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Aperiodic crystals and their atomic structures in superspace: an introduction

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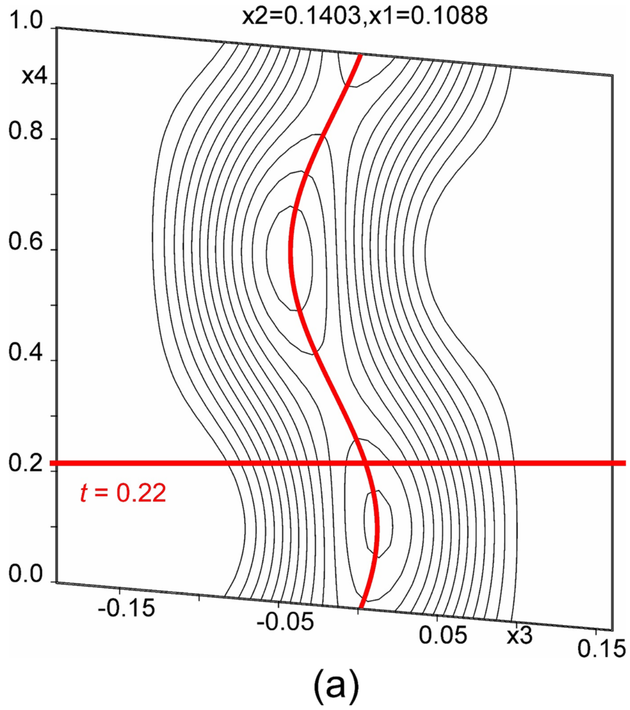
Abstract

Aperiodic crystals are ordered matter without three-dimensional (3D) translational symmetry. They encompass quasicrystals, incommensurate composite crystals and incommensurately modulated structures. Their crystal structures are described by the so-called superspace theory, in which hidden periodicity is uncovered as translational symmetry in a space of dimensions higher than three. Here, I give an introduction to the structural features of aperiodic crystals and to the superspace theory for describing those structures. Applications, in particular *t*-plots, are demonstrated for the charge-density wave (CDW) materials $Er_2Ir_3Si_5$ and $EuAl_4$.

Graphical abstract



Keywords Aperiodic crystals · Modulated crystals · Quasicrystals · Crystal structure

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This paper belongs to the topical collection ”Quasicrystals: State of the art and outlooks” originated from an international conference organized by the Accademia dei Lincei, held in Rome on November 18, 2022 in the frame of the 2022 International Year of Mineralogy.

Extended author information available on the last page of the article

1 Introduction

The present contribution is based on a presentation given at the conference ”Quasicrystals: State of the art and outlooks,” that took place on 18 November 2022 at the Accademia Nazionale dei Lincei in Rome, Italy (Bindi and Parisi 2023). Here, I will provide an overview of aperiodic order in crystals, and I will give a brief introduction to the superspace theory for the description of the atomic structures of aperiodic crystals. Furthermore, the use of *t*-plots as most important tool for crystal–chemical analysis will be illustrated by two examples. I will provide these descriptions with a minimum of mathematics. For a rigorous treatment of the superspace theory, I refer to textbooks (van Smaalen 2012; Steurer and Deloudi 2009; Janssen et al. 2007).

The crystalline state of matter is important for many branches of science, including mineralogy, solid state physics, solid state chemistry and the pharmaceutical sciences. Many crystalline materials possess an atomic structure with translational symmetry. That is, the atomic arrangement in space—called crystal structure—is completely determined by the positions of the atoms in a unit cell, together with a lattice of translations. The latter is based on three basic vectors, {**a**, **b**, **c**}, that are the edges of the unit cell. Most crystalline materials have relatively few atoms in the unit cell. For example, for pharmaceutical compounds, the unit cell may accommodate precisely one molecule.

By way of construction, the three-dimensional (3D) translational symmetry of periodic crystals implies long-range order for their crystal structures. In the middle of the twentieth century, it became apparent, that solid materials with long-range order may exist, which do not have translational symmetry. Crystals with this property are now called aperiodic crystals. Three modes of long-range order without 3D translational symmetry have been found up to the present date. They are incommensurately modulated crystals, incommensurate composite crystals and quasicrystals. The crystal structures of these materials are most favorably described with the aid of the superspace theory, which was developed by Aloysio Janner, Ted Janssen and Pim de Wolff (de Wolff 1974; de Wolff et al. 1981).

