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Chapter 1 : Framework structure crystalline materials and Rigid Unit Modes (RUMs)

Introducing the new concept of MLRUMs and skeletons

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Abstract : This article reviews Framework Structures (FWs), defined as crystalline materials built of rigid AX_n polyhedra sharing vertices (like perovskites, tungsten bronzes, Dion-Jacobson, Ruddlesden-Popper, and Aurivillius phases, quartz, silicates, and others), and their peculiarities resulting from this linkage. The situation of rigid units linked by common vertices may allow the units to accomplish concordant rotations without deformation, which gives rise to soft phonon modes called "Rigid Unit Modes" (RUMs). The condensation of a RUM can trigger structural phase transitions to a structure of lower symmetry, with tilted polyhedra, at the origin of spontaneous ferroic or multiferroic properties. We overview results precedently obtained on RUMs in perovskites, tetragonal tungsten bronzes, and quartz, and detail new results on "maximally localized RUMs" (MLRUMs), a fundamental new concept in the physics of RUMs. We introduce also the related new concept of "skeletons" that allows to generate all ferroelastic phases found in these systems.

Keywords : PEROVSKITES, TUNGSTEN BRONZES, DION-JACOBSON, RUDDLESDEN-POPPER, AURIVILLIUS, QUARTZ, SILICATES, TILT SYSTEMS, FRAMEWORK STRUCTURES, FERROIC, MULTIFERROIC, RIGID UNIT MODES, PHONON MODES, PHASE TRANSITIONS, LATTICE DYNAMICS, SYMMETRY BREAKING

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I. Overview on main framework structure (FWS) crystalline materials

The Framework Structures (FWSs) are defined as crystalline materials built of rigid AX_n polyhedra (thereafter named as “rigid units”) linked by common vertices, edges, or faces ^[1]. In most common cases these materials contain rigid units of octahedral or tetragonal shape as encountered in numerous oxides, fluorides, oxyfluorides, but also chlorides, bromides, iodides, and mixed compounds.

Figure 1: Perovskite structure in parent (cubic) phase

In these systems of ABX_3 chemical formula, rigid units are BX_6 octahedra sharing corners. From structure data of $PbTiO_3$ ref. [3]

When the rigid units are linked by corners the system has maximal degrees of freedom whereas a connection through edges allows only a rotation of rigid units around an axis parallel to the common edge. A link through a common face between two rigid units fixes the geometry and no rotation is permitted. It is why in the following we focus on most interesting systems where the link between adjacent rigid units is achieved through a common vertex. The most known example of this type is that of perovskites ^[2] where the corresponding units are octahedra that share corners as in $PbTiO_3$ (Figure 1), and in the first discovered mineral of this type, $CaTiO_3$. The general chemical formula for perovskite compounds is ABX_3 , where A and B are two cations of very different sizes, or molecular groups, and X is an anion (O, F, I,...). Mention also the “antiperovskites” ^[4] in which the positions of the cation and anion are reversed in the

unit cell structure in comparison with perovskites, the overall structure being identical. In both cases the parent crystalline structure is cubic, and many distortions of this structure are observed in relation with phase transitions as a function of temperature, pressure, or other external parameters. As explained later in this volume, the notion of “tolerance factor” t , based on a geometrical analysis of the relation between ionic radii, is a useful indicator for the stability of structures. Perovskites (and antiperovskites) are well known for the numerous possibilities of rotation of octahedra, that may induce a large variety of crystalline phases ^[5].

Among systems where rigid units are octahedra there exist in nature different structural arrangements and it is important in these systems, to focus on the way how the rigid units are linked to each others.

Figure 2: Arrangement of octahedra (of oxygen or fluor in most cases) in perovskite phase (a) and in tetragonal tungsten bronze phase (b)

In the TTB phase (Fig. 2-b) there occur square, triangular, and pentagonal channels the last two being absent in perovskites; the arrangement around square channels (center of Fig.2-b) is identical with that in perovskites. Along c the octahedra share corners in a similar way in both cases (Data from refs [2] and [6]).

Another important crystalline family is that of tetragonal tungsten bronze (TTB) type ^[6], in their parent phase, along the high symmetry axis, octahedra share corners in a similar way as in perovskites, forming linear chains of octahedra. However in the basal plane, the octahedra are disposed in such a way that there appear three types of

channels (Figure 2-b). In perovskites there exist only square channels between octahedra (Fig.2a), whereas in tungsten bronzes besides square channels, there are triangular channels and distorted pentagonal channels (Figure 2b) (or hexagonal channels in “hexagonal tungsten bronzes” HTB). Both in perovskites and in tungsten-bronze type materials, all corners of a given octahedron are shared with neighbours, but the ratio of shared corners may be different in other FWSs.

Figure 3: Examples of single-layer structures

(a) In KFeF_4 the centers of FeF_6 octahedra lie in a plane, note that at room temperature octahedra are tilted around crystallographic axis a (setting Cmcm , from [7]). The high symmetry phase with non-tilted octahedra is not realized in this system. (b) in BaMF_4 -type phase MF_6 octahedra form puckered sheets in a $\text{Cmc}2_1$ symmetry (from [8]).

Thus an interesting parameter that deserves attention, is the ratio of common vertices. There exist systems in which only a part of corners is shared, which leads to a more pronounced anisotropy of the structural organization of the FWS, with the appearance of layer structures or of wired structures. When octahedra share four of their vertices, there occur layer structures with one octahedron in the thickness. Examples of such structures are KFeF_4 where the Fe atoms at the center of FeF_6 octahedra lie in a plane [7], and BaMF_4 [8,9] ($\text{M}=\text{Co}, \text{Zn}, \text{Mn}, \dots$) where MF_6 octahedra form puckered sheets (Figure 3).

Figure 4: example of Ruddlesden-Popper (RP) phase

The considered example is that of $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n=2$). (a) Perspective view of the conventional unit cell. (b) Perspective view of several unit cells. Space group $I4/mmm$, data from ref. [14].

