

Crystallography of Modulated Structures in Superspace

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Abstract: Since the discovery of X-ray diffraction, it was believed that the discrete distribution of diffracted intensities was a direct consequence of the periodic arrangement of atoms in the three dimensions of space. However, in the last thirty years many examples of new types of crystals have been found which do not fulfil this criterion but nevertheless give perfectly discrete diffraction patterns. The new category of crystals which exhibits this property is called aperiodic. It includes incommensurate crystals, quasicrystals and composite crystals. These structures are best described in superspace, an extension of the three-dimensional space up to six dimensions. Aperiodic structures can be interpreted as three-dimensional cuts of higher dimensional periodic objects. The description of an incommensurate structure in 3+1 dimensions along with the concept of symmetry in superspace is presented as an example.

Keywords: Aperiodic crystals · Incommensurate structures · Modulated structures · Superspace groups.

Introduction

The three-dimensional periodic arrangement of the atomic constituents (atoms, molecules, ions, ...) of crystalline phases was believed to be one of the most fundamental principle underlying the architecture of condensed matter. As a consequence of this characteristic periodicity, only a finite number of possible symmetric arrangements of the atomic building blocs are possible in three-dimensional space. The periodicity (translational symmetry) imposes, for example, limitations on the rotational symmetries: pentagonal and higher than hexagonal symmetries can never occur. The possible 230 types of arrangements are each characterised by their three-dimensional space group.

By means of X-ray, neutron or electron diffraction, the atomic structure, *i.e.* the spatial arrangement of the atoms, can

be elucidated by exploiting the diffracted intensities. In this process, one takes advantage of the particular conditions imposed on the diffraction pattern by the space group symmetry. For example the rotational symmetries can be observed in the diffraction patterns.

Another consequence of the three-dimensional periodicity is that the diffracted intensities, *i.e.* the *Bragg peaks*, can be expressed in terms of a linear combination of integer multiples of *three* independent vectors, the reciprocal basis vectors. On a macroscopic level, each face of a crystal can be uniquely characterized by *three* integers, the *Miller indices*. There exists an intricate relation between the Miller indices and the three integers associated with the diffracted intensities.

This concept of periodicity and symmetry represents a powerful tool for structural studies and is at the origin of the very successful investigations of crystals by optics and diffraction. Nevertheless some indications appeared questioning this paradigm of three-dimensional periodicity of crystals. One of the earliest examples was the attempt to assign Miller indices to the faces of the mineral calaverite $\text{Au}_{1-p}\text{Ag}_p\text{Te}_2$ ($p < 0.15$) [1]. Following a very careful study of more than 100 samples, the authors came to the conclusion that 'das Gesetz der rationalen Indizes [...] nicht ein allge-

meines Gesetz ist'. The law of rational indices expresses the fact that the Miller indices of each crystalline face are uniquely characterised by three small integers. Obviously, this general law was not applicable to calaverite. Later, the diffractogram of $\gamma\text{-Na}_2\text{CO}_3$ resisted every attempt to find combinations of three integers [2] to characterise each reflection. More recently, the discovery of quasicrystals [3] with diffraction patterns exhibiting pentagonal, octagonal, decagonal or dodecagonal symmetries (see [4]) also contributed to the serious questioning of the three-dimensional periodicity paradigm.

The few examples mentioned here are just a small selection among numerous other cases, which continue to inflate the list at a rapid pace.

In this article we would like to show the consequences of the departure from three-dimensional periodicity on the structure of condensed matter. In a first part, we shall present the generalised concept of periodicity which goes beyond three-dimensional space and the tools which have been developed recently in order to deal with it. In a second part, we shall illustrate this new concept with an example selected from organic compounds and finally, we shall deal with the consequences of this new development.

