axis are A–E, B–F, C–G and D–H (redrawn from [82]).

The structure of cholesterol serves as example with $Z' = 8$ for the room-temperature phase [82]. A twofold rotational *pseudo*symmetry along the crystallographic $\boldsymbol{c}$-axis was reported. In Fig. 13 the eight independent molecules are shown. The high-temperature phase at $T = 310$ K has even a double amount of independent molecules in the asymmetric unit, *i.e.* $Z' = 16$. Also in this phase the molecules are related to each other *via* non-crystallographic *pseudo*-screw axes [83].

The interactions between the independent molecules are important for the understanding of the crystal packing of the Z' structures in special, but also for the understanding of order and packing in solid state matter in general [84]. The origin of the large Z' structures in alcohols and steroids was seen in the "*conflicting driving force towards achieving saturated hydrogen bonding of the hydroxyl functionalities on the one hand and close van der Waals packing of the large lipophilic substituent on the other*" [84]. And again, "*This complexity and pseudosymmetry was rationalised as resulting from the fact that the steric demands of the steroid portion of the molecule are quite different from the optimal arrangement of ionic or hydrogen bonding moieties yet both must be simultaneously accommodated*" [84].

All this resembles somehow to the situation which is also present in modulated crystal structures and there might be a good chance to describe (and perhaps to better understand?) those structures with large Z' as commensurately (or incommensurately) modulated structures while applying the higher-dimensional superspace approach. In such case it might be necessary to chose the modulation wave vector $\boldsymbol{q}$ not along one of the crystallographic axes (to generate a simple superstructure) but maybe, depending on the structure under investigation, in a diagonal way. An example (the pharmaceutical compound already discussed at the end of Section 3.2 in the context of rigid-body refinement) is discussed in detail in [12] with 35 independent molecules, the modulation wave vector $\boldsymbol{q}$ in the superspace model lying in the $(\boldsymbol{a}^*, \boldsymbol{c}^*)$ plane with $\boldsymbol{q} = (0.143, 0, 0.384)$.

The $[M(H_2O)_2(\text{15-crown-5})](NO_3)_2$ complexes with $M =$ Mg, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pd, are a good example for structures with large Z' and strong hydrogen bonds. Intensive investigations have been performed by Brock and coworkers in this family of compounds including structures with large Z', polymorphism, disorder and modulation [85–89]. Some attempts to understand and describe several of those structures as (commensurately modulated) superstructures are presented.

A model to describe the structure of $[Cu(H_2O)_2(\text{15-crown-5})](NO_3)_2$ with $Z' = 10$ in $(3+1)$-dimensional superspace is proposed in [90]. For the $Z' = 10$ superstructure in space group Pn the crown complexes are ordered but present two different orientations. They reveal a staircase like periodic pattern in the $(\boldsymbol{a}, \boldsymbol{c})$-plane: along the $\boldsymbol{a}$-axis the two orientations alternate and along the direction $-3\boldsymbol{a} + 2\boldsymbol{c}$ the two orientations form a 10 molecules "periodic unit" with five consecutive crowns in one and the following five in the other orientation. By treating the weaker superstructure reflections as satellite reflections, the structure can be described in the superspace approach as a commensurately modulated structure. The closest strong superstructure reflections next to the mains reflection have been defined as first order satellites. Hence the modulation vector is $\boldsymbol{q} = (^1\!/_2, 0, -^2\!/_5)$. As superpspace group the non–centrosymmetric $Pc(\sigma_1 0 \sigma_3)\,s$ was applied.

3.3.2 Commensurate *vs.* incommensurate

A first hint, if a structure has to be treated as a commensurately modulated or as an incommensurately modulated structure, is given in the diffraction pattern by the peak positions of the satellite reflections. As explained in Section 2.2 in Eq. (3), those positions are described with respect to the reciprocal lattice $\Lambda^* = \{\boldsymbol{a}^*, \boldsymbol{b}^*, \boldsymbol{c}^*\}$ by the components of the modulation wave vector $\boldsymbol{q} = (\sigma_1, \sigma_2, \sigma_3)$. If at least one of the components has a value, which can not be expressed by the ratio of two small integer numbers, then the structure is incommensurately modulated (and does not show three-dimensional periodicity). On the other hand, also variation of at least one of the components $\sigma_1, \sigma_2, \sigma_3$ with temperature, pressure or another external parameter is a clear sign for incommensurability (even though at a certain temperature, for example, then this value might be rational).