There exist also layer structures in which the layers are thicker, comprising two or more octahedra along the thickness. Among such layered structures derived from perovskites mention the Dion-Jacobson and Ruddlesden-Popper (RP) phases^[10], the

(a)

b)

Figure 5: Example of Aurivillius phase with 3 octahedra in the thickness of perovskite blocks

(a) perspective view of conventional unit cell. At the difference with RP phases the perovskite blocks are separated by Bi_2O_2 layers instead of single anions; (b) perspective view of several cells showing the alternative layers of perovskite and of Bi_2O_2 . Space group $I4/mmm$, data from ref. [17].

Aurivillius phases ^[11], and various structures where octahedra are linked to each others in a bidimensional arrangement. Analogous layered structures exist also as derived from tungsten-bronze structures as in $\text{Cs}_2\text{NaAl}_3\text{F}_{12}$ (single HTB layers separated by Cs^+ and Na^+ in the hexagonal direction) ^[12] or in $\text{Rb}_2\text{NaAl}_6\text{F}_{21}$ ^[13] (double layers of HTB type separated by Rb^+ and Na^+ ions). The Dion-Jacobson (DJ) and Ruddlesden-Popper (RP) phases consist of two-dimensional perovskite-like layers separated by cations

(single cation sheet for the DJ phases, double cation puckered sheet for the RP phases) ^[10] (Figure 4). Their general formula are respectively $MA_{n-1}B_nX_{3n+1}$, and $M_2A_{n-1}B_nX_{3n+1}$, where M, A and B are cations (or molecular groups), X is an anion (oxygen for most of known compounds), and n is the number of layers of octahedra in the perovskite-like block. The Aurivillius phases of general formula $[Bi_2O_2]^{2+}[A_{n-1}B_nO_{3n+1}]^{2-}$ first mentioned in 1949 by B. Aurivillius may be considered as deriving from Ruddlesden-Popper (RP) phases in which the layers of separating cations are replaced by layers of $[Bi_2O_2]^{2+}$; these structures ^[11] may thus be described as alternative layers of $[Bi_2O_2]^{2+}$ and perovskite-type blocks comprising n octahedra (usually in the range 1–5) in the layer thickness (Figure 5). Simplest examples are Bi_2WO_6 (n=1) ^[15], $SrBi_2Ta_2O_9$ (n=2) ^[16] and $Bi_4Ti_3O_{12}$ (n=3) ^[17], but the family comprises numerous compounds associating A chosen among uni-, di- or trivalent cation (K^+ , Ca^{2+} , Sr^{2+} , Ba^{2+} , Pb^{2+} , La^{3+} , Bi^{3+}) and B among small transition metal (Ti^{4+} , Nb^{5+} , Ta^{5+} , W^{6+}). Organo-metallic compounds are also found in this family.

Figure 6: Example of structures with wires of octahedra

(a) Conventional unit cell of $Rb_2AlF_5 \cdot H_2O$. AlF_6 octahedra share two corners and form isolated wires. H and O are not represented in the figure. Setting $Cmcm$, data from ref. [19];

(b) Conventional unit cell of an hexagonal phase of $CsAlF_4$ in which wires of octahedra are connected in a triangular arrangement. Space group $P\bar{6}2m$, data from ref. [20]

Crystalline materials having a layered structure built from layers of interconnected rigid units (as Aurivillius phases or micas) correspond to an intermediate situation between solids and clays and could allow a better understanding of some physical properties of materials as smectites. The existence of FWS materials with a 2D pronounced structural organization, where the intralayers links are strong and interlayer forces much weaker, opens also the interesting possibility of existence of materials consisting

of a single layer or block of rigid units, in an analogous way as in graphene ^[18]. Such single layers of octahedra or tetrahedra should present singular properties differentiating these materials from bulk materials in reason of size effects including quantum localizations and confinement effects.

Varying the connectivity between octahedra can lead also to structures where octahedra are sharing only two corners in one direction, forming octahedra wires isolated from others. This is the case of such compounds as Rb_2AlF_5 , H_2O ^[19] and of others of chemical formula A_2BF_5 (Figure 6-a). Several existing structures with octahedral rigid units may be seen as lattices of such wires as in CsAlF_4 ^[20] (Figure 6-b) or in layered structures as $\text{K}_3\text{Zn}_2\text{F}_7$ ^[21].

Figure 7: Example of structures with tetrahedral rigid units

(a) High quartz (β phase)

(b) High cristobalite phase "C9" (space group $Fd\bar{3}m:2$)

After these examples of framework structures built with octahedra as rigid units, consider examples of structures built with tetrahedral rigid units. The most known examples are from quartz phases, namely so called β -quartz ^[22] and cristobalite C9 ^[23], respectively of hexagonal and cubic symmetry (Figure 7). Tetrahedral rigid units occur in quartz-like materials and more generally in silicates ^[24] (minerals such as feldspar, mica, amphibole, pyroxene, olivine, and a great variety of clays) ^[25]. In some minerals as nesosilicates (olivine, garnets, etc) tetrahedra are isolated from others ^[26], or form pairs in sorosilicates ^[27] so that these structures cannot be considered of FWS type. In

other silicates, tetrahedra form rings^[28], single chains^[29] (inosilicates like pyroxenes and wollastonite), double chains (amphiboles)^[30], or sheets (micas, clays, serpentine, ...) ^[31, 32, 33]. Mention in particular the interesting cases of pyrochlore compounds^[34], feldspar^[35], and of zeolites^[36] where tetrahedra are interconnected in several directions. The nature reveals also interesting materials built with a mixture of octahedral units of different types as cubic spinel structure, weberite $\text{Na}_2\text{NiFeF}_7$ ^[37], elpasolites^[38], $\text{SrAl}_2(\text{PO}_4)_2\text{F}_2$ ^[39], and tetrahedral units of different types such as LaBGeO_5 ^[40], etc .

The framework structures are of great interest for several reasons:

- many mineral-forming compounds widely spread in the Earth crust belong to this family;
- many FWSs exhibit phase-transition behavior under temperature or pressure variation;
- many FWSs are ferroic or multiferroic materials, some of them exhibit anomalous thermal dilatation properties;
- numerous crystalline materials with interesting applications in various domains, belong to this family.
- The number of phases and crystal symmetries encountered in FWSs is considerable and may be understood by models of tilting rigid units analogous to those for perovskites ^[43].