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Extension in Superspace

One of the common features of the examples described above is that the full set of reciprocal vectors can be described by integer multiples of more than three basis vectors. In mathematical terms, each reciprocal lattice vector \mathbf{H} can be expressed as

$$\mathbf{H} = \sum_{i=1}^n h_i \mathbf{a}_i^* = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^* + \dots + h_n \mathbf{a}_n^*$$

where n can vary up to six in the case of *icosahedral quasicrystals* and up to five for some *incommensurate* or other quasicrystal structures. For $n > 3$, the relation

$$\mathbf{a}_{3+d}^* = q_{d1} \mathbf{a}_1^* + q_{d2} \mathbf{a}_2^* + q_{d3} \mathbf{a}_3^*$$

must be satisfied with at least one irrational value of q_{ij} . By generalising the concept of space dimension, the vectors \mathbf{H} can be interpreted as reciprocal vectors in n dimensions. At this point, one could ask whether there exists a periodic structure in n dimensions ($n > 3$) which would transform according to the reciprocal space expressed by the vector \mathbf{H} . The extension of the space of this type of crystal structures in higher dimensions, the so-called *superspace*, has been extensively studied during the last three decades [5] and is currently under further development.

We shall illustrate the extension principle with the example shown in Fig. 1. The periodic structure described in higher dimensional space, *i.e.* the superspace is defined by the two basis vectors \mathbf{a}_{S1} and \mathbf{a}_{S4} . In each unit cell, an atom is expressed as a string, which is periodic along \mathbf{a}_{S4} . Although this structure is perfectly periodic in superspace, this is in general not the case in the one-dimensional cut (which represents our three-dimensional space) along the line defined by R . If this line is a rational cut of the two-dimensional periodic array, the resulting one-dimensional structure is periodic and is usually called a *superstructure*. If on the contrary this line is not a rational cut (as shown in the Figure) the resulting structure is non-periodic or *aperiodic*. The aim of this superspace approach, the extension of the three-dimensional space to $(3+d)$ -dimensional space, is to study the characteristics of aperiodic crystal structures derived from the three-dimensional cut of periodic pattern of up to six dimensions. One should note that the shape of the modulation function represented in Fig. 1 is arbitrary and must be