2 Incommensurately modulated crystals

Incommensurately modulated crystals were the first kind of aperiodic crystals described in the literature. Their crystal structures can be derived from periodic structures, for example, CrOCl at ambient conditions with 3D periodic orthorhombic symmetry *Pmmn* and two formula units in the unit cell (Fig. 1a) (Forsberg 1962).

Modulated structures can be understood if we first assume that all atoms bear small displacements out of their lattice-periodic positions. However, these displacements are correlated with each other such that they follow as the values of a wave, which are obtained at the respective lattice-periodic positions. The latter is called basic structure. For CrOCl,

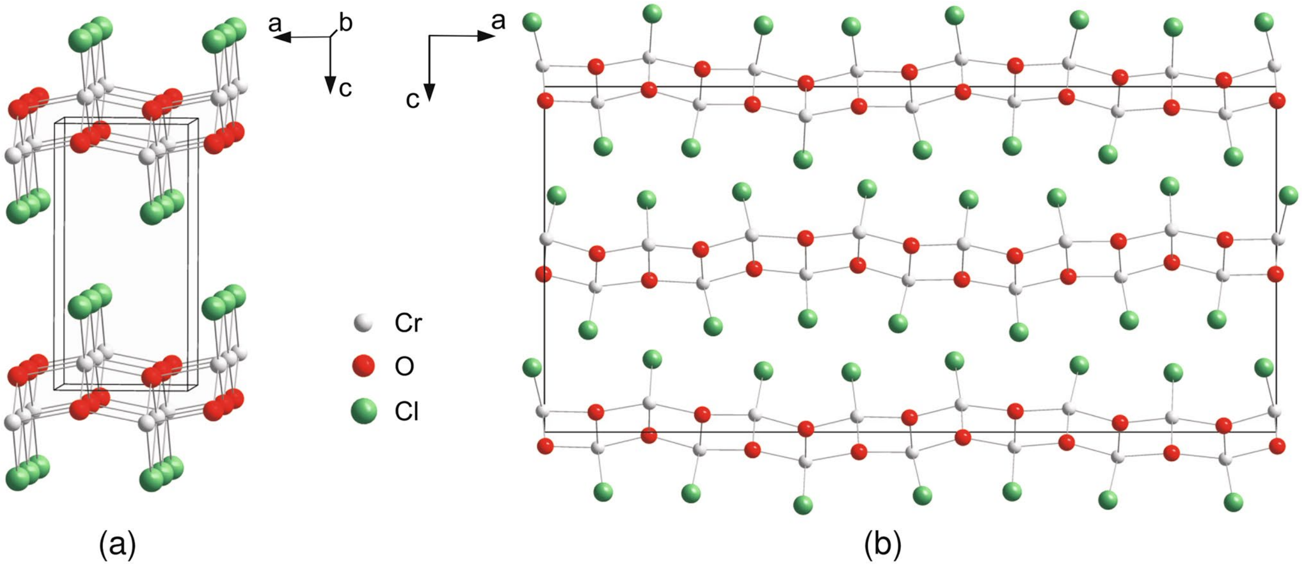

Fig. 1 Crystal structures of CrOCl at two different pressures. **a** Perspective view along the **b**-axis of the ambient-pressure crystal structure. **b** Approximate $7a \times b \times 2c$ superstructure at 30.3 GPa. Adapted from Fig. 1 in Bykov et al. (2015) Sci. Rep. **5**, 9647. DOI: 10.1038/srep09647 (color figure online)

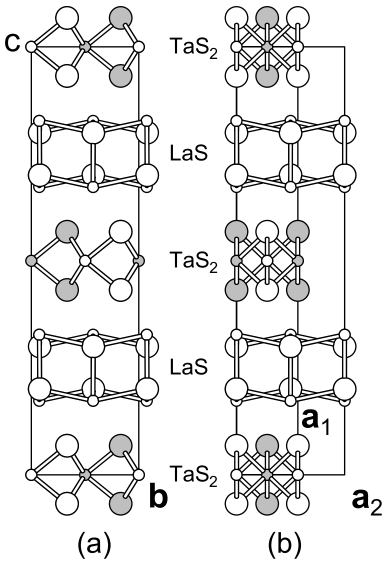

Fig. 2 The crystal structure of the incommensurate composite crystal $(LaS)_{1.13}TaS_2$. **a** Projection along the incommensurate **a** axis, and **b** projection along the common **b** axis. Large circles denote S atoms; small circles represent the metal atoms. Shaded and white circles represent atoms at different positions of the projected coordinate. Reproduced from Jobst and van Smaalen (2002). https://doi.org/10.1107/S0108768101019280