The linkage of the units by common vertices or edges allows the units to accomplish concordant rotations without internal deformation, which gives rise to the soft phonon modes called Rigid Units Modes (RUMs) ^[43]. The condensation of a RUM can trigger the symmetry breaking structural phase transition which results in the emergence of a new structure with tilted polyhedra and consequently in new spontaneous physical (ferroic or multiferroic) properties as a result of symmetry lowering.

The list of mentioned FWS materials shown above is not exhaustive, it only aims at showing different typical situations concerning the configuration of rigid units. The existence of FWS materials differentiating themselves from others by the connectivity between rigid units, opens a new approach to these systems in terms of rigid units behaviour that governs a number of properties. This raises the problem of how to approach these systems globally, to understand common features and differences between different structures, classical approaches being perhaps not relevant to solve the question.

The analysis of rigid unit modes as performed and described further in this article, seems to be a relevant approach that should help understanding common properties and differences between various FWS compounds with different connectivity and configuration.

The aim of what follows is to resume the problem of Rigid Units Modes in FWSs, and describe essential approaches to RUMs and results obtained by different methods. We will show how this approach can lead to a new vision of the crystalline structures of FWSs and of their dynamics.

II. Overview on rigid unit modes in FWS

The idea of RUMs emerged after the pioneering work of Glazer on perovskites^[43]. As seen in precedent paragraph, these materials of formula ABX_3 , are built with BX_6 octahedra sharing corners (Figure 1). The idea of Glazer was to propose classifying the different phases found in this crystalline family according to rotations of undistorted octahedra around different axes (Glazer introduced notations for phases according to triads $(a^*, b^\#, c^\$)$ where $^*, ^\#, ^\$ = +, -, \text{ or } 0$: $+$ superscript means rotations in phase when following the axis or rotation, $-$ superscript stands for anti-phase octahedron rotations, and superscript 0 means no rotation. So for instance the triad (a^0, b^+, b^-) means no rotation around **a**, a rotation by angle b around **b**, in phase following the **b** direction, and a rotation by angle b around **c**, antiphase when following the **c** direction). This approach contained implicitly the idea that the phases that are most likely to occur, are those characterized by the absence of elastic energy for octahedra distortion and it appeared in the numerous experimental studies that followed, on perovskites, « double perovskites », and related systems, that the description of structures in terms of Glazer scheme, was relevant and convenient to classify the immense majority of phases encountered in different regions of pressure-temperature phase diagrams of these systems^[5].

The predisposition of a FWS to phase transitions is customarily explained by the presence of the RUMs: the RUM phonon modes involve concordant rotations of the AX_n polyhedra without deformation. The restoring forces of the RUM deformations are primarily related to rigidity of the A-X-A bridges which are quite flexible, resulting in low frequencies of the RUM modes. The condensation of a RUM can trigger the symmetry breaking structural transformation which results in the emergence of a new structure with tilted polyhedra. Such crystal structures are often referred as 'partly collapsed' structures because the RUM-induced distortions inevitably are accompanied by a

volume reduction^[43, 44]. Once the whole spectrum of RUMs is determined, one can describe the whole variety of the partly collapsed structures and predict all possible scenarios of the related phase transitions.

Figure 8: Illustration of the impossibility of rotation of octahedra around the 4-fold axis without deformation in TTB structure

Curved arrows represent rotations around the 4-fold axis; in figure 8(a) the concordant rotations are possible in the perovskite structure. Figure 8(b) shows that in TTB such rotations would face a situation of frustration, in an analogous manner as in antiferromagnetic systems in a triangular lattice.

The paper by Glazer^[43] was a first example of the approach as applied to the ideal cubic perovskite lattice. As seen precedently, another interesting crystalline family, the tungsten bronzes, is also built on the AX_6 octahedra which share their corners, but in a way that differs from that in perovskites (see Figure 2). In that family of tetragonal tungsten bronzes (TTB) it is obvious, from symmetry and rigid unit considerations, that the constraints are stronger than in perovskites, for instance a rotation around the high symmetry axis is forbidden due to a frustration situation in the basal plane (Figure 8). The concept of frustration was first introduced by Toulouse^[45] in systems with antiferromagnetic interactions. In these magnetic materials such a situation is known to favour modulated phases in the basal plane^[46]. The RUMs existing in this crystalline family were studied in ref. [47]. Much attention was also paid to the FWS built of corner-sharing tetrahedra. The most thoroughly studied is the α - β phase transition in quartz. Historically, it was the first example of the soft-mode behavior induced by a RUM^[48]. The idea on the concordant tetrahedron tilting as a driving mechanism of the α - β SPT was originally declared by Grimm and Dörner^[49] and later developed by

Vallade et al ^[50]. Soon afterwards, the same idea was applied to the α - β phase transition in cristobalite^[51]. And finally, the RUM concept was extended for other tetrahedron-based FWS ^[52, 53].

III. Different technical approaches to RUMs

A RUM is defined as a small structural deformation which does not distort (in linear approximation) the AX_n polyhedra. It is evident that an arbitrary combination of RUMs is also a RUM. Thus the problem of description of all possible partly collapsed structures consists in the determination of the whole RUM spectrum and in the examination of possible combinations.

We developed the analysis of RUMs using an original lattice dynamics approach^[47]: we have simulated the phonon states of a model system geometrically identical to the oxide framework in a perovskite and in a TTB lattice (in its para-phase structure) with regular XO_6 octahedra that are assumed to be mechanically rigid. Using the lattice-dynamical simulations one can easily determine the presence of RUMs in any point of the Brillouin zone (BZ) ^[47, 51-53].

Technically, the rigidity was guaranteed by supposing high values of bond stretching force constants for the intra-octahedron X-O bonds and the O-O edges. Some of simulated vibrational eigenstates of such model system were found to possess zero eigenvalues: these are the RUMs. So, the search for the whole RUM spectrum consists in scanning phonon states of the model system throughout the entire Brillouin zone (BZ).