It was shown above in this section, that commensurately modulated structures can be described either as a three-dimensional superstructure or within the higher-dimensional superspace approach. The other way around also incommensurately modulated structures can be described not only within the higher-dimensional superspace approach, but also by applying the superstructure approach, while approximating the irrational component of the modulation wave vector $\boldsymbol{q}$ by a rational number. As larger the superstructure, as better the approximation. It was, however, already stated by de Wolff in the early days of modulated structures [6], that the resulting space groups of the approximated superstructure might lack symmetry relations, which are present in the higher-dimensional superspace groups. Such description then do not adequately account for the true nature of the modulated structure. Some indication to this might be given in the diffraction pattern, when the superspace group can explain systematic absences of reflections, which might not be possible with the three-dimensional space group of the (approximated) superstructure [21]. In addition, to choose a rational approximation can be rather ambiguous, too. Might *e.g.* the irrational number $f = 0.1832\ldots$ be better described by the rational approximation $a = ^1\!/_5 = 0.2$ or better by $b = ^1\!/_6 = 0.166\bar{6}$? The first one will give a five-fold, the latter one a six-fold superstructure. A better choice (closer approximation) for this example is the rational number $c = ^2\!/_{11} = 0.0.1\overline{18}$ in an 11-fold superstructure (but from a practical point of view, is an 11-fold superstructure still feasable in the crystal structure refinement process with respect to number of parameters and with respect to *CPU* time?). And what is the effect for the resulting five-, six- or 11-fold superstructure approximation, which do represent three different models for just one and the same structure under investigation? A simple model is given in Fig. 14, showing, that the three models result in different orientations of the molecules. It can be

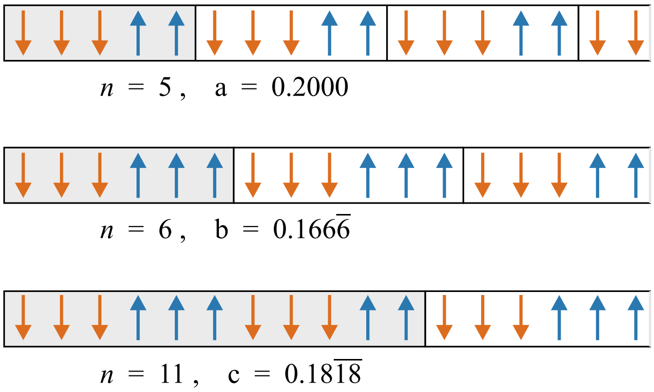

Fig. 14. Schematic drawing on three simple superstructure approximations while describing the irrational number $f = 0.1832\ldots$ by the rational approximation $a = {}^1\!/_5$, $b = {}^1\!/_6$ and $c = {}^2\!/_{11}$. Those approximations result in n-fold superstructures with $n = 5, 6$ and 11, respectively. The arrows represent one molecule in two different orientations or conformations (orange down and blue up). Please note, that the three models are significantly different while they shall describe the same aperiodic crystal structure under investigation.

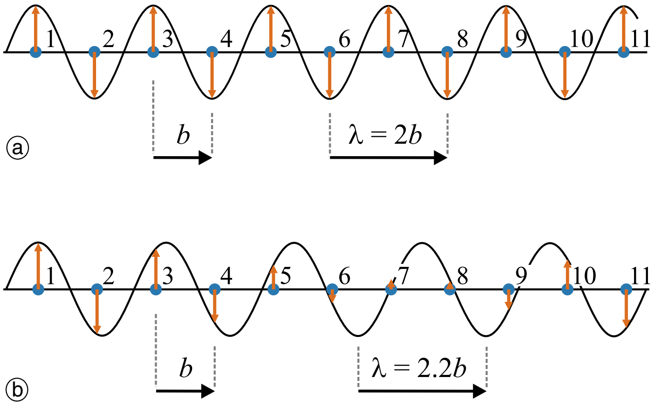

Fig. 15. Schematic drawing representing the problem of a superstructure approximation. The sinusoidal wave represents the modulation of the torsion angles, the blue circles the molecular positions along ***b*** and the orange arrows the corresponding magnitude and direction of their torsion angles ϕ. In (**a**) the approximation is shown, with the (commensurate) wavelength of the modulation wave vector being $\lambda = 2b$. As result all molecules have equal, *i.e.* maximum magnitudes of their torsion angles. In (**b**) the true (incommensurate) wavelength $\lambda = 2.2b$ is applied, and the magnitude of the torsion angles varies throughout the whole crystal (redrawn from [61]).

seen immediately, that due to the different periodicities the resulting pattern of the orientations of the molecules differ significantly (but all three models are approximations to the same aperiodic structure under investigation). A deeper discussion on that is given in [91].