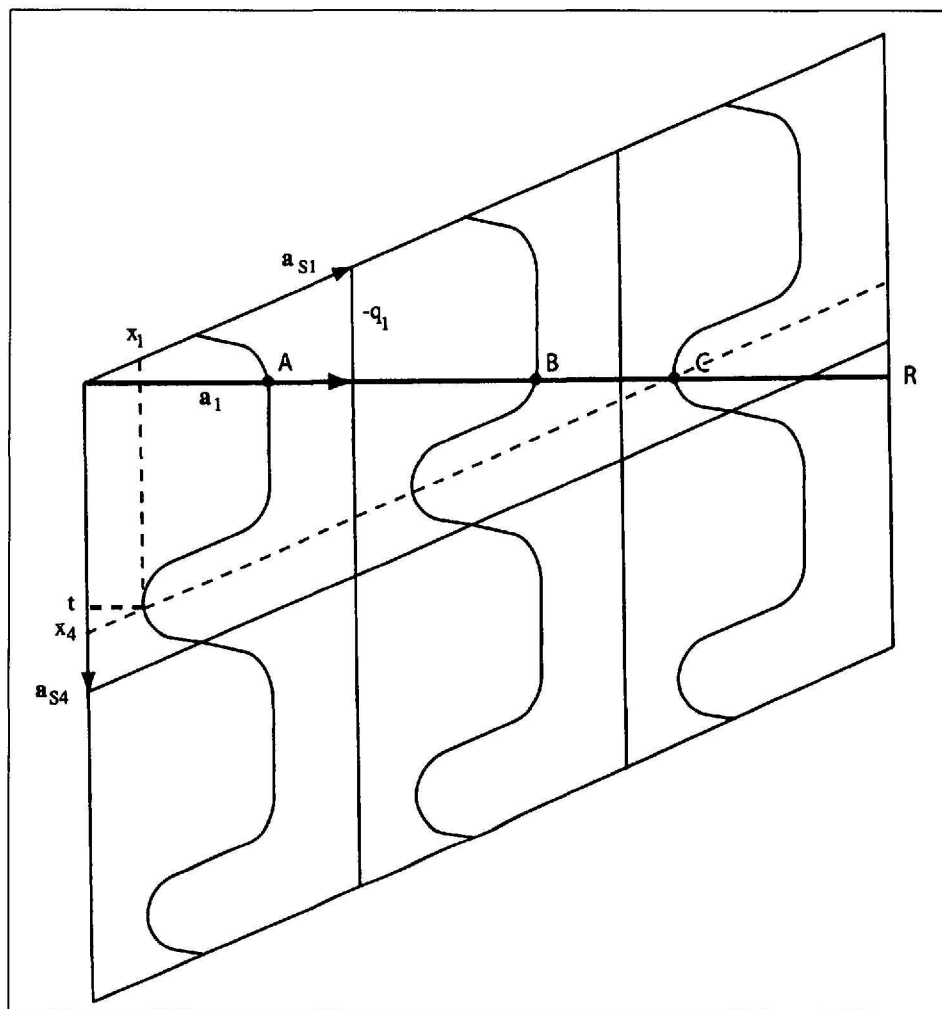


Fig. 1. Extension of a crystal structure in superspace. The atomic modulation function is periodic with the basis translation vectors \mathbf{a}_{S1} and \mathbf{a}_{S4} . The one-dimensional cut R indicated by the points A , B and C represents the real atomic structure. Along this line, the periodicity is lost, the distance between A and B is different than the distance between B and C .

determined experimentally for each structural parameter. This function must however be periodic along \mathbf{a}_{S4} . On the figure, the variable t is also defined and in some cases is more convenient to use instead of x_4 .

At this point one might wonder if the expression *aperiodic crystal* is not an oxymoron. This would at least be the case in the classical definition of a crystal. One of the main discoveries of the recent research of modern crystallography [6] is that (three-dimensional) periodicity is not a *sine qua non* condition for the existence of crystals. Their long-range order, which gives rise to the discrete diffraction pattern, can be realised not only by periodicity but also by other means of which the Penrose pattern [7] is just an example!

In classical crystallography, the concept of symmetry is so fundamental that any structure description is associated with its space group symmetry. The identification of its space group is a prerequisite for the solution of a crystal structure.

Fortunately, for aperiodic crystals also, the superspace formalism can take advantage of symmetry considerations. For the particular case of one- and two-dimensionally *modulated* structures, *i.e.* structures for which all the reciprocal space vectors can be described by four, respectively five integers, the full set of superspace groups has been tabulated [8]. Here also, the specific superspace group can be selected on the basis of selection rules characterized by systematic absences of the diffracted intensities. The resolution of the structure occurs in superspace. The main difficulties reside in the characterisation of the modulation curves as represented in Fig. 1 or more generally the *atomic surfaces* for each atom in the unit cell.

In order to illustrate some of the concepts presented above, we shall discuss one example of an organic compound, which exhibits the characteristics of a non-periodic crystal structure and identify the structural features which are at its origin.