This is one more approach besides those described in the overview by A.E. Phillips ^[54] who reported the spring model of Giddy et al ^[55] and the algebraic approach of Campbell et al ^[56]. Results obtained by these different methods are very similar, as can be seen by comparing our results of 2014 on the predicted crystal structures shown for instance in figures 2a and 2c of Ref [47] and figures 4 and 5 of Ref. [56] published four years later, in 2018.

It is more interesting to focus on the comparison, made in Ref. [47], between predicted RUM-induced phases and those found in the published experimental studies. In some cases there is a perfect coincidence: observed crystal structures correspond well to structures expected from RUMs condensation. However it is noteworthy that some other structures, for which the experiments have predicted disordered atomic positions, may be interpreted as resulting from simultaneous condensation of several

RUMs. We think that such experimentally observed structures can be considered as averaged over several RUM-induced structures and should be reinvestigated accordingly.

The results reported by Campbell et al in 2018 confirm our results published in 2014. It seems however, that it escaped from the attention of corresponding researchers, that besides the prediction of structures induced by the RUM condensation, we highlighted the existence of basic deformations whose combinations allow generating all possible RUMs. In the TTB structure these basic deformations are localized in the layers perpendicular to (110) and (1 -1 0) direction, we named them ρ and σ -deformations (see Figure 2 of ref.[47]). It is noteworthy that all existing RUMs can be represented as combinations of the ρ and σ -deformations localized in different layers.

In perovskites, the situation is analogous but slightly different. Due to the cubic symmetry, the layers containing RUMs are stacked in three directions, namely (100), (010) and (001), whereas in TTB lattice they are stacked only in two directions, namely (110) and (1-10).

The consequence of the existence of the spatially localized RUMs has not yet been completely investigated. It is not yet clear if such objects may exist in a 'frozen' state and what may be their signature. These issues require further experimental and theoretical studies. It is obvious that the determination of all $\mathbf{k}$ -points containing RUMs is insufficient for the comprehensive description of the RUM-induced structural distortions. A uniform description of the RUM-induced distorted structures can be achieved by using the Maximally Localized Rigid Unit Modes (MLRUM). After having determined the atomistic model of these modes, we can use them as basic elements to build (just as in a Lego toy) all possible RUMs and all possible tilted structures.

The idea of representing the lattice vibrations not as usual extended plane waves (normal modes) but as a set of localized vibrational states was first proposed in Ref [57]. This concept was inspired by the electronic state theory which can be formulated either within the extended basis functions (Bloch waves) or alternatively within the localized basis functions (Wannier functions). The localized lattice vibrations appeared to be of interest for the treatment of defects and other problems calling for a localized description. In particular, this concept was successfully used for studying the ferroelectric phase transitions^[58].

Figure 9: RUM localized within a plane (a) and within a chain (b)

Localized RUMs give rise to the RUM phonon branches covering whole directions and planes in the BZ respectively. The localization areas are planes in (a) and rods in (b).

However, applications of the concept were restricted by few particular cases till the sound theoretical background for determining the Maximally Localized Wannier Function (MLWF) was reported in Ref [59]. This finding opened wide perspectives for applying the Wannier functions as an efficient tool for the electronic-structure theory as well as for the phonon excitations in the photonic crystals, and the cold-atom containing optical lattices. Some applications of the MLWF concept to the phenomena related with the phonon states were discussed in Ref. [60]. In the present paper we demonstrate that the use of the MLRUM is easily applicable for the most studied FWS structures.

IV. Theoretical background

Due to corner-sharing linkage, any rotation of a polyhedron in the framework lattice forces the neighboring polyhedra to move. This means that any RUM is a collective motion of ensemble of the polyhedra. The ensembles may include the whole lattice.

However, it is important to notice that if the axis of the polyhedron rotation passes through one or two polyhedron apexes, the apexes remain immobile during the rotations. Hence, not all neighboring polyhedra are bound to participate in this

collective motion. This gives rise to RUMs localized within some restricted area – within a plane or a chain. These cases are schematically shown in Figure 9a and 9b respectively.

The existence of RUMs localized within a plane results in the appearance of the RUM phonon branches in the BZ direction perpendicular to the plane. The eigenvector of the RUM corresponding to an arbitrary $\mathbf{k}$ -vector is determined by the expression:

$$e(\mathbf{k}, \mathbf{R}) \sim w(0) \exp[i(\mathbf{k}_\perp \cdot \mathbf{R})] \quad (1)$$

in which $\mathbf{k}_\perp$ denotes the $\mathbf{k}$ -vector component perpendicular to the plane of localization.

The existence of the RUM localized within a chain results in the appearance of the RUM phonon branches in the BZ planes perpendicular to the chain direction. Eigenvectors of the RUMs corresponding to arbitrary $\mathbf{k}$ -vector is determined by the expression:

$$e(\mathbf{k}, \mathbf{R}) \sim w(0) \exp[i(\mathbf{k}_1 \cdot \mathbf{R}) + i(\mathbf{k}_2 \cdot \mathbf{R})] \quad (2)$$

in which $\mathbf{k}_1$ and $\mathbf{k}_2$ denote two mutually orthogonal $\mathbf{k}$ -vector components perpendicular to the chain of localization.

It is noticeable, that the Eqs. 1 and 2 coincide with the expression which relates the Bloch functions $e(\mathbf{k}, \mathbf{R})$ and the Wannier functions $w(0)$ in the electronic band theory^[61].

The theory provides us with the inverse relation which allows to determine $w(0)$ from $e(\mathbf{k}, \mathbf{R})$ ^[60]:

$$w(0) = \frac{V}{(2\pi)^3} \int_{BZ} d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{R}} e(\mathbf{k}, \mathbf{R}) \quad (3)$$

Integration in (3) may be restricted to the direction or a plane in the BZ for the cases (a) and (b) respectively. The Eq (3) allows an exact analytic definition of the MLRUM.

The concept of MLRUM allows us to describe arbitrary RUM at arbitrary $\mathbf{k}$ -point as a combination of the MLRUMs localized within different planes or chains. This provides us with a basis for unified classification of the whole RUM spectrum and allows the uniform classification of all tilt structures induced by the RUM condensation.

