Compositional uniformity, domain patterning and the mechanism underlying nano-chessboard arrays

Santiago González¹, J M Perez-Mato¹, Luis Elcoro¹, Alberto García², Ray L Withers³ and Laure Bourgeois⁴

¹ Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, Universidad del País Vasco (UPV/EHU), Apartado 644, E-48080 Bilbao, Spain
² Institut de Ciència de Materials de Barcelona, (ICMAB-CSIC), Campus de la UAB, E-08193 Bellaterra, Spain
³ Research School of Chemistry, The Australian National University, Canberra, ACT, Australia
⁴ Monash Centre for Electron Microscopy (MCEM) and Department of Materials Engineering, Monash University, Clayton, Victoria, Australia

E-mail: wmppemam@lg.ehu.es (J M Perez-Mato)

Received 6 July 2012, in final form 27 September 2012
Published 9 November 2012
Online at stacks.iop.org/JPhysCM/24/495301

Abstract

We propose that systems exhibiting compositional patterning at the nanoscale, so far assumed to be due to some kind of ordered phase segregation, can be understood instead in terms of coherent, single phase ordering of minority motifs, caused by some constrained drive for uniformity. The essential features of this type of arrangement can be reproduced using a superspace construction typical of uniformity-driven orderings, which only requires the knowledge of the modulation vectors observed in the diffraction patterns. The idea is discussed in terms of a simple two-dimensional lattice-gas model that simulates a binary system in which the dilution of the minority component is favoured. This simple model already exhibits a hierarchy of arrangements similar to the experimentally observed nano-chessboard and nano-diamond patterns, which are described as occupational modulated structures with two independent modulation wavevectors and simple step-like occupation modulation functions.

(Some figures may appear in colour only in the online journal)

1. Introduction

Domain self-patterning on the nanoscale, particularly if the nanoscale chemical ordering can be engineered or tuned, is the goal of much research in the nanoscience and nanotechnology area. Potential applications include the use of the surfaces of such materials as templates for the assembly of molecular monolayers, for the reliable synthesis of functional nano-structured materials or for the structured adsorption of gas species. The recent discovery that tunable nanoscale ordering occurs spontaneously in the wide range, non-stoichiometric Li₁/₂−₃ₓNd₁/₂+ₓTiO₃, 0.02 ≤ x ≤ 0.12, solid solution [1] as well as in a variety of other A-site ordered perovskite-related phases [2, 3] is thus of intense current research interest. Guiton and Davies [1] demonstrated the existence of 2D, nanoscale compositional ordering in the Li₁/₂−₃ₓNd₁/₂+ₓTiO₃, 0.02 ≤ x ≤ 0.12, system via high angle annular dark field (HAADF) imaging and interpreted this result in terms of phase segregation arising from some kind of ‘ordered’ spinodal decomposition into Li₁/₂−₃ₓNd₁/₂+ₓTiO₃ nano-chessboard regions separated by narrow Nd₂/₃TiO₃ boundary regions. As an example, figure 1 shows the kind of nano-patterns that can be observed in this compound.

The 2D apparent phase separation into compositionally distinct areas described above is strongly reminiscent of the 1D atomic order that takes place in many compositionally flexible ordered phases. The list is very extensive, but one can cite for instance many binary and/or ternary alloy systems [4–6], reduced rutile structures such as the Ti₆O₂₇–₁ system [5, 7], ReO₃ related compounds such as
Figure 1. (a) A typical low resolution TEM image of the chessboard type nano-structure characteristic of a Li$_{1/2}$Nd$_{1/2}$TiO$_3$, $x=0.067$, sample. (b) A high resolution Bright field STEM image of this nano-chessboard array. The lighter regions are presumed to be Nd-poor and correspond to regions of stoichiometry Li$_1$NdTiO$_3$ while the darker boundary regions are presumed to be Nd-rich and correspond to the stoichiometry Nd$_2$TiO$_3$, according to [1].

Figure 2. HRTEM image of a striped ordering in B$_{1-x}$Ca$_x$FeO$_{1-x/2}$, $\sim$0.20 $< x < \sim$0.49, a perovskite-related phase viewed along an [001] projection direction. Stripes of width 5$a_p$ are realized for this particular grain (for details see [13]).

In this paper we show that these findings can be extended to the case of intrinsically two-dimensional patterns, which need two modulation vectors for their superspace description. These 2D pseudouniform arrangements appear in certain ranges of composition, and in some cases exhibit nano-chessboard-like features similar to those observed in the compounds mentioned at the beginning of this section. These patterns, resulting again from a basic drive to uniformity or maximal dilution within a lattice, involve a coherent arrangement of structural motifs, which is rather different from the idea of ordered spinodal decomposition or phase segregation that has been previously proposed.