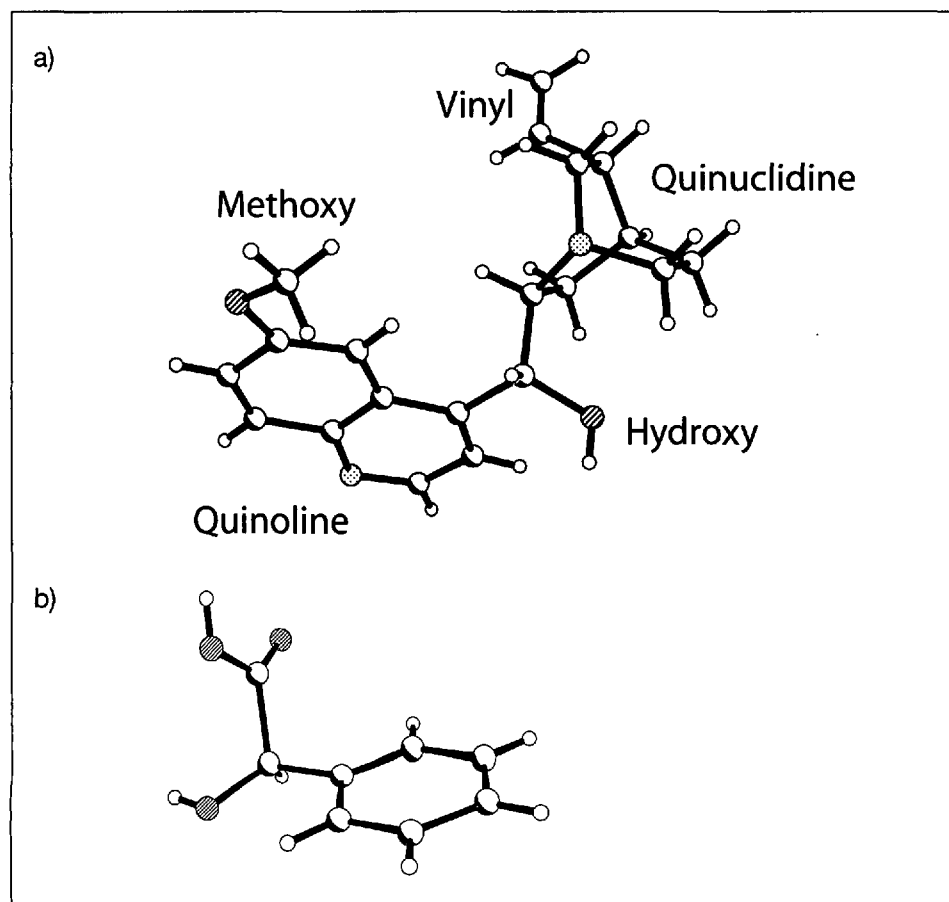


Fig. 2. The molecules of quinine, $C_{20}H_{24}N_2O_2$, (a) and mandelic acid, $C_8H_8O_3$, (b). Carbon atoms are indicated by shaded spheres, oxygen atoms by lines inside a circle and nitrogen atoms by dotted circles, the hydrogen atoms by small open circles.