MLRUMs being localized within planes or chains, their symmetry cannot be described by one of the 230 space groups. The adequate concept to describe their symmetry is that of subperiodic groups (of space groups)^[62], that contain the frieze groups, the layer groups and the rod groups. A layer group collects all symmetry operations leaving invariant a given object extending in the three-dimensional space, but having a two dimensional translation symmetry. A rod group describes the symmetry of an object also extending in the three-dimensional space, but having a one-dimensional translation symmetry. Frieze groups are two-dimensional groups with one-dimensional translations. The symmetry properties of MLRUMs will be described in more details in another article, but we shall present in the following the most important points related with symmetry based on the example of perovskites.

V. Analysis of RUMs in important systems

V.1 MLRUMs in perovskites

The framework lattice of the perovskites is formed by the corner-sharing octahedra (see Figure 1). There exist RUM branches covering special lines in the BZ^[55]. They are shown in Figure 10. Application of Eq. (3) to the M-R RUM branch allowed revealing the MLRUM shown in Figure 11.

Figure 10 : Brillouin zone (BZ) of perovskite crystals.

The BZ directions corresponding to RUM branches are along R-M-R lines, namely coincide with the cube edges.

Figure 11 : Eigenvector of MLRUM in perovskites.

(a) The MLRUM is perpendicular to the figure plane. + and – signs represent respectively shifts up and down with respect to the plane of the figure. Tilting octahedra are highlighted.

(b) The MLRUM is represented in the figure plane. Eigenvectors are shown in the upper left octahedra by small arrows. Octahedra rotated clockwise are shown in grey, those rotated counter-clockwise are left in white. $\vec{A}$ and $\vec{B}$ are elementary translations leaving the RUM pattern invariant.

Our simulations show that in the case of perovskites, there exists only one MLRUM, the pattern of which is presented in Figure 11. In fact this is an abuse of language to speak about “one MLRUM” because one should in fact more adequately say that there is one class of symmetry equivalent MLRUMs.

Consider the map shown in Figure 11-b and suppose that the plane of the shown MLRUM (MLRUM₁ noted η_1), is normal to crystallographic axis $\vec{c}$. The plane of this MLRUM is defined by $\vec{a}$ and $\vec{b}$ the basic vectors of the unit cell of parent phase, but translations by $\vec{a}$ and $\vec{b}$ do not leave the MLRUM pattern invariant: as shown in Fig. 11-b the elementary translations leaving the pattern invariant are $\vec{A}$ and $\vec{B}$:

$$\vec{A} = \vec{a} - \vec{b} \text{ and } \vec{B} = \vec{a} + \vec{b} \quad (4)$$

Along crystallographic direction $\vec{c}$ no translation leaves the pattern of Figure 11-b invariant. With respect to the translation group of the parent phase, the translations by $\vec{a}$, $\vec{b}$ and $\vec{c}$ are lost in the structure of an isolated MLRUM. As a consequence, applying lost translations to the patterns of Figure 11 allows to generate all translational variants of MLRUM₁ namely:

$$\begin{aligned} \text{MLRUM}_a &= \mathcal{T}_a(\eta_1); \text{MLRUM}_b = \mathcal{T}_b(\eta_1); \text{MLRUM}_c = \mathcal{T}_c(\eta_1); \dots \\ \text{MLRUM}_{nc} &= \mathcal{T}_{nc}(\eta_1), n \text{ taking all integer values between } -\infty \text{ and } +\infty \\ \text{MLRUM}_{a+nc} &= \mathcal{T}_{a+nc}(\eta_1) = \mathcal{T}_{nc}(\text{MLRUM}_a) \end{aligned}$$

where $\mathcal{T}_x$ is the operation of translation by vector x .

The two-dimensional cell defined by **A** and **B** being twice larger than the cell defined by **a** and **b**, there are two translational variants and MLRUM_a and MLRUM_b coincide. As can be seen in Figure 13 the eigenvectors differentiating MLRUM_a from MLRUM_b are opposite, so that we write $\text{MLRUM}_b = -\text{MLRUM}_a$

Along **c** naturally all structures generated by translations are different, and are distinguished from others by their position with respect to the origin.

As a conclusion there exist two patterns deduced from each other by a translation by **a** in the basal plane, and each of them may be located at different **c**-coordinates.

The same analysis can be performed with all symmetry operations of space group $Pm\bar{3}m$. Among symmetry operations belonging to a layer group, there are two types:

- side preserving operations, mapping each half space on both sides of the planar object into itself (keeping the normal invariant)
- side reversing symmetry operations (mapping the normal to its opposite)

In the space group $Pm\bar{3}m$ for the considered orientation of MLRUM (we consider the orientation normal to **c**, namely to z direction), the side preserving operations are mirrors containing z and rotations around z, namely 4z and 2z. Among them symmetry operations keeping the pattern of Figure 11 b invariant can be seen in Figure 12 so that they belong to the layer group of the MLRUM, together with mirrors m_x and m_y .

Figure 12: Layer group describing the MLRUM symmetry

(a) Pattern of rotated octahedra of fig. 11-b and symmetry operations leaving it invariant

(b) Corresponding layer group (No 63, $p4/mbm$) in its standard orientation according to the ITC vol. E (subperiodic groups)^[62]. $\vec{A}$ and $\vec{B}$ are the elementary translations shown in Figure 11-b. Fig. 12-b is rotated by 45° from Fig. 12-a and Fig. 11.

Side reversing operations are mirror m_z , and rotations $2_x, 2_y, 2_{xy}$. All belong to the layer group (keep the pattern invariant) as shown in Figure 12. Other operations of the space group not belonging to the layer group transform the MLRUM pattern in a symmetry equivalent variant: applying any of them to $MLRUM_1$ allows to generate symmetry equivalent MLRUMs (of different orientation along $\langle 100 \rangle$ directions). In a given direction one can easily see that there are only two variants as shown in figure 13 a&b. As mentioned, the interest of MLRUMs is that combining them allows to generate all possible phases characterized by rotations of octahedra. From the considerations above, it appears that the unique knowledge of the structure of the cell ($\vec{A}, \vec{B}$) allows to generate all tilt phases. We call **skeleton** the pattern of eigenvectors within the cell ($\vec{A}, \vec{B}$), from which all structures can be built.