the modulation wave of, for example, the positions of the Cl is obvious, when seven basic structure unit cells are plotted (Fig. 1b). Actually, if the modulation wave has a period of exactly seven basic translations, it is commensurate, and the seven-fold supercell is exact. In case the wave slightly deviates from a seven-fold period, it is incommensurate, and no true supercell can be found for the modulated crystal structure. The superspace theory needs to be applied (see below).

In general, an incommensurately modulated structure can represent the minimum of the Free Energy. This happens in particularly if competing interactions are present, which cannot be simultaneously satisfied in an optimal way. For example, as proposed in Bykov et al. (2015), the incommensurately modulated crystal structure of CrOCl allows a denser packing of Cl atoms within the van der Waals gap than is possible with any periodic structure derived from the orthorhombic *Pmmn* 3*D* periodic structure.

3 Incommensurate composite crystals

The incommensurability of composite crystals is at a more fundamental level than that of modulated crystals. Figure 2 shows the principle of composite crystals by the example of the layered compound $(LaS)_{1.13}TaS_2$. Layered compounds can be described as the stacking of a single layer type, where there is strong chemical bonding within the layers and weak Van der Waals interactions between the layers, as it is found, for example, for CrOCl (Fig. 1a) and NbS_2. In a variation of this principle, two different kinds of layers are alternately stacked, e.g., along the **c**-axis (Fig. 2).

The two layer types share a common **c**-axis.[1] They might also have the same **b**-axis, with the result that a projection along **a** appears like the projection of a periodic crystal (Fig. 2a). However, the projection along **b** reveals two independent **a**-axes for the two layer types (Fig. 2b). Accordingly, the crystal structure lacks 3D translational symmetry, and it is an aperiodic crystal. It is important to realize that a composite crystal does not possess two separate ”unit cells.” Space is covered by the unit cells of the TaS_2 subsystem, where there is empty space for accommodating the LaS layers. The other way around, the LaS unit cells also cover space, and they have empty space where the TaS_2 layers are located. In a similar way, columns of mutually incommensurate periodicity can be put on a common 2D grid. Or a framework structure can be made, in which channels are filled with molecules or atoms with their own periodicity along the channel axis.

The amplitude of the modulation wave (that is the maximum displacement of the atoms) can be made arbitrary small for modulated crystals. In this way, a 3D periodic basic structure can be defined, as the structure with modulation amplitudes sets to zero. A 3D periodic basic structure does not exist for composite crystals. Each subsystem has its own periodicity that is incommensurate with the periodicity of the other subsystem. Actually, the interactions between the layers of $(LaS)_{1.13}TaS_2$ result in two subsystems, that are by themselves incommensurately modulated structures. The periodicity of the modulation wave in the TaS_2 subsystem is provided by the **a**-axis of the LaS subsystem, and the periodicity of the modulation wave in the LaS layers is provided by the **a**-axis of the LaS subsystem.

4 Symmetry and diffraction

The symmetry group of a periodic crystal always includes a 3D lattice of translations, that is defined by three basis vectors {**a**, **b**, **c**}. The diffraction of such a structure produces sharp Bragg reflections with scattering vectors that are given by the reciprocal lattice vectors (Fig. 3a).

The latter are based on three reciprocal basis vectors {$\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$}. Accordingly, Bragg reflections are indexed by three integer indices (h, k, l).

Sharp Bragg reflections are the result of long-range order. Sharp Bragg reflections are thus obtained in the diffraction of all three types of aperiodic crystals. For incommensurately

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[1] More correctly, the layers are perpendicular to $\mathbf{c}^*$; for orthorhombic and higher symmetries reciprocal and direct axes are parallel.