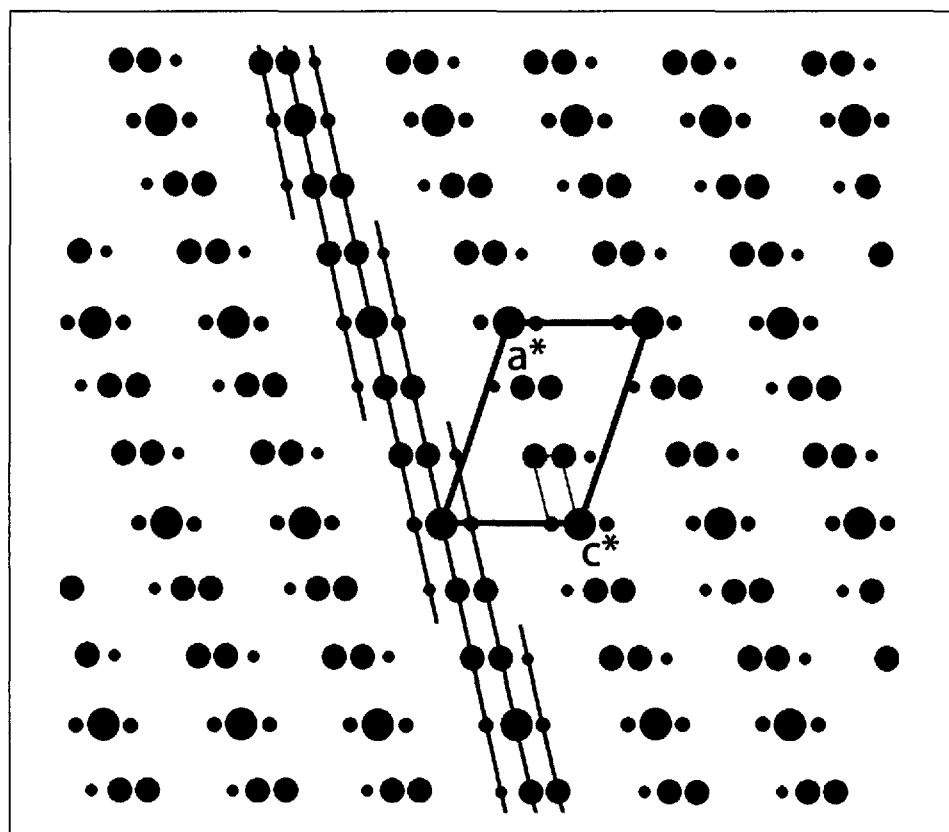


Fig. 3. Schematic view of the (a^* , c^*) reciprocal layer with main reflections (black dots) and satellite reflections up to 4th order (grey dots). The diagonal lines indicate the assignment of the satellite reflections to the corresponding main reflection. Also shown in this figure are the basic cell (defined by main reflections only) and a supercell approximation (defined by main and satellite reflections).

The Modulated Structure of Quininium (*R*)-Mandelate

In addition to the main reflections, the diffraction pattern of quininium (*R*)-mandelate, $C_{20}H_{25}N_2O_2^+ \cdot C_8H_7O_3^-$, exhibits a series of satellites of which many orders can be observed [9][10]. The molecules of quinine and mandelic acid are shown in Fig. 2, a schematic view of the diffraction pattern in Fig. 3. The main reflections can be indexed in a monoclinic cell with one formula unit per asymmetric unit: $a = 6.57 \text{ \AA}$, $b = 18.46 \text{ \AA}$, $c = 10.26 \text{ \AA}$ and $\beta = 107.23^\circ$. Setting the modulation vector $\mathbf{q} = 0.33\mathbf{a}^* - 0.27\mathbf{c}^*$, the complete set of reflections can be uniquely defined with the four integers $hklm$.

Without entering into the practical details of the resolution, the results of the refinement can be illustrated with two examples. Fig. 4 indicates the modulations associated with two specific atoms of the quininium ion, C(3) and C(15). The (x_2 , x_4) sections of the electron density illustrate the variety of the modulation curves which can result from the refinement in superspace (for a three dimensional periodic structure, this curve would be just a straight line). The shape of the modulation indicated in Fig. 4(a) is close to a step function whereas the modulation in Fig. 4(b) is very close to a zig-zag function. The modulation functions which are periodic along x_4 are obtained by adjusting a number of terms in the Fourier series. The maximal order of the terms is limited by the number of observations which can be measured. As an example, the variation of the torsion angle defining the position of the vinyl group is illustrated in Fig. 5. The shape of the function is very close to a step function with two positions differing by approximately 120° . One of the positions is adopted by 65% of the molecules whereas the other is adopted by the remaining 35%.