The paper is organized as follows. In section 2 we review briefly the basic ideas and results on pseudouniform stripe orderings in a simple two-dimensional A$_{1-x}$B$_x$ binary model presented in [17]. In section 3 we discuss the features and superspace description of a different family of pseudouniform A$_{1-x}$B$_x$ orderings which are intrinsically two dimensional, including the determination of their two modulation vectors.
and their direct correspondence with the composition of the system. Finally, in section 4 we show how the above ideas can be useful to describe orderings in real systems.

2. Pseudouniform 1D stripe compositional ordering

The basic patterns appearing due to a drive to maximal dilution of minority motifs, abstracted from any other effects present in real systems, can be studied using a simple model of a square lattice with binary composition \( A_1 \cdots B_1 \), in which the B ‘atoms’ represent the minority motifs. In [17] the dilution drive was originally mimicked by isotropic Yukawa-type repulsive interactions between the B particles, and a simple lattice-gas simulated-annealing method was used to explore and generate pseudouniform patterns by minimizing the repulsion energy. For most compositions, stripe orderings of the type shown on figure 3 were found to optimize the lattice-ordered dilution of the B atoms. The stripes are formed by the concatenation of tiles, parallelepipeds delineated by B atoms, with a fixed composition and orientation within a stripe. For example, in figure 3(a), the B atoms (the larger black dots) are present in the proportion \( x = 5/12 \) and they achieve an ordered distribution as close as possible to uniformity by forming a sequence of B-rich and B-poor stripes of tiles with composition 1/2 and 1/3 respectively (the smaller, square tile contains one A and one B atom, while the larger tile contains one B and two A atoms). As the overall B fraction \( x = 5/12 \) is closer to 1/2 than to 1/3, the 1/2 stripe regions are dominant (by a ratio 3:2), and the 1/3 stripes have minimal width and are isolated, as if they could be considered minority motifs themselves, subject to a dilution drive. The stripe sequence and makeup follow strict rules based on the decomposition of the overall B fraction \( x \) in irreducible terms according to the Farey tree construction [17, 18]; for example, \( x = 5/12 \) can be decomposed as \( 1/2 \oplus 1/2 \oplus 1/3 \oplus 1/2 \oplus 1/3 \), where the \( \oplus \) notation indicates a simultaneous addition of numerator and denominator in the fractions (e.g. \( n_1/m_1 \oplus n_2/m_2 = (n_1 + n_2)/(m_1 + m_2) \)), which physically corresponds to the concatenation of two subsets of motifs of concentrations \( x_1 = n_1/m_1 \) and \( x_2 = n_2/m_2 \). This leads to the so-called uniform sequence [22323], which compactly indicates the composition and arrangement of the basic tiles in a pseudouniform stripe configuration.

Figure 3(b) shows an analogous stripe ordering for \( x = 3/14 \), where stripes with composition 1/5 and 1/4 are arranged according to the uniform sequence [554]. The stripe pseudouniform sequence corresponding to any other composition can be derived using the Farey tree construction, and in most cases it involves irreducible tiles of compositions \( 1/n \) and \( 1/(n + 1) \) bracketing the overall B fraction \( x \) [17]. These tiles can be seen as encoding at a local level the drive for dilution, and their overall arrangement according to the rules results in a pseudouniform intergrowth. Variations in the repulsive model potential cause small changes in the relative stability of different arrangements, so a purely repulsive criterion does not univocally lead to a single solution in two dimensions. Hence our consistent use of the term pseudouniform to refer to these orderings. Fine differences in stability are in practice irrelevant when one takes into account that the drive for dilution is a convenient but rough simplification of the state of affairs in real systems. This suggests that a fruitful approach to the problem of cataloguing pseudouniform orderings in two dimensions is to abstract the basic ingredients, which are the irreducible, locally uniform, tiles, and their juxtaposition into intergrowth arrangements following appropriate rules.

A key result of [17] is that the arrangements of the type shown in figure 3 can be considered as compositionally modulated structures with a single composition-dependent primary modulation wavevector (a 1D modulation). The Fourier spectra (square modulus of the geometric structure factor) of these two examples are shown in figures 3(c) and (d). One can see that the wavevectors \((5/12)(1, 1)\) and \((3/14)(2, 1)\), respectively, which are approximately orthogonal to the stripe direction, determine the location of the most intense satellite reflections stemming from the ordering. Within the superspace formalism originally developed to describe incommensurately modulated structures [19–21], these pseudouniform orderings can be described as long period but commensurate structures with a simple step-like occupational modulation, with values either ‘atom A’ or ‘atom B’ in the relevant proportion, and using those vectors as primary modulation wavevectors.
3. Pseudouniform 2D compositional ordering in a prototype A$_{1-x}$B$_x$ model

3.1. The snub-square ordering

In some circumstances more complex, essentially two dimensional, ordered configurations in the A$_{1-x}$B$_x$ system can become competitive and prevail (in the sense of maximal dilution) over the 1D striped arrangements studied in [17]. For the case of a square lattice and an ideal isotropic dilution drive this happens for compositions within the interval 1/5 < x < 1/4. This composition interval is special because the basic tiles corresponding to the compositions x = 1/4 and x = 1/5 can be juxtaposed with different orientations (the two sides of the two tiles have the same length), forming two-dimensional patterns (tilings). These 2D patterns were already considered in [22] in a simple context. Here we present a more complete picture of this family of orderings, their generating principles, and their description as modulated structures.