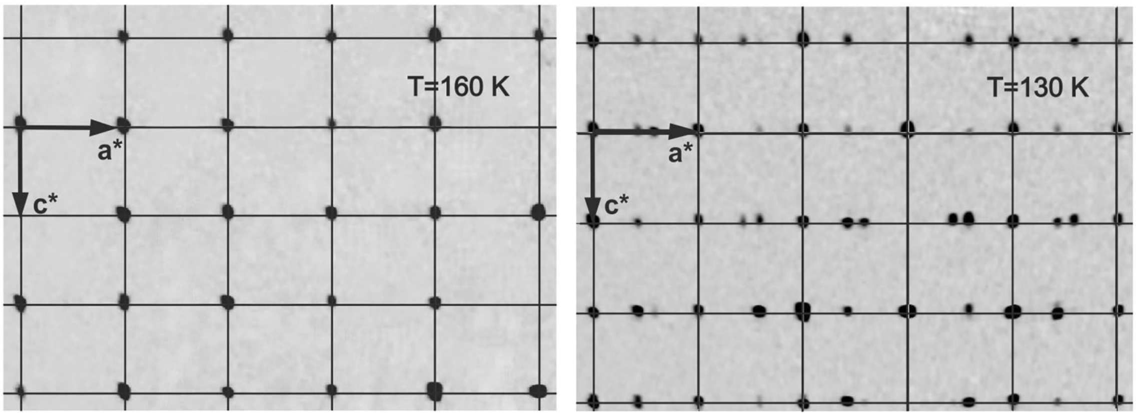

Fig. 3 Diffraction by morpholinium tetra-fluoro-borate. **a** reconstructed ($h\,4\,l$) reciprocal layer for the periodic structure at T = 160 K. **b** Reconstructed ($h\,4\,l\,m$) reciprocal layer for the modulated structure at T = 130 K. Satellite reflections are visible with $\mathbf{q}$ = (0.4219, 0, 0). Notice the *mmm* point symmetry. Figure 1 from Noohinejad et al. (2017) reproduced with permission of the IUCr. https://doi.org/10.1107/S2052520617009398

modulated crystals, Bragg reflections are found on the reciprocal lattice of the 3D-periodic basic structure (main reflections). Additional Bragg reflections—called satellite reflections—appear at positions ±**q** from the main reflections (Fig. 3b). Any of these reflections can uniquely be indexed by four integers (h, k, l, m), where (h, k, l, 0) are main reflections and (h, k, l, m) with $m \neq 0$ are satellites. The vector **q** is the wave vector of the modulation wave; its length is the reciprocal of the wave length. The modulation wave vector **q** thus characterizes the modulation as present in the aperiodic crystal. The example of Fig. 3 pertains to a one-dimensional modulation (d = 1) with one modulation wave vector. Modulated crystals have also been found for d = 1, 2 or 3 modulation wave vectors.

The space group of a periodic crystal includes rotational symmetry in addition to translational symmetry. This symmetry directly translates into point symmetry of the diffraction pattern. For example, the diffraction in Fig. 3a possesses *mmm* point symmetry, where both the mirror perpendicular to $\mathbf{a}^*$ and the mirror perpendicular to $\mathbf{c}^*$ map a Bragg reflection onto another Bragg reflection of the same intensity or onto itself. The same is true for the diffraction of the modulated crystal (Fig. 3b). An additional feature is, that the point symmetry maps a main reflection onto a main reflection, and it maps a satellite onto a satellite.

The point symmetry thus observed in the diffraction of an aperiodic crystal eventually becomes part of the superspace group (superspace symmetry). At this stage, it is important to notice that the point symmetry of an aperiodic crystalline phase cannot be anything else than a 3D point group. No restrictions on the possible point groups exist for aperiodic crystals, unlike the restriction to so-called crystallographic rotations of order n = 1, 2, 3, 4, 6 (where n = 1 represents the identity operator). Despite an infinite number of these symmetries, the structure is simple: in analogy to crystallographic point groups 4/*mmm* and 6/*mmm*, the only point symmetries are *n*/*mmm* (n is even) and their subgroups. 3D space is special, in that it furthermore allows the crystallographic cubic and the non-crystallographic icosahedral groups.

Incommensurately modulated structures and incommensurate composite crystals have symmetries according to a crystallographic point group. Quasicrystals are loosely defined as aperiodic crystals based on non-crystallographic point symmetry. Actually observed have been quasicrystals with icosahedral, octagonal, decagonal or dodecagonal symmetries. Several higher-order rotations have been found for soft-matter quasicrystals (Fischer et al. 2011).