It is straightforward to transform the structural information from superspace to real space. From Fig. 1, the position of each individual atom in a specific cell can be derived in order to reconstruct the non periodic structure in three dimensions. Such an example is presented in Fig. 6 for a specific part of the structure, *i.e.* the vinyl group already mentioned in the previous figure. In this particular case, the modulation function refined in superspace translates into the presence of steps which breaks the three-dimensional periodicity of the structure. In the same structure, many other types of modulations can also be found as a result of the indi-

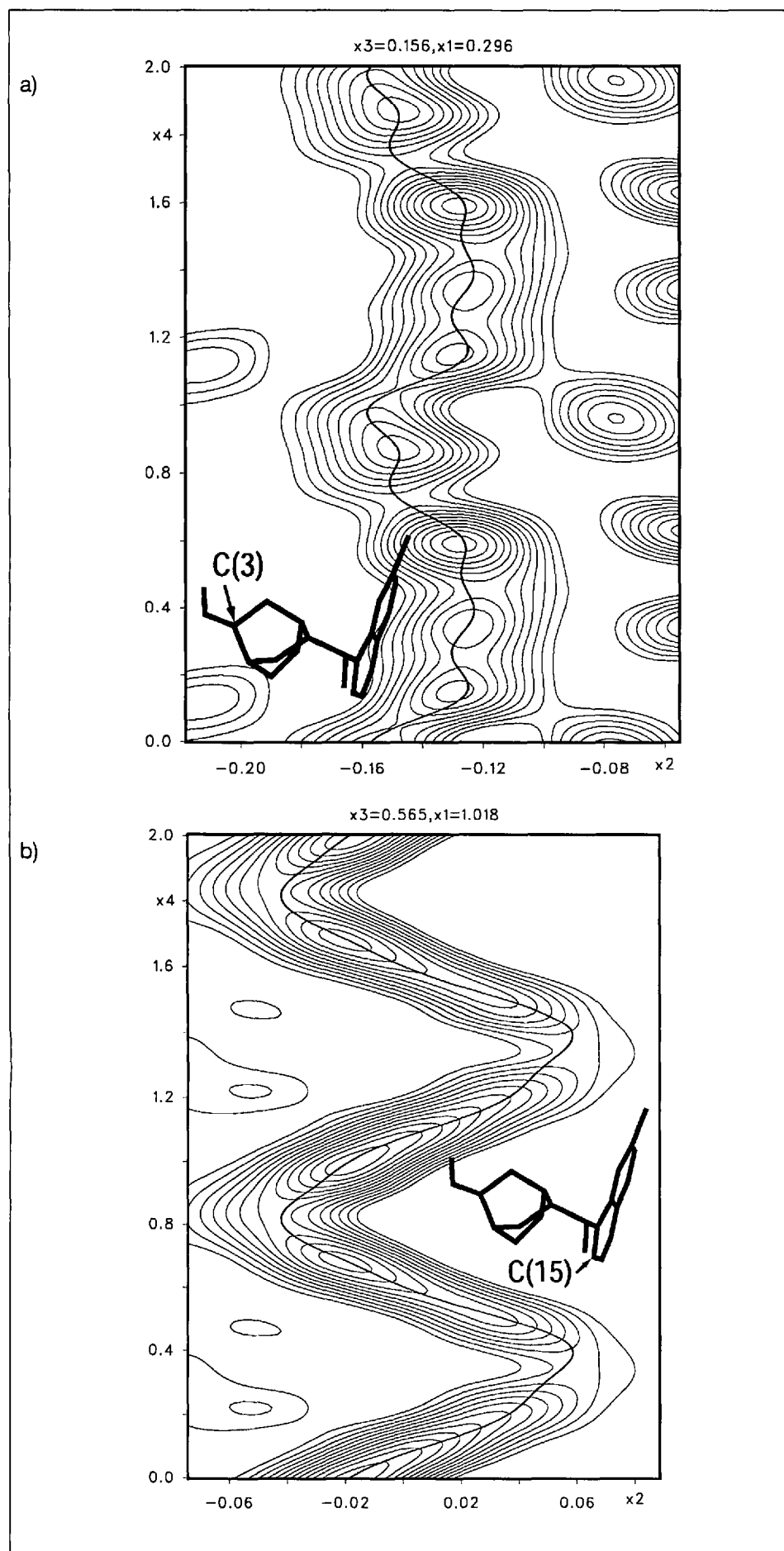


Fig. 4. Electron density distribution in the (a_{S2}, a_{S4}) plane illustrating the positional modulations (indicated by the continuous grey line) of the two carbon atoms C(3) (a) and C(15) (b). While the modulation of C(3) is close to a step function, the modulation of C(15) can be better described by a zigzag function.

vidual shapes of the modulation functions refined for each atomic parameter.