Simulations for the repulsive lattice-gas model mentioned in section 2 indeed confirm the apparition of intrinsically 2D ordered patterns in this composition range. Figure 4 shows the ground states obtained for a composition x = 2/9 for two different sizes of the simulation supercell (subject to periodic boundary conditions). The pseudouniform stripe arrangement with sequence [45], in agreement with the rules explained in section 2, was obtained for a minimal 9 × 9 supercell (figure 4(b)). But for a 12 × 12 supercell, a completely different ordering pattern is stabilized (figure 4(a)). It has the form of a so-called snub-square tiling (as in [23], but with a slight modification: the rhombic 1/4 tile is formed by two isosceles triangles instead of the equilateral triangles of the canonical snub-square tesselation). This ordering pattern (henceforth SSQ ordering) prevails in the simulations over the stripe arrangement if the boundary conditions are compatible with both types of orderings.

A comparison of the distribution of B–B distances points to the main reason for the prevalence of the SSQ ordering over the striped one. As pointed out by Watson [22], both have the same distribution of B–B interatomic distances up to $\sqrt{10}$ (in cell parameter units of the underlying square lattice), but the SSQ ordering avoids the next distance $\sqrt{13}$ associated with neighbours separated by a vector (3, 2) or (2, 3), which is present in the striped arrangement. Figures 4(c) and (d) presents sketches of the Fourier spectra of the SSQ ordering and of the competing striped arrangement. They clearly show the primary modulation wavevector(s) that can be identified in each case. The superstructure reflections of the striped arrangement can be indexed as linearly arranged satellites, with the strongest one being given by the modulation wavevector $\mathbf{q} = (2/9)$ (2, 1), in accordance with the rules established in [17]. The diffraction pattern of the SSQ ordering requires instead two primary wavevectors for a simple indexation of the satellite reflections, and the strongest satellites indicate the most obvious choice: $\mathbf{q}_1 = (1/2, 1/6)$ and $\mathbf{q}_2 = (-1/6, 1/2)$.

The relevance of the SSQ-type arrangements as 2D orderings that could maximize somehow the uniformity of the distribution of a minority component for some specific compositions was pointed out in [22]. We stress here that these configurations are indeed observed as ground states in simulations of lattice-gas models with repulsive interactions that mimick an isotropic drive to uniformity. In the following we will show their hierarchical structure when they are interpreted in terms of uniform sequences, and how they can produce nano-chessboard and nano-diamond patterns. In this framework, it will be shown that this type of arrangements, when described as compositional modulated structures, have some simple basic common ingredients which
can be generalized and applied to explain and rationalize orderings in real systems generated at least in part by a drive to maximal uniformity, including ordered patterns in the nanoscale.

3.2. Generalization of the snub-square ordering for any composition between 1/4 and 1/5.

The SSQ ordering for \( x = 2/9 \) can be seen as a perfect array of intercrossing ribbons, each one formed by single tiles arranged in a 1/4 \( \oplus \) 1/5 sequence. (From now on, to emphasize the actual arrangement of motifs in a sequence, we will use a slightly modified notation: \{45\} indicates in this case an alternating sequence of 1/4 and 1/5 tiles, while the \{\} form will be reserved for pure numerical Farey term sequences for a specific concentration. In the stripe-ordering cases both notations are equivalent.) This topology, which avoids the distance \( \sqrt{13} \) present in the stripe arrangement, can be generalized to any other composition in the interval \( 1/5 < x < 1/4 \) [22]. For compositions different from 2/9, it is not possible to avoid the \( \sqrt{13} \) distance completely, but in general the B–B distance distribution will still be favourable when compared to the stripe ordering. Following the argument in section 3.1, we will discuss these generalized SSQ orderings in terms of our basic mechanism of juxtaposing appropriate tiles following certain rules, and we will not be concerned any more with detailed questions of maximal stability within a repulsive model. Figure 5(a) shows an example of a generalized SSQ ordering with \( x < 2/9 \). It corresponds to the case \( x = 9/41 \), and is characterized by the crossing of two kinds of ribbons, one corresponding to the tile sequence \{554\} (shown in the figure with shaded 1/5 tiles) and the other to the sequence \{445\}. In each ribbon, the minority tiles appear in a proportion 1/3, and the \{445\} ribbons are also a minority in a proportion 1/3. The minority ratio 1/3 (which we will henceforth denote by \( \alpha \)) is thus a key parameter in the construction of a pattern. In fact, if we take abstract motifs \( a \) and \( b \), both the tile sequence in each ribbon and the ribbon arrangement sequence are instances of the physical sequence \{aab\} (uniform sequence [3]), as befits a concentration \( \alpha = 1/3 \). By comparison, for the SSQ ordering for \( x = 2/9 \) in figure 4(a), \( \alpha = 1/2 \), which corresponds to a simple alternation of 1/4 and 1/5 tiles on each (identical) ribbon and a simple alternation in the ribbon arrangement (uniform sequence [2]) for \( \alpha = 1/2 \).