And how is the relation between superstructure approximation and the true incommensurately modulated structure? The incommensurately modulated low-temperature phase of biphenyl (Section 3.1) will serve again as example. The structure below $T = 20$ K was described in a twofold superstructure, *i.e.* the modulation wave vector component $\sigma_2 = 0.46$ as can be found in the diffraction pattern was approximated to the rational value $\sigma_2 = {}^1\!/_2$ [60]. As consequence, in this case the wavelength λ of the modulation wave was shortened from $\lambda = |\frac{1}{\sigma_2 b^*}| = \frac{1}{0.46b^*} \approx 2.2b$ to $\lambda = |\frac{1}{0.50b^*}| = 2b$. By doing so, a twofold superstructure approximation with unit cell $\boldsymbol{a} \times 2\boldsymbol{b} \times \boldsymbol{c}$ with respect to the unit cell at room temperature is generated. Main characteristic of this superstructure approximation is the torsion of the molecule with the torsion angle between the planes of the phenyl rings $\phi = 10.2°$. Neighbouring molecules along ***b*** show an opposite sense for the torsion, while neighbouring molecules along ***a*** and ***c*** have the same sense of torsion. Also in the superstructure this torsion of the molecule results in a loss of the inversion symmetry of the molecular structure and of the crystal structure. The resulting space group of the superstructure is *Pa* [60]. The structure refinement of the superstructure however suffered by the fact, that different scale factors had to be applied for the main and for the satellite reflections.

This approximation has as direct consequence that all molecules show a "complete distortion" with a torsion angle of $\phi = \pm 10.2°$ (for neighbouring molecules along ***b*** in opposite directions). The values of this torsion angle ϕ is schematically illustrated in Fig. 15a as the amplitude of a sinusoidal function with wavelength $\lambda = 2b$. The maxima (and minima) of this function superpose with the molecular positions. In contrast in the incommensurately modulated structure the wavelength of the sinusoidal function has the proper value $\lambda = 2.2b$, the maxima and minima are shifted away from the molecular positions (Fig. 15b). As consequence, a large number of molecules are almost undistorted [61], *i.e.* the molecules are more or less planar ($\phi = 0°$). It can be seen in Fig. 15, that in a short range, *i.e.* for the molecules $1, 2, 3$ the superstucture approximation can reproduce the molecular conformation in a decent way. But this does not work in a long range, the superstructure approximation fails completely to reproduce the torsion angles of the molecules $6, 7, 8$ and for the molecules $9, 10$ it even predicts torsion angles with opposite directions.

A better approach, but still an approximation are the models discussed by Dzyabchenko [67], describing the modulated structure of biphenyl at low temperature with a 13-fold and 14-fold superstructure, respectively, approximating the incommensurate component of the modulation wave vector with $\sigma_2 = {}^6\!/_{13} = 0.4615$ and $\sigma_2 = {}^6\!/_{14} = 0.4286$.

The superstructure approximation for an incommensurately modulated structure can give a first glance on the structure and can serve as a starting model to understand the crystal packing and establish some rough ideas on molecular interactions. But – as it is only an approximation, which superposes a periodicity on an aperiodic structure – it is not reflecting the true nature of the crystal structure. It can not account for the structural flexibility of the molecular conformation.

3.4 Macromolecular compounds and "bio-crystals"

It was shown up to now, that an aperiodic crystal structure is not limited to inorganic compounds and metals but also takes place in structures composed by small molecules – and perhaps the modulation of a molecular crystal structure occures more often then generally expected.

It is worth mentioning that there are also reports on superstructures and weak additional reflections in the diffraction pattern of protein crystal structures. Some of them shall be briefly discussed here as kind of representative examples:

Aschaffenburg *et al.* [92] observed in the precession photographs of goat α-lactalbumin additional sharp reflections along the crystallographic $\boldsymbol{a}^*$-direction, appearing in pairs and being equidistant from the main reflections. The authors "eliminated" those reflections by soaking the crystals in 1 mM-potassium chloroplatinite.

Gouaux and Lipscomb observed in the diffraction pattern of native aspartate carbamoyltransferase (EC 2.1.3.2, from *Escherichia coli*) ligated with l-aspartate and phosphate clearly visible but weak superlattice reflections [93]. These superlattice reflections have been interpreted by the authors to arise maybe from some periodic perturbation of the molecular conformation or packing.