Do We Need Superspace?

At this point one may wonder if the conventional methods, *i.e.* solving the structure in a three-dimensional space group, could not yield the same results. For this purpose, a change of the unit cell is in order so that all peaks can be indexed by three integers. This new cell is represented by the small cell in Fig. 3. Setting $A^* = 0.33 \cdot a^* - 0.27 \cdot c^*$ and $B^* = b^*$, we very soon face the difficulty of selecting C^* . Two possible approximations can be used: $C^* = 1/5 \cdot c^*$ or $C^* = 1/6 \cdot c^*$. Independently of the choice, an error in the cell dimensions is introduced. Another difficulty resides in some space group symmetry operations which depend on the parity of the dividing factors 5 or 6 for this particular case. The use of superspace thus eliminates the need for this selection. The advantages of working in superspace are even more notorious in the presence of a continuous change of a modulation vector with *e.g.* the temperature.

In many cases, the superspace group approach is a very sensitive tool to reveal detailed atomic interactions. The existence of a structural modulation often results from competitive forces which can be much better identified from a precise knowledge of the structure. In this respect, the refinement in superspace is in a better position than a commensurate approximation to deliver the required detailed information.

New Trends of Research in Superspace

We have shown above that incommensurate structures are better described in superspace. The use of superspace is not only limited to their descriptions but can also be applied to the description of superstructures, *i.e.* commensurate structures, which often occur in phase transition phenomena. In general and for a single compound, the full sequence of phases occurring at various temperatures or pressures can be described with a single superspace group independently of the specific values of the modulation vector being commensurate or incommensurate.

Recently, the use of superspace has even been extended to the description of a complete family of compounds exhibiting some compositional changes [11].

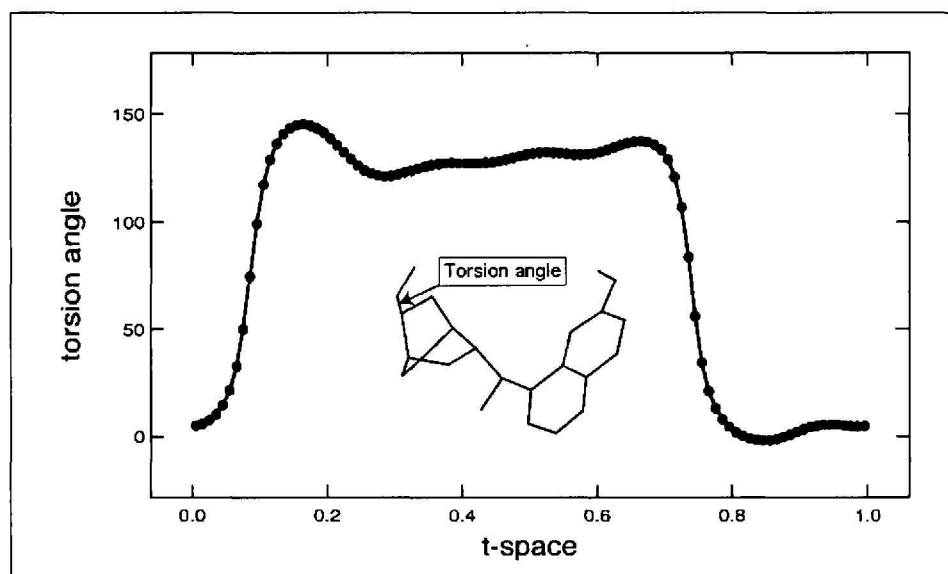


Fig. 5. The torsion angle of the vinyl group as a function of t . One can identify two preferred orientations, the first with a torsion angle of about 130° (65% of the t -space), the latter of about 10° (35% of the t -space).