The parameter \( \alpha \) fully characterizes the generalized SSQ orderings by determining the hierarchical tiling arrangement, both at the level of each ribbon, and at the level of ribbon kinds. As it relates to a minority concentration, we can take without loss of generality \( \alpha \leq 1/2 \), and the general relation between \( \alpha \) and \( x \) is given by [22]:

\[
x = 2 \frac{\alpha^2}{9 \pm (1 - 2\alpha)^2}
\]

where the plus sign in the denominator corresponds to \( 1/5 < x < 2/9 \) (with 1/4 tiles underrepresented), and the minus sign to \( 2/9 < x < 1/4 \) (with relative abundance of 1/4 tiles).

Figure 5(b) shows the corresponding arrangement for a composition much closer to 1/5, \( \alpha = 1/9 \) (\( x = 81/389 = 0.208 26 \)). This ordering optimizes the distribution of B–B interatomic distances towards larger values by forming large squares of composition \( x = 1/5 \), separated by single ribbons with an inverted 1/9 proportion of 1/5 tiles, in an effective sequence \{444444445\}. Despite the large size of the square blocks, the system cannot be considered subject to phase segregation. On the contrary, the regions with different local composition are coherently interleaved and ordered as a single phase. Paradoxically, it is the quest for uniformity that can drive the system into this type of chessboard orderings. For \( \alpha \) values of type \( n/m \), the patterns become more complex, as the ribbons with a proportion \( n/m \) of basic tiles of type either 1/4 or 1/5 must be ordered according to a 1D nontrivial pseudouniform sequence of the type explained.
in the section 3.1. The presence of 1D uniform sequences (derived from the Farey tree construction) along the individual ribbons is in fact the signature that the ordering is being driven by a uniformity quest. Figure 6 shows two examples for $\alpha = 2/7$ and $3/7$. One can see in this figure that a more complex uniform sequence is realized in the way the $1/4$ and $1/5$ basic tiles are arranged along each oblique ribbon, with either $1/4$ or $1/5$ tiles as minority in a proportion $\alpha$. For $\alpha = 2/7 = 1/3 \oplus 1/4$, the relevant abstract uniform sequence is $\{aabaaab\}$ (i.e. [34]), leading to interlocking ribbons of the form $\{4454445\}$ and $\{5545554\}$, which themselves are in a proportion $2/7$ with the same sequencing.

For a rational value of $x$, the corresponding $\alpha$ according to (1) is in most cases irrational, and therefore the generalized SSQ ordering for that $x$ is incommensurate with respect to the underlying lattice. The ribbons of basic tiles will follow an aperiodic uniform sequence corresponding to the irrational value of $\alpha$, still according to the Farey tree construction [17]. Thus, the tendency to uniformity could conceivably stabilize 2D incommensurate orderings of minority motifs even if their proportion is a simple rational value. For instance, the generalized SSQ ordering for $x = 3/14$, which competes with the stripe arrangement shown in figure 3(b), would be an incommensurate ordering with $\alpha$ having an irrational value close to $2/9$.

Within the interval $2/9 < x < 1/4$ the number of $1/4$ tiles is larger than that of $1/5$ tiles, and the ordering patterns follow then the same rules but with the roles of the two types of basic tiles interchanged, such that the ribbons having a proportion $\alpha$ of $1/5$ tiles become majority. As $x$ approaches the composition limit $x = 1/4$, blocks of density $1/4$ increase in size, forming patchwork patterns of diamond shape, as shown in figure 7.

We see that the $\alpha$ parameter acts as an auxiliary ‘minority concentration’, controlling the arrangement of the $1/4$ and $1/5$ basic tiles, which in themselves encapsulate a maximal local uniform ordering. The only other essential ingredient that makes the SSQs orderings more uniform than the stripe arrangements for the same composition is the intercrossing feature that tends to eliminate as much as possible the $\sqrt{13}$ distance.