5 Direct and reciprocal superspace

Inspection of the atomic structures immediately reveals the absence of translational symmetry for aperiodic crystals (e.g., see Fig. 1). On the other hand, the diffraction of aperiodic crystals does exhibit rotational symmetry (Sect. 4). The latter will provide symmetry of the atomic structure of the aperiodic crystals through the use of superspace groups.

The first step towards the superspace description is the indexing of the diffraction pattern by four or more integers, employing four or more reciprocal vectors. For example, in the case of incommensurately modulated morpholinium tetra-fluoro-borate, an integer indexing of the diffraction requires four reciprocal vectors, {$\mathbf{a}^*$, $\mathbf{b}^*$, $\mathbf{c}^*$, $\mathbf{q}$} (Fig. 3b). It was observed by De Wolff, Janner and Janssen (1981), that a set of points described by (3 + d) integer indices forms a (reciprocal) lattice in (3 + d) space. Accordingly, superspace is defined as a space of dimension (3 + d). For the example

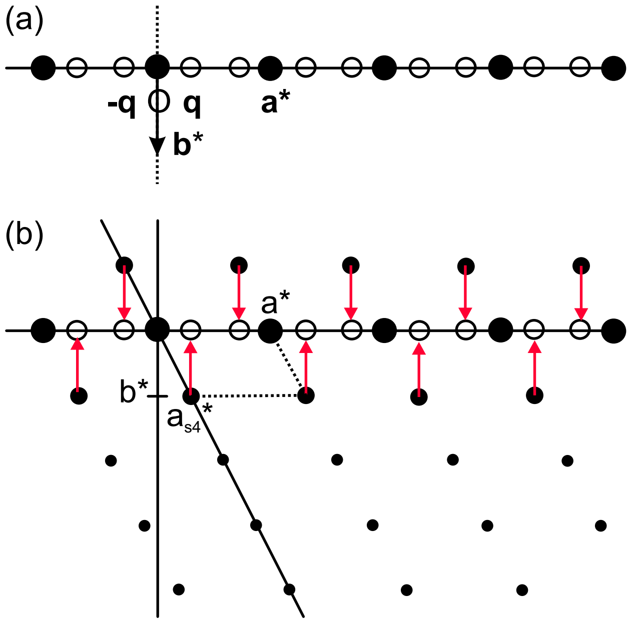

Fig. 4 Reciprocal superspace. **a** 1D section of the diffraction of a modulated structure. The reciprocal vector $\mathbf{b}^*$ is perpendicular to physical space. **b** 2D section of the reciprocal superspace lattice. Dotted lines indicate the reciprocal unit cell in superspace. Satellite reflections in physical space are the projections of reciprocal lattice points in superspace (red arrows for first-order satellite reflections.) (color figure online)

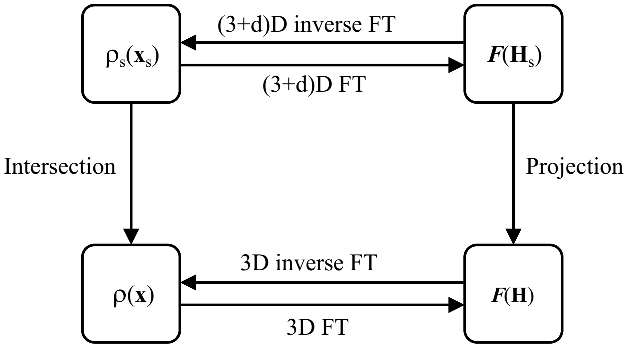

Fig. 5 Relations between direct and reciprocal spaces and between physical space (bottom row) and superspace (top row). $\rho_s(\mathbf{x}_s)$ is the electron density in superspace, which is a function of the $(3+d)$ coordinates of the position $\mathbf{x}_s$ in superspace. $\mathbf{H}_s$ stands for the reflection indices (h, k, l, m). FT is Fourier Transformation. Figure 2.4 in Incommensurate Crystallography (van Smaalen 2012) reproduced by permission of Oxford University Press

of an incommensurately modulated structure with a one-dimensional modulation (a single modulation wave vector), Fig. 4 shows the relation between observed Bragg reflections in physical, 3D space, and the reciprocal lattice points in (3 + 1)D space.

There is no theoretical bound on the number of modulation waves in an incommensurately modulated structure, but only $d = 1$, 2 and 3 have been found experimentally (van Smaalen et al. 2013). The same is true for incommensurate composite crystals. Icosahedral quasicrystals have $d = 3$; decagonal and dodecagonal quasicrystals have $d = 2$.