A (commensurately modulated) twofold superstructure along the crystallographic $\boldsymbol{c}$-axis was reported for the F_{420}-dependent methylenetetrahydromethanopterin dehydrogenase by Warkentin *et al.* [94]. In this structure the translational symmetry is broken by small reorientations of the hexameric structural units, while the reorientations are related to the crystal packing. It was reported that the additional superstructure reflections do account for roughly 14% of the overall diffraction intensity.

Lovelace, Borgstahl and coworkers reinvestigated an incommensurately modulated structure of a bovine profilin: β-actin complex from calf thymus [95–97]. This modulated structure was dicovered by Schutt *et al.* [98] and shows an extensive intermolecular network with satellite reflection in the diffraction pattern and a superstructure with *pseudo*symmetry. The modulation occurs along the crystallographic $\boldsymbol{b}$-axis, which corresponds to an 'actin ribbon' formed by the crystal lattice. For the origin of the modulation it was assumed, that the protein is undergoing a conformational change affecting the neighbouring molecules [96]. The intensities of the satellite reflection are about 15 × weaker then those of the main reflections.

4. Conclusions and outlook

The crystal-chemical analysis of incommensurately modulated crystal structures can be performed in an elegant way applying the higher-dimensional superspace approach. This approach allows the recovery of higher-dimensional translational symmetry, *i.e.* periodicity, which is lost in the three-dimensional aperiodic crystal structure. The superspace approach has been extensively used during the last three decades, is now well established and can be applied to all kinds of materials: inorganic matter, metals and alloys, organic and organometallic compounds with small molecular and macromolecular structures, or even magnetic structures.

Concerning modulated molecular compounds one has to respect some internal freedom in the molecules. The individual molecules might be built by several molecular segments, which act themselves as rigid-units. These rigid units have some possibility, some freedom to rotate or bend with respect to each other. Very important for a better understanding is also to analyse the intermolecular interactions as function of the phase of the modulation, like crystal packing and hydrogen bonding scheme, as both might strongly influence the molecular conformation. Applying the superspace formalism, an exact crystal-chemical analysis of the crystal structure as function of the phase of the modulation t is therefore possible.

The application of the superspace approach is, however, not limited to the analysis of aperiodic crystal structures. It can also be applied to the analysis of the relations between modulated and non-modulated structures and between incommensurately modulated structures and (commensurately modulated) superstructures. In many cases an incommensurately modulated structure transforms to a three-dimensional periodic high-symmetry phase on increasing temperature and/or to a commensurately modulated phase, the so-called lock-in phase, on decreasing temperature. The superspace approach represents the tool to describe this sequence of phases with one unique model, independent of the specific value of the modulation wave vector components being irrational or rational numbers, *i.e.* independent of the structure being incommensurately or commensurately modulated.

The structures with large Z' are promising candidates to be described within the higher-dimensional superspace approach. Some of those structures can be interpreted as (commensurately modulated) superstructures, and some might be incommensurately modulated. The superspace approach can help to clarify the relation between the molecules, their interactions and the general principles of crystal packing. And it also might help to clarify the relation between different modifications and different members of families of compounds with different stoichiometry.

As it is stated in [96], the general approach in protein crystallography is to discard a sample, when a modulated diffraction pattern, *i.e.* a diffraction pattern with strong main reflections and additional weak satellite reflections, is observed, and to go for another sample, which "*behaves better*". … The reason might be mainly seen in the lack of computer programs for data integration and reduction and also for structure solution and refinement – and in some lack of consciousness within the concerned community, too. But as those problems are already identified, the general situation will probably improve within the next years.

One can therefore conclude, that in general the application of the superspace approach to the description and crystal-chemical analysis of superstructures and of incommensurately modulated structures for molecular compounds will become more and more familiar to a larger community. This trend is supported by the technical development: Today diffractometers with two-dimensional detectors like CCD detectors and image plates are widespread available. With such detectors large data sets of high accuracy even for weak intensities can be measured in feasable time. Also computers and processors can handle now such large data sets with up to several tenthousand reflections without problems. And finally – and maybe most important – computer programs and software have been developed, which make it possible also for non-experts to apply the higher-dimensional superspace approach for treating the measured data and for interpreting the modulated structures under investigation in the crystal-chemical analysis. Today, within the higher-dimensional superspace approach a complete picture of the true nature of the compounds and an accurate structural model for aperiodic crystal structures can be established by everybody, who has to do so.

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