3.3. Description of uniformity-driven 2D orderings as modulated structures

Although the generalized SSQ orderings discussed above present a large variety of arrangements, their diffraction
patterns are very similar. They exhibit a strong hierarchy in the intensity of the superstructure reflections, characteristic of modulated structures (see figures 4, 5, and 7). The strongest superstructure reflections can be taken as first-order satellites, and define the primary modulation vectors, while the remaining ones can be indexed as higher-order satellites. In section 3.1 we showed the primary modulation wavevectors that can be associated with the \( x = 2/9 \) SSQ ordering. These are particular values among those that can be obtained for generalized SSQ arrangements, which depend on the composition according to simple rules of geometrical origin. In figure 5(c), for example, the second-order satellite (11) lies along the line joining two first-order satellites, and at distances from them which are fractions \( \alpha \) and \( 1 - \alpha \) of the length of the line. This constraint, together with a simple symmetry argument (existence of a symmetry plane for \( x > 2/9 \), and tetragonality for \( x < 2/9 \)), is enough to fix the modulation vectors. To be short, we only describe those corresponding to the cases with \( 1/5 < x < 2/9 \). In this interval, the two modulation wavevectors are given by the equations:

\[
\begin{align*}
q_1 &= \left( \frac{1}{2} - \frac{x(1-2\alpha)}{2}, \frac{1-3x}{2} \right) \\
q_2 &= \left( \frac{1}{2} + \frac{3x}{2}, \frac{1}{2} + \frac{x(1-2\alpha)}{2} \right)
\end{align*}
\]

and are an explicitly tetragonal and right-handed set, best suited for the construction of the superspace model to follow. (There is an alternate choice of modulation vectors \( k_1 = q_1 \) and \( k_2 = (1, 0) - q_2 \), with the extra property that \( k_1 \times k_2 = x \). Also, these ‘natural’ vectors are reciprocal to the real-space vectors defining a ‘virtual’ monatomic unit cell that best approximates the uniform motif distribution with density \( x \) (in correspondence with the concept described in [17]).)

The SSQ ordering can now be described as a modulated structure with the modulation vectors of equation (2) and with an occupational modulation defined by a function \( f(x_4, x_5) \), of period 1 for both variables, such that the atom occupying a given lattice site \( m = (m_1, m_2) \) is determined by the value (either ‘atom A’ or ‘atom B’) of \( f(x_4, x_5) \) for \( x_4 = q_1 \cdot m \) and \( x_5 = q_2 \cdot m \). Maps of the function \( f(x_4, x_5) \) sampled at the discrete values of \( x_4 \) and \( x_5 \) that correspond to the SSQ orderings considered so far are shown in figure 8. As it happens in the 1D case, the domain with value ‘atom B’, corresponding to the minority motifs, forms a single compact/dense region with an area equal to their proportion \( x \) in the lattice. Thus the minority atoms B aggregate in the internal space of the occupational modulation function in order to describe arrangements in which these atoms are maximally scattered in real space. (As remarked above, for irrational \( \alpha \) one would obtain from equation (2) incommensurate wavevectors, and the sampling of the A- and B-valued domains would be continuous.) The B atomic domains have in all cases a form which avoids the occupation by B atoms of two neighbouring lattice sites. This restriction is ensured by the geometrical condition shown in figure 8: The B atomic domains, if translated on the plane \((x_4, x_5)\) by either \((q_1 \cdot (1, 0), q_2 \cdot (1, 0))\) or \((q_1 \cdot (0, 1), q_2 \cdot (0, 1))\), juxtapose with the original one, with no superposition. Within the superspace formalism this is termed ‘closeness condition’, and is known to be satisfied by the atomic domains describing some quasicrystals [24, 25]. The atomic domain borders can be taken parallel to the basis vectors of the point lattice in internal space formed by the points \((q_1 \cdot m, q_2 \cdot m)\), where \( m \) represents the direct lattice points. This, together with the closeness condition and equation (2), is sufficient to define the appropriate atomic domain B for any composition \( x \), and to construct with it its corresponding SSQ ordering.

4. Uniformity-driven orderings in real systems

We have considered above an idealized A\(_1\)\dots B\(_m\) model for which the optimal ordering within a lattice depends only on the maximization of the dilution of minority motifs. In real systems this factor can be one among many others. For instance, intrinsic anisotropies of the underlying crystalline lattice, energy constraints on possible orderings (for instance, compatibility with rigid unit modes, chemically forbidden geometries, etc) can play a fundamental role in favouring a particular ordering pattern. Nevertheless, if an effective dilution still retains a main role in these realistic scenarios, some of the features of the purely uniformity-driven orderings are very likely to be maintained. One of the features which are present in the above discussion is the possibility of constructing the orderings through the juxtaposition (intergrowth) of basic tiles. These encapsulate at the local level the drive for dilution, and their combination, as we have seen, can lead to a variety of patterns, depending on the...
geometrical flexibility involved. Figure 9(a) shows a sketch of the ordering pattern of oxygen vacancies observed in layers of the compounds La$_8$–$_5$Sr$_3$Cu$_9$O$_{20}$. (La, Sr)$_3$Cu$_8$O$_{18}$ and La$_2$Sr$_2$Cu$_9$O$_{16}$ [26]). To our knowledge, this is the first time that this ordering is interpreted as a tiling, similar to the SSQ, but with tiles of composition 1/3 and 1/5, so that the global vacancy density is 1/4. In this case the ordering is not optimizing a purely repulsive interaction (which would lead for this composition to a monatomic superlattice of vacancies), but the drive for dilution is still obviously present. Considered as an abstract geometrical and numerical exercise, the combination rules for the 1/3 and 1/5 tiles lead to the same kind of regularities discussed above for the 1/5, 1/4 tiles, including the appearance of coherent generalized nano-patches (nano-rhombi in this case) [27]. Crucially, all the arrangements produced through the 1/5–1/3 tile combinations are also describable as occupationally modulated structures, with compact atomic domains in the superspace construction, and with modulation vectors that can be read directly from the diffraction diagram. For the case of the vacancy distribution in figure 9(a), the primary modulation wavevectors can be chosen as $q_1 = (1/2, 1/4)$ and $q_2 = (-1/4, 1/2)$, as seen in the diffraction diagram of figure 9(b), and the corresponding modulation function is shown in figure 9(c). The four independent vacancies within the 16 atomic sites form again a single simple B-valued atomic domain fulfilling the closeness condition described above. This real example shows once more that these modulation functions are very efficient for distributing regularly minority motifs in real space.