In perovskites, all tilt-phases can be constructed by combining the unique skeleton to

its symmetry-related variants.

Figure 13: MLRUM states in a given orientation

(a) MLRUM₁ (see text)

(b) The second MLRUM state, obtained from (a) by lost translations in the plane, or by lost point group operation leaving the plane invariant

V.2 MLRUMs in TTB

Our simulation results show that there exist RUM branches covering special lines in the BZ^[47]. They are shown in Figure 14 by thick lines R-S-R and Z-S-A. The unit cell of the TTB lattice and the corresponding BZ are shown in Figure 2b and Figure 14. Special points within BZ are $Z=(00\frac{1}{2})$, $A=(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and $R=(0\frac{1}{2}\frac{1}{2})$. For all these $\mathbf{k}$ -points, our calculations revealed the existence of two RUMs. Moreover, the calculations indicated the presence of two RUM branches along the Z-A and R-S-R directions. Application of Eq. (3) to the RUMs corresponding to the Z-A branch allowed revealing the MLRUM shown in Figure 15-a.

Figure 14: Upper half of Brillouin zone (BZ) of TTB crystal

The Γ point is at the center of BZ. Orientation is given in central part of figure but arrows do not indicate the length of reciprocal vectors.

The BZ directions corresponding to RUM branches are shown as thicker coloured lines along R-S-R and Z-S-A directions.

Analogously, application of Eq. (3) to the RUMs corresponding to the R-S branch allowed revealing the MLRUM shown in Figure 15-b. We see that there exists no symmetry operation of the parent phase relating both structures, that are described by different layer group symmetries.

In TTB all tilt structures can be generated by the combination of two RUMs, namely by the combination of two distinct skeletons and their symmetry related variants, a situation more complex than in perovskites.

V.3 MLRUMs in quartz

Quartz is the most widely spread modification of silica. The corner-sharing tetrahedra in the quartz lattice form the hexagonal lattice with the three-membered and six-

Figure 15: Eigenvectors of two independent MLRUMs in TTB crystals.

The RUMs are localized within the layers perpendicular to the figure plane. Tilting octahedra are highlighted.

(a) MLRUM corresponding to RUM along the Z-A branch

(b) MLRUM corresponding to RUM along the R-S branch

(adapted from ref. [47])

Figure 16: Brillouin zone BZ of β -quartz crystal

The BZ plane corresponding to RUM branches is shown in different color (plane $\Gamma - K - M$). One RUM exists at any arbitrary $\mathbf{k}$ -point in this plane, another RUM branch exists along the $A - H - L - M$ path, and one triply degenerate RUM exists along $\Gamma - A$ line.

membered infinite spirals. The non-tilted quartz structure (called β -quartz) is shown in Figure 7-a. The total set of the RUMs in β -quartz is rather large^[55]. The totality of corresponding $\mathbf{k}$ -points is shown in Figure 16.

Analysis of RUMs has also been performed with a special attention to the case of quartz analog FePO_4 [63].

Simulation results show that one RUM exists at any arbitrary $\mathbf{k}$ -point belonging to the whole Γ -K-M plane (shown in Figure 16 in different color). In addition, one RUM branch exists along the A-H-L-M path (see Figure 16). Besides, one triply degenerate RUM exists along the Γ -A line (see Figure 16).

In view of these facts, the foregoing considerations allow the following suggestions:

1. There must be one MLRUM localized within a chain parallel to z-axis. This MLRUM gives rise to the RUMs with $\mathbf{k}$ -points covering the Γ -K-M plane.
2. There must be one MLRUM localized within a plane perpendicular to the $(\xi 00)$ direction. This MLRUM gives rise to the RUMs with $\mathbf{k}$ -points on the Γ -M line.
3. There must be three MLRUMs localized within planes perpendicular to the (00ξ) direction. This MLRUM gives rise to the triply degenerate RUM with $\mathbf{k}$ -points on the Γ -A line.

The identification of atomistic pattern of the MLRUMs in quartz is not evident. We have solved the problem by analyzing eigenvectors of the RUM along various BZ directions.

It is relatively easy to determine the atomistic pattern of the MLRUMs localized within the planes. Such a MLRUM perpendicular to the (00ξ) direction is shown in Figure 17-a. One can see that the localization area is a layer which includes three successive planes of tetrahedra.

The tetrahedra in the two exterior planes swing, and the tetrahedra in the interior plane (shown in white) rotate. There are three planes of tetrahedra per one unit cell of β -quartz. Each of them can be taken as the interior one. Correspondingly, the MLRUMs corresponding to $\mathbf{k}$ -vectors in the Γ -A direction are triply degenerate. The MLRUM localized within the layer perpendicular to the $(\xi 00)$ direction is shown in Figure 17-b. One can see that the localization area also includes three successive planes of tetrahedra.

The tetrahedra in the two exterior planes swing, and the tetrahedra in the interior plane rotate. Summarizing, we can conclude that atomistic patterns of the MLRUMs which give rise to the tilt structures modulated in the $(\xi 00)$ and (00ξ) directions are three-layered sandwich-like excitations. Patterns shown in figure 17 have symmetries described by layer groups (subperiodic groups with two-dimensional translations).

Figure 17: Eigenvectors of MLRUM localized within the layer perpendicular to the (00ξ) direction (a) and the $(\xi 00)$ direction (b) in β -quartz.

Atomic displacements are shown by arrows, tilting tetrahedra are highlighted, rotating tetrahedra are shown as white.

Figure 18: Eigenvectors of MLRUM localized within chain-like area perpendicular to the $(\xi\xi0)$ plane in β -quartz.

Atomic displacements are shown by arrows. The tetrahedra accomplishing large tilting displacements are those in the center of the figure, their eigenvectors are shown as bold arrows.