The diffraction pattern assigns an intensity value to each of the Bragg reflections (reciprocal points) in 3D space. After solving the phase problem, each reciprocal point gets assigned a structure factor. The atomic structure then is the inverse Fourier transform of these structure factors. This allows a general scheme to be given for the superspace description of aperiodic crystals. In reciprocal space, 3D and (3+d)D spaces are related by a projection, while the structure in 3D space is the intersection of the superspace structure (Fig. 5).

The crystal structure in superspace is periodic. The superspace equivalent of a point atom in physical space is a wavy string that precisely has the shape of the modulation wave. This is illustrated by one unit cell of the Fourier map in superspace for the example of $Er_2Ir_3Si_5$ with a 1D modulation (Fig. 6).

The trace of the maximum of the Fourier map in Fig. 6a is a wavy line that represents the atomic string in Fig. 6b. Each section labelled t = constant represents physical space. It is perpendicular to the fourth axis, but makes irrational angles with at least one other axis, such that physical space lacks 3D translational symmetry.

Quasicrystals have a different superspace. One reason is the lack of a periodic basic structure in physical space. The superspace equivalents of point atoms are occupation domains of dimension d, which exist perpendicular to physical space.

6 *t*-Plots and crystal chemistry

By construction, the fourth coordinate axis in superspace is perpendicular to physical space (Figs. 4 and 6). The fourth coordinate $\bar{x}_{s4}$ of a point in superspace then is

$$\bar{x}_{s,4} = t + \mathbf{q}\cdot\bar{\mathbf{x}}(\mu) \tag{1}$$

where $\bar{\mathbf{x}}(\mu)$ are the three coordinates of atom μ in the basic structure. The parameter t can be considered as the initial phase of the modulation wave. Different t gives shifted, but entirely equivalent representations of physical space. As such it is related to the phason degree of freedom. For crystal structures, the variation of environments of a particular atom of the basic structure can be obtained by the consideration as a function of t of structural parameters, like atomic displacements, atomic distances, bond angles, torsion angles, direction of magnetic moment, and occupation of atomic

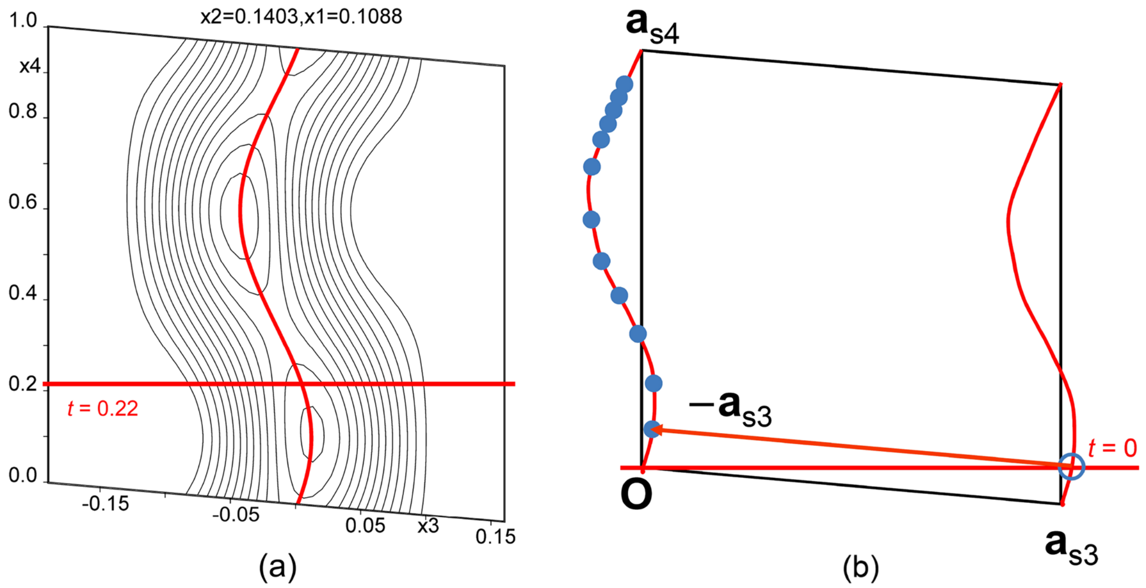

Fig. 6 (x_{s3}, x_{s4})-Section of superspace of the incommensurately modulated structure of $Er_2Ir_3Si_5$, showing the atom Er at basic position $\bar{x}_{s3} = 0$. **a** Section from the Fourier map, and **b** Schematic drawing of the superspace atom. Drawn with data from Ramakrishnan et al. (2020) (color figure online)