With all the evidence presented so far (here and in the previous work over several years [28, 9, 29–32]) we can say that in a real system the knowledge of the relevant modulation vectors (extracted from its diffraction diagram) is sufficient to design, through the rules explained above, a compositionally modulated model which corresponds to an atomic ordering with a high degree of uniformity in the distribution of some specific motif. Thus we can postulate an atomic distribution model with a specific composition and a maximal dilution consistent with the observed modulation vectors. If a drive for dilution is at work, this a priori model should approximate the experimental arrangement. This clearly occurs in the example shown in figure 9, and also seems to happen in the nano-chessboard arrangements observed in the compounds mentioned in section 1. As shown below, the basic features of the latter can be reproduced in a simplified binary system by postulating a compositionally modulated arrangement with step-like atomic domains that fulfill the closeness condition, and are consistent with the observed modulation vectors. This would indicate that the observed arrangements represent some optimization of the dilution of the atoms within the underlying perovskite lattice, but subject to some anisotropic constraints that force the possible modulation vectors.

Let us consider for instance the compound Li$_{1/2}$–$_{3y}$Nd$_{1/2+y}$TiO$_3$ mentioned in the introduction. Figure 10 shows a [001] zone electron diffraction pattern (EDP) of this material with $y = 0.067$ (we change the letter for the composition variable to avoid confusion with that employed in our binary toy model). The primary modulation wavevectors can be identified directly from the EDP diagram as $q_1 = (1/2 - \epsilon, -1/2)$ and $q_2 = (1/2, 1/2 - \epsilon)$ with $\epsilon$ about 1/30. One cannot pretend to derive from this information a quantitative structural modelling of this compound, but we can determine for our simple 2D A$_1$–B$_x$ binary system a pseudouniform ordering of the B atoms consistent with these modulation vectors. Using the rules explained above, we have to consider an occupational modulation function $f(x_4, x_5)$ fulfilling the closeness condition for these modulation vectors (see figure 11(b)). This simple step-like function yields the
atom ordering shown in figure 11(a), which vividly recalls the nano-chessboard arrangements observed in this compound. The square patches have composition AB, while the global excess of A atoms are localized at the interfaces, which are made only of A atoms and are limited to two unit cells of the underlying lattice. By construction, the composition of this \( \text{A}_{1-x}\text{B}_x \) nano-chessboard arrangement is fully determined by the modulation vectors, and is given by the relative area of the B atomic domain in figure 11(b), which is \( x = 1/2 - \epsilon + \epsilon^2 \), i.e. \( x = 421/900 = 0.467778 \). Obviously this composition is not comparable with that of \( \text{Li}_{1/2-\epsilon}\text{Nd}_{1/2+\epsilon}\text{TiO}_3 \). The arrangement of figure 11 is far from the real system, not only due to the reduction to a 2D \( \text{A}_{1-x}\text{B}_x \) arrangement, but also because the vacancies accompanying the Nd/Li substitution and the expected very large positional relaxations are ignored.

But nevertheless, this simple occupational modulation, with an intrinsic tendency to uniformity and consistent with its modulation vectors in a binary system, is sufficient to reproduce basic features of the real system. Notice for instance the shift of the A and B occupation sites in contiguous patches of composition \( \text{A}_{1/2}\text{B}_{1/2} \) of the chessboard, as proposed in the model for \( \text{Li}_{1/2-\epsilon}\text{Nd}_{1/2+\epsilon}\text{TiO}_3 \) of [1]. Figure 11(c) shows the geometric diffraction pattern of this 2D \( \text{A}_{1-x}\text{B}_x \) nano-chessboard arrangement. It is remarkable that despite the strong anharmonicity of the occupational modulation only odd-order satellites are observable. This is consistent with the Fourier decomposition of the underlying two-dimensional step-like occupational modulation. In the real system even-order satellites close to the main reflections are also significant, which is probably due to the strong displacive modulations in the perovskite framework (mainly tiltings), induced by the cation ordering. This can be a plausible explanation, since by just introducing a small displacive sinusoidal modulation with wavevectors \( \mathbf{q}_1 \) and \( \mathbf{q}_2 \), and \( \mathbf{q}_1 - \mathbf{q}_2 \) of the A and B positions in the configuration of figure 11(a), we can produce a diffraction diagram similar to the experimental one of figure 10.