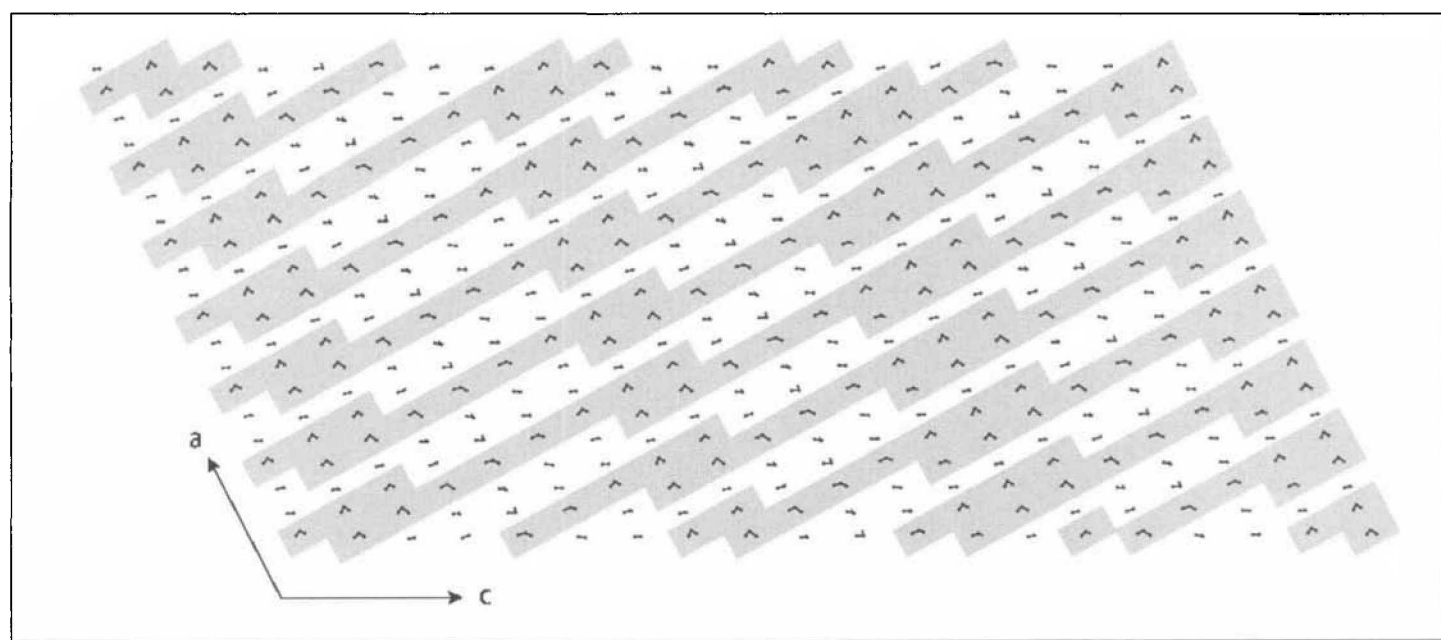


Fig. 6. Reconstruction of the vinyl group of the modulated structure to three-dimensional space. Shown are 20×20 unit cells. One can distinguish the two different orientations (corresponding to the two different torsion angles of Fig. 5). It also can be observed that this pattern is non-periodic.

This work shows very elegantly how at least seven known phases with the general composition $\text{LaTi}_{1-x}\text{O}_3$ can all be described with a single superspace group. This example is not unique and some more have been described in the most recent literature.

The trend to generalise the use of the superspace description is obviously growing. The potential of this new paradigm is certainly larger than initially expected. In the future, we can expect new and innovative developments in the field of structural sciences.

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