To reveal the MLRUM localized within a chain-like area running along the (00ξ) direction, we have analyzed eigenvectors of the RUMs along the Γ -K direction. The results are shown in Figure 18. One can see that, strictly speaking, the eigenvector of this MLRUM is delocalized over the whole lattice. However, displacements of the atoms within one spiral chain (shown by bold arrows, center of the figure) are markedly larger than in the rest of the lattice. The mode can be roughly characterized as tilting of the tetrahedra localized within the six-membered spirals (the 6 octahedra in the center of fig. 18). This MLRUM may give rise to doubly modulated tilt structures with the modulation vectors within the ab -plane, as observed in quartz^[64] and its analog AlPO_4 ^[65] in a narrow temperature interval between α and β phases.

This structure is also interesting because it is an example of linear structure the symmetry of which is described by a rod group (subperiodic group with one-dimensional translations).

VI. Facing experimental results

As already mentioned, the analysis of RUMs allows to find all Glazer's tilt phases in perovskites, but it allows to predict more than that due to the forecasting of RUMs not only at particular points R and M, but also all along the lines joining these points (the computed phonon modes show a zero frequency along these lines).

This "softness" allows to expect the appearance of an infinity of distorted phases modulated with incommensurate wave vectors or modulated with commensurate wave vectors possibly of high order.

Temperature-composition, temperature-pressure phase diagrams and various dopings have been investigated in perovskites, and results reveal a large variety of different phases. Modulated phases were observed in the phase diagram of PZT^[66], of PZS^[67], and as the result of doping, in particular by La^[68]. Complex stars of modulation wave vectors were reported around M point of BZ^[69] in PZT for low concentration of Ti (R point of BZ is also involved in this region) and a competition between different tilt-modes (namely RUMs) was invoked to explain the structure of an incommensurately modulated phase in layered perovskite, $\text{Li}_{0.5-3x}\text{Nd}_{0.5+x}\text{TiO}_3$ (LNT)^[70].

The availability of low energy branches along R-M-R directions opens the possibility that small perturbations of the structure as due to doping, or composition changes, could lead to a complete softening at general points between R and M points. The underlying mechanism could be of the same type as that evoked by Levanyuk and Minyukov several years ago^[71] that led them to predict the existence of modulated phases in solid solutions of ferroelectric materials. The mechanism involved a coupling between an atomic concentration C and the soft phonon (polar) branch in the form of a Lifshitz-like invariant (see eq. (5) where P_z is the polarization) that may lead to the appearance of a modulated phase, predicted on the basis of minimization of the thermodynamic potential:

$$P_z \frac{\partial \delta C}{\partial z} - \delta C \frac{\partial P_z}{\partial z} \quad (5)$$

Such mechanisms require the presence of low energy phonon branches the presence of which may be considered in general case as questionable. Most evident candidates in general case are soft phonon, and acoustic branches. However in the case of FWSS we now established that such low frequency phonon branches exist and are RUMs.

In **TTB systems** the comparison between predicted structures and observed ones is interesting, this work was done for niobates in ref.[47]. Let us remark that RUM induced phases are ferroelastic – we named them “substructures” in ref. [47].

Considering polar subgroups of substructures allows to deduce all possibilities for RUM-induced ferroelastic-ferroelectric phases at low temperature.

As follows from above considerations we expect that RUM induced phases are characterized by a doubling of crystallographic **c**-axis, so that the phases in which the **c** parameter is unchanged, cannot result from a RUM condensation (see Table 1). Among phases in which the **c** axis is doubled, those in which the **a** and **b** crystal parameters are kept unchanged, cannot either result from a RUM condensation (except the phase with space group Pbnm (No 62, D_{2h}^{16}) in which **c** is doubled and **a** and **b** are unchanged [47]). On this basis we can conclude that cases presented in lines 1, 2, 3, and 11 of Table 1 are not directly related to a RUM condensation.

However we can notice an important aspect : if one considers the tilting oscillations of octahedra involved in RUMs (see Figure 15 and 19), it is obvious that the equatorial oxygen atoms move mainly in vertical direction (along c-axis) whereas the apex oxygen atoms move in horizontal direction (in **ab**-plane). Looking at atomic displacement parameters in the published TTB structures which do not involve the **c** parameter doubling [72, 73] allows to see that these features are observed. We can interpret this as due to a hidden doubling of the **c** parameter, which leads us to propose to reinvestigate those materials by means of techniques that would allow to evidence this doubling easily (for instance electron diffraction). This may thus apply to the

case of P4bm space group (line 1 in Table 1). This symmetry, polar along (001), could well correspond to the absence of any rotation, but XRD data and structure refinements show that oxygens present also a disorder^[74] that is consistent with RUM condensation as discussed above, which suggests that there is a hidden doubling of crystalline parameter in **c** direction. The same remark applies in fact to all cases “not directly related to RUM condensation” in Table 1, so that it would be interesting to

Figure 19: schematic representation of motion of corner atoms in RUMs
(compare with figure 15- **c** axis is in vertical direction)

reconsider these cases by searching carefully for evidence of cell parameters multiplication. Studying electron diffraction patterns on small single crystals should allow to determine if additional diffraction spots may be observed.

The second zone in Table 1 presents cases corresponding clearly to RUM condensation; related results of crystallographic studies reveal indeed unambiguously that the described phases are induced by rotations of octahedra.

In the third zone of Table 1 are presented “ambiguous cases” for which :

- the volume of the cell is larger than in the parent phase, consistently with a mechanism of RUM condensation
- deduced symmetries are not predicted by RUM condensation.

First this situation could be due in some cases to mistakes in the identification of space groups: for instance the structure of line 10 in Table 1, is close to the RUM induced structure $Ic2m$, that of $Bmm2$ (line 6) is very resembling with the RUM induced one with $Bbm2$ ^[47]. The cases of lines 4 and 7 (BNN and PKN) could dissimulate a doubling of c . It would be interesting to reinvestigate these cases, in particular that of line 4 where disorder on oxygens observed in BNN can be described as the superposition of two ordered $Ccm2_1$ or $Bbm2$ RUM-induced structures ^[47, 75].

Mention once again that when constructing possible phases generated by combining the skeletons and their symmetry-related variants, it is possible to find modulated phases. The modulation directions of these RUM-induced IC phases, given by the orientation of skeletons or MLRUMs, must be according to (110) and (1 -1 0).