Nano-chessboards of the type reported in [1–3] may therefore originate in a drive for maximal uniformity in the

---

**Figure 10.** [001] zone electron diffraction pattern of the (3 + 2)-D incommensurately modulated, nano-chessboard phase of \( \text{Li}_{0.30}\text{Nd}_{0.657}\text{TiO}_3 \), indexed with respect to the basis set \( M^* = (a^* = a^p_1, b^* = b^p_0, c^* = 1/2c^p_0, \mathbf{q}_1 = 1/2a^p_1 + (1/2 - \epsilon)b^p_0, \mathbf{q}_2 = (-1/2 + \epsilon)a^p_1 + 1/2b^p_0 \) }, where the subscript \( p \) stands for parent perovskite, and \( \epsilon \sim 1/30 \).

**Figure 11.** (a) Chessboard nano-pattern in a square lattice of composition \( \text{A}_{1-x}\text{B}_x \), obtained as a compositional modulated structure with modulation wavevectors \( \mathbf{q}_1 = (1/2, 1/2 - \epsilon) \) and \( \mathbf{q}_2 = (-1/2 + \epsilon, 1/2) \) with \( \epsilon = 1/30 \) (i.e. those present in \( \text{Li}_{1/2-\epsilon}\text{Nd}_{1/2+\epsilon}\text{TiO}_3 \) ), and a step-like A/B occupational modulation function fully determined by the closeness condition of the B domains for these modulation vectors. This modulation function is shown in (b), where A and B-valued domains are depicted as dark and clear regions, respectively, within a 2D period of the function (i.e. a unit cell of the internal space in the superspace construction). The closeness condition satisfied by the neighbouring B-valued domains in the superspace description is shown by means of continuous lines corresponding to their projected borders. The corresponding geometric diffraction pattern is shown in (c).
distribution of a minority motif. If this were indeed the mechanism, the width of the interface regions between the chessboard patches, although clearly wider than in our model due to structural displacive relaxations, should be independent of the size of the patches, i.e. of the system composition. A careful check of the fulfilment or not of this property by the nano-chessboards observed in real systems would be a key feature for the validation of a uniformity-drive mechanism.

5. Conclusions

We have shown that a drive towards dilution of minority structural motifs constrained to an underlying lattice is sufficient to produce two-dimensional orderings with local composition variations in the nanoscale. The dilution can be achieved in practice by the combination or intergrowth of basic tiles that encapsulate a local repulsion of minority motifs. This combination principle is able to generate orderings that are hierarchically structured, adopting for certain compositions the form of nano-chessboards or diamond-like patches. In all cases, regions of two different effective compositions are interleaved coherently, with long-range order.

The mechanism leading to composition patterning from a dilution drive has already been documented in other systems: layer arrangement in compositionally flexible layered compounds [28, 9, 29–32], and two-dimensional systems exhibiting effectively 1D stripe patterns [17]. Here we find what appears to be a segregation of phases instead of a pseudouniform distribution, but these arrangements are in fact near-optimally uniform by any reasonable criterion, and their underlying structure (now essentially two dimensional instead of effectively 1D) can be described by the same recipe at work in the pseudouniform systems previously studied: modulation vectors directly and simply determined from the intensity distribution in the diffraction diagram, and step-like occupational modulations satisfying a closeness condition for these modulation vectors.

The description in terms of occupational modulations, best represented using the tools of the superspace formalism, is thus seen as the unifying structural principle in a wide variety of systems which exhibit in some degree a dilution drive. The key idea is that minority motifs maximally scattered in real space are represented by compact regions in the internal coordinates of the superspace construction.

We have shown that this powerful principle seems to be at work for two kinds of relevant experimental systems. In the case of the distribution of vacancies in La₈₋ₓSrₓCu₈O₂₀₋₄₋ₓ, (La,Sr)₂Cu₉O₂₄ and La₂Sr₆Cu₁₀O₁₆ [26], the resulting pattern can be seen also as a direct example of the tiling rules in real space. The nano-chessboard arrays, and similar patterns exhibiting composition patterning, that have been recently observed in composition flexible systems such as Li₁₋ₓ/₂₋₃₋ₓNd₁₋ₓTiO₃ are strongly reminiscent of the kinds of hierarchical real-space orderings that appear in uniformity-driven simple models. They reproduce basic features of the observed nano-chessboard arrangements, and their Fourier spectra exhibit the kind of strong hierarchical satellite structure present in the experimental diffraction diagrams. We can thus suggest that the observed compositional changes at the nanoscale in these compounds have their origin, at least partially, in a drive for uniformity, maintaining the coherency of a single phase, and are not, as previously proposed, due to any kind of phase separation.