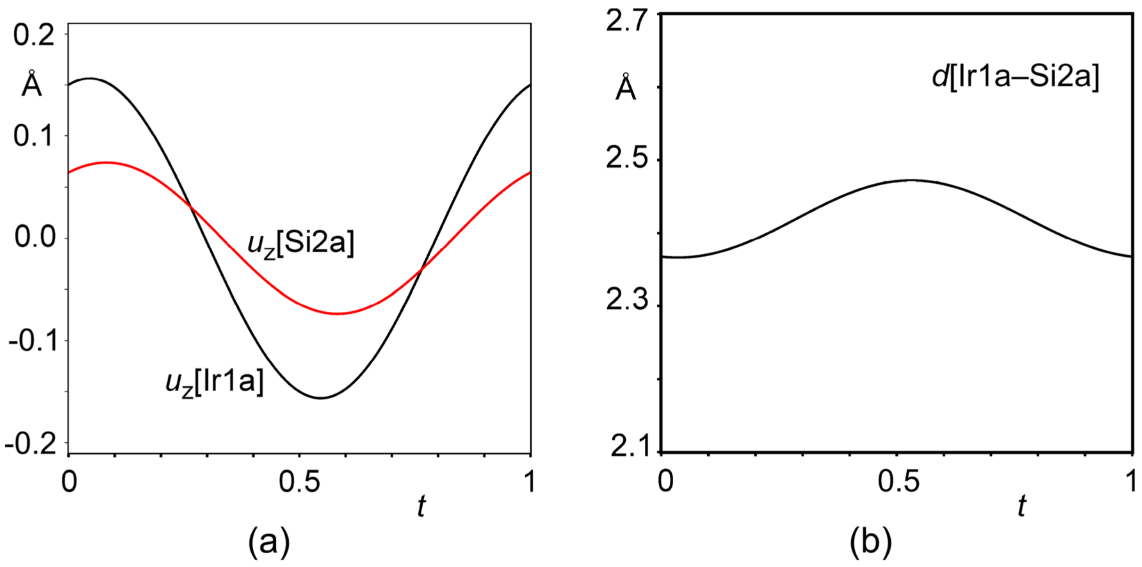

Fig. 7 **a** *t*-Plot of displacements along $z \mathrel{\widehat{=}} x_3$ of atoms Ir1a and Si2a in the incommensurately modulated structure of $Er_2Ir_3Si_5$. **b** *t*-Plot of the distance between atoms Ir1a and Si2a. Drawn with data from Ramakrishnan et al. (2020)

site,⋯ As an example, the z components u_z are given for the modulation functions of the atoms Ir1a and Si2a in the incommensurately modulated crystal structure of $Er_2Ir_3Si_5$ (Fig. 7a).

In the basic structure, a chemical bond exists between the atoms Ir1a and Si2a. Figure 7a reveals that the modulation displacements of these atoms are in phase, i.e. the modulation functions u_z of Ir1a and Si2a attain minimum and maximum values for almost the same values of t. Accordingly, the *t*-plot of the interatomic distance Ir1a–Si2a exhibits but a small variation of this distance as a function of t (Fig. 7b), and the chemical bond Ir1a–Si2a persists in the modulated structure.

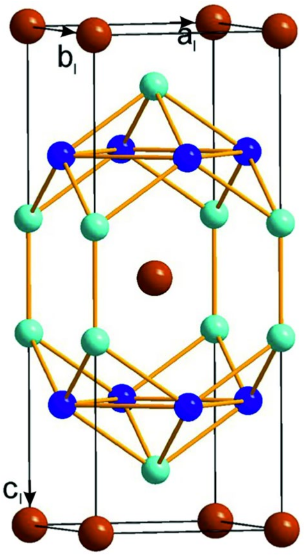

Fig. 8 The basic structure of $EuAl_4$. One *I*-centered unit cell is shown with Eu (red), Al1 (blue) and Al2 (green) atoms. Reproduced with permission from Ramakrishnan et al. (2022) (color figure online)