Observed IC phases among the TTB compounds are precisely with modulation vectors along these directions, as seen in the cases of BNN ($Ba_2NaNb_5O_{15}$) of SBN, etc^[77, 78, 79]. This is in agreement with our proposition that IC phases in the TTB family could be induced by RUM condensation.

It is also noteworthy that the TTB family reveals temperature-composition phase diagrams rather similar to those observed in the perovskite family (compare for instance results of ref [66] and [86]). On the basis of this analogy, some regions in

Table 1: RUM induced phases, predicted and observed

(from results of ref. [46], numbering of lines is the same than in this ref.). SP means spontaneous polarization

	Compounds (*)	Space group	a_s, b_s, c_s	SP direction	Order /disorder	Reference
Cases not directly related to RUM induced ferroelastic structure						
1	BNN, BSN, PKLN	<i>P4bm</i> (No 100)	1, 1, 1	c_s	<i>o</i>	[72, 73, 76]
2	BNN, PKLN	<i>Pba2</i> (No 32)	1, 1, 1	c_s	<i>o</i>	[76], [80]
3	SBN	<i>P4bm</i> (No 100)	1, 1, 1	c_s	<i>d</i>	[74, 81]
11	SBN	<i>P4bm</i> (No 100)	1, 1, 2	c_s	INC	[78]
RUM induced ferroelastic structures						
5	BNN, SBN	<i>Ccm2₁</i> (No 36)	$\sqrt{2}, \sqrt{2}, 2$	c_s	<i>o</i>	[82], [83]
8	BNN	<i>Bbm2</i> (No 41)	$2\sqrt{2}, \sqrt{2}, 2$	c_s	<i>o</i>	[84]
9	SBN	<i>Im2a</i> (No 46)	$2\sqrt{2}, 2\sqrt{2}, 2$	b_s	<i>o</i>	[85]
Ambiguous cases						
10	BRTN	<i>Im2a</i> (No 46)	$\sqrt{2}, \sqrt{2}, 2$	c_s	<i>o</i>	[77]
4	BNN	<i>Cmm2</i> (No 35)	$\sqrt{2}, \sqrt{2}, 1$	c_s	<i>d</i>	[75]
6	SBN, CBN	<i>Bmm2</i> (No 38)	$\sqrt{2}, 2\sqrt{2}, 2$	c_s	<i>O</i> , INC	[83], [86]
7	PKN	<i>Cm2m</i> (No 38)	$\sqrt{2}, \sqrt{2}, 1$	b_s	<i>o</i>	[87]

(*) BNN: $\text{Ba}_4\text{Na}_2\text{Nb}_{10}\text{O}_{30}$; BSN: $(\text{Ba}_{0.67}\text{Sr}_{0.33})_5\text{Nb}_{10}\text{O}_{30}$; PKLN: $\text{Pb}_2\text{K}_4\text{Li}_2\text{Nb}_{10}\text{O}_{30}$; SBN: $(\text{Sr}_{0.67}\text{Ba}_{0.33})_5\text{Nb}_{10}\text{O}_{30}$; PKN: $\text{Pb}_4\text{K}_2\text{Nb}_{10}\text{O}_{30}$; CBN: $(\text{Ca}_{0.28}\text{Ba}_{0.72})_5\text{Nb}_{10}\text{O}_{30}$; BRTN: $(\text{Ba}_{0.67}\text{Re}_{0.33})_5(\text{TiNb})_{10}\text{O}_{30}$

phase diagrams of TTB, could also correspond to modulated phases.

Further investigations are needed to clarify this point. Another possibility that was mentioned on the basis of predictions based on RUM analysis, is a chaotic distribution of MLRUMs along (110) and (1 -1 0) crystallographic directions. Such a distribution whatever it is static or dynamic, should appear in diffuse scattering data, as diffuse

lines along the same directions. Precisely data of diffuse scattering obtained by X ray or electron diffraction, reveal such lines in those directions in various compounds with TTB structure, in particular in BNN and SBN of various compositions^[88, 89]. These data may be considered as a serious evidence of the corresponding new chaotic (static) states described in terms of RUMs, or of fluctuations “structured” by RUMs. A new phenomenon, not yet observed in any system, could also be a fluctuation of the modulation vector modulus itself in a given region of reciprocal space (in form of a breathing of the superlattice of MLRUMs).

These fascinating aspects will require further studies to be analyzed at the light of results of RUM simulations.

VII. Conclusion

The analysis of RUMs seems to be a relevant method to understand common features and differences between different compounds of various FWS types.

The idea of the localized Wannier excitations being applied to the Rigid Unit Modes leads to the concept of the Maximally Localized Rigid Unit Modes. Such modes have been already considered in studies of the different framework structures: perovskites [63], cristobalites [64] and tetragonal tungsten bronzes [46]. The application of the MLRUM concept to the quartz lattice is presented in this paper. It is asserted that the MLRUM concept is useful as universal basis for description of the whole RUM spectrum. Besides, the knowledge of the atomistic patterns of the MLRUM provides us with the tool to describe all possible tilt structures including the incommensurate ones, generated from the elementary objects called skeletons and their symmetry variants.

The existence of localized RUMs allows to assume that in certain circumstances there may occur disorder in their distribution along the soft branches direction, which leads to consider the possibility of existence of new states that would be chaotic, more disordered than usual incommensurate phases, and not periodic in one or several directions. Such phases were not predicted till now and could exist as a result of interactions between MLRUMs and defects of crystal lattice.

Incommensurate phases with multiple modulation vectors not belonging to the same star, were also reported recently, in a region with phases induced by RUMs^[68].

To conclude, the field of RUMs opens several interesting problems of crystallography and of physics of condensed matter. The main crystalline families concerned, concentrate quasi all interesting properties found in solid state physics, both from fundamental and practical points of view, and, in reason of the recent development of ferroic and multiferroic materials, it will be important to understand the details of structural properties of these materials, an argument more to bet on the development of the physics of RUMs.

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Simulations were performed by means of the open source software LADY^[91]

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