Acknowledgments

This work has been supported by the Spanish Ministry of Science and Innovation (projects MAT2008-05839 and FIS2009-12721-C04-O3) and by the Basque Government (project IT-282-07). Technical and human support provided by IZO-SGI SGiker (UPV/EHU, MICINN, GV/EJ, ERDF, ESF) is gratefully acknowledged. RLW acknowledges financial support from the Australian Research Council in the form of ARC Discovery Grants. LB also acknowledges use of the facilities within the Monash Centre for Electron Microscopy.

References

[1] Guiton B and Davies P K 2007 Nature Mater. 6 586–91
[2] Garcia-Martín S, King G, Urones-Garrote E, Nenert G and Woodward P M 2011 Chem. Mater. 23 163–70
[3] Licurce M W, Borisevich A Y and Davies P K 2012 J. Solid State Chem. 191 220–4
[4] Schubert K, Kiefer B, Wilkens M and Hauffler R 1955 Z. Metallk. 46 692–715
[5] Terasaki O and Watanabe D 1971 Japan. J. Appl. Phys. 10 292–303
[6] Watanabe D and Takashima K 1975 J. Appl. Crystallogr. 8 598–602
[7] Bursill L A and Hyde B G 1971 Acta Crystallogr. B 27 210–5
[8] Bursill L A 1969 Proc. R. Soc. A 311 267–90
[9] Elcoro L, Perez-Mato J M and Withers R 2000 Z. Kristallogr. 215 727–39
[10] Schmid S, Thompson J G, Rae A D, Butler B D, Withers R L, Ishizawa N and Kishimoto S 1995 Acta Crystallogr. B 51 698–708
[11] Rae A D, Schmid S, Thompson J G, Withers R L and Ishizawa N 1995 Acta Crystallogr. B 51 709–21
[12] Michiue Y, Yamamoto A, Onoda M, Sato A, Akashi T, Yamane H and Goto T 2005 Acta Crystallogr. B 61 145–53
[13] Schiemen J, Withers R, Noren L, Liu Y, Bourgeois L and Stewart G 2009 Chem. Mater. 21 4223–32
[14] Janner A and Janssen T 1980 Acta Crystallogr. A 36 399–407
[15] Janner A and Janssen T 1980 Acta Crystallogr. A 36 408–15
[16] de Wolf P M 1974 Acta Crystallogr. A 30 777–85
[17] González S, Perez-Mato J M, Elcoro L and Garcia A 2011 Phys. Rev. B 84 184106
[18] Farey J 1816 Phil. Mag. 47 385–6
[19] Janssen T, Chapuis G and de Boissieu M 2007 From Modulated Phases to Quasicrystals (Oxford: Oxford University Press)
[20] Janssen T, Janner A, Looijenga-Vos A and de Wolf P M 1992 International Tables for Crystallography vol C, ed J A C Wilson (Dordrecht: Kluwer Academic) pp 797–835
[21] van Smalen S 2007 Incommensurate Crystallography (Oxford: Oxford University Press)
[22] Watson G I 1997 Physica A 246 253–74
[23] Grünbaum B and Shephard G C 1987 Tilings and Patterns (New York: Freeman)
[24] Cornier-Quiquandon M, Grattias D and Katz A 1992 Methods of Structural Analysis of Modulated Structures and
Quasicrystals ed J M Perez-Mato, F J Zúñiga and G Madariaga (Singapore: World Scientific) pp 313–32

[25] Katz A and Gratias D 1993 J. Non Cryst. Solids 153/154 187–95

[26] Hadermann J, Tendeloo G V and Abakumov A M 2005 Acta Crystallogr. A 61 77–92

[27] González S, Perez-Mato J M and Elcoro L 2011 unpublished

[28] Perez-Mato J M, Zakhour-Nakhl M, Weill F and Darriet J 1999 J. Mater. Chem. 9 2795–808

[29] Boullay P, Trolliard G, Mercurio D, Perez-Mato J M and Elcoro L 2002 J. Solid State Chem. 164 252–60

[30] Darriet J, Elcoro L, Abed A E, Gaudin E and Perez-Mato J M 2002 Chem. Mater. 14 3349–63

[31] Michiue Y, Yamamoto A and Tanaka M 2006 Acta Crystallogr. B 62 737–44

[32] Izaola Z, Gonzalez S, Elcoro L, Perez-Mato J M, Madariaga G and Garcia A 2007 Acta Crystallogr. B 63 693–702