7 The charge density wave in $EuAl_4$

The metal $EuAl_4$ develops a charge density wave (CDW) at temperatures below the phase transition at $T_{CDW} = 145$ K (Nakamura et al. 2015; Shimomura et al. 2019). The CDW is a modulation of the electron density of the conduction band, coupled with a displacement modulation of the atoms. The latter modulation has been determined by temperature-dependent single-crystal X-ray diffraction (Ramakrishnan et al. 2022). $EuAl_4$ is tetragonal with space group *I*4/*mmm* and lattice parameters $a = 4.395$ and $c = 11.161$ Å at $T = 250$ K (Fig. 8).

An alternative setting is *F*4/*mmm*, with $a = 6.215$ and $c = 11.161$ Å. The CDW modulation is incommensurate with modulation wave vector $\mathbf{q} = (0, 0, 0.1781)$ at 70 K. The CDW phase transition is accompanied by a reduction in point symmetry from tetragonal to orthorhombic *Fmmm* for the basic structure. The (3 + 1)D superspace group for the modulated structure is $Fmmm(0\,0\,\sigma)s00$ (Ramakrishnan et al. 2022).

Both *I*4/*mmm* and *Fmmm* have three crystallographically independent atoms in the basic structure: Eu1, Al1 and Al2 (Fig. 8). The shortest distances are two Al2–Al2 contacts and four contacts each of Al2–Al1 and Al1–Al1. The largest atomic displacements of the modulation wave are along **a**; they are in-phase and they are nearly equal for all atoms. Only Al1 has a sizeable modulation along **b**. This modulation is responsible for a strong variation of two out of four Al1–Al1 contacts, as shown in Fig. 9a.

Other distances are nearly constant over the modulation wave. These observations have led to the conclusion, the CDW resides on the Al1 type atoms (Ramakrishnan et al. 2022).

8 Outlook

Aperiodic crystals encompass ordered materials without translational symmetry, including incommensurately modulated structures, composite crystals, and quasicrystals. The crystal structures of aperiodic crystals are described by the superspace theory, originally developed by Janner,

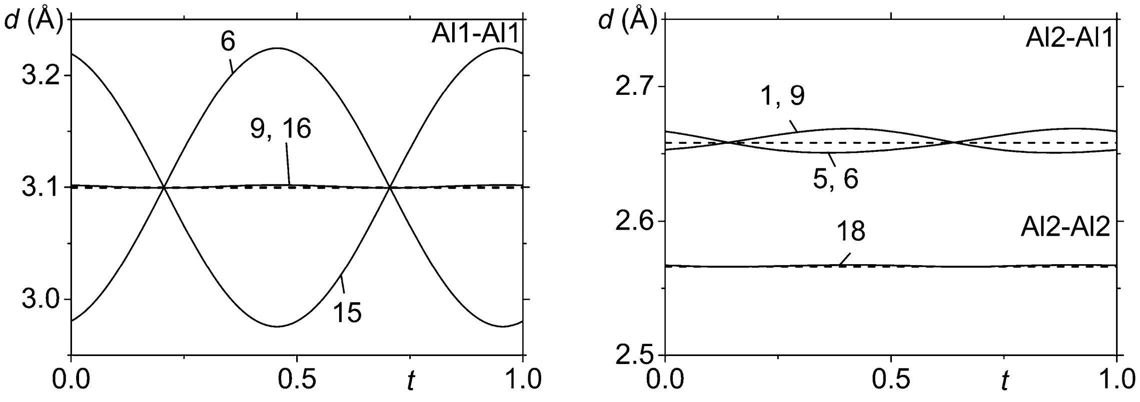

Fig. 9 *t*-Plot of interatomic distances in the CDW modulated crystal structure of $EuAl_4$. (Left) Al1–Al1 distances, and (right) Al2–Al1 and Al2–Al2 distances. Numbers indicate the symmetry operators that were applied to the second atom of each pair (see original publication). Reproduced with permission from Ramakrishnan et al. (2022)

Janssen and de Wolff (van Smaalen 2012; Steurer and Deloudi 2009; Janssen et al. 2007). Superspace structure models may reveal important properties of aperiodic materials, not the least their symmetries.

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Declarations

Conflict of interest The author has no relevant financial or non-financial interests to disclose. The author has no competing interests to declare that are relevant to the content of this article.

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