

Superspace description of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ (a perovskite-related compound of the type $A_nB_nO_{3n+2}$) as a modulated layered structure

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The recently determined structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ is reanalyzed within the superspace framework. The material follows the general features of the superspace model proposed for the perovskite-related compounds of the general formula $A_nB_nO_{3n+2}$ [Elcoro *et al.* (2001). *Acta Cryst.* **B57**, 471–484]. It can be described as a commensurate modulated structure with discontinuous atomic domains given by occupational crenel functions. These atomic domains automatically introduce the layered configuration of the actual structure in real space. However, the displacive modulations follow a quite different pattern from that observed in the $\text{Sr}_n(\text{Nb,Ti})_n\text{O}_{3n+2}$ series, discussed in the above-mentioned reference. The superspace group relevant in this new case has been identified through a systematic search of all the possible groups and a comparison of the resulting superspace embeddings of the experimental three-dimensional structure. Being a commensurate structure, the fundamental ambiguity of the superspace description was broken by choosing the highest possible symmetry that yields smooth displacive atomic modulations and hence minimizes the number of parameters. The efficiency of the proposed superspace model is demonstrated with a new refinement of the structure. Assuming the model's general relevance, symmetry properties for the whole $[\text{Ca,Na}]_n\text{Nb}_n\text{O}_{3n+2}$ series are predicted.

1. Introduction

The structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ at room temperature has been determined recently (Zúñiga & Darriet, 2003). This compound is formed by perovskite slabs stacked along the $[110]_p$ direction, where the symbol p refers to the reference unit cell of the cubic perovskite structure. The compound can be considered as belonging to the general formula $A_nB_nO_{3n+2}$, with $n = 5$, and is related to the homologous series $\text{Sr}_n[\text{Nb,Ti}]_n\text{O}_{3n+2}$. All these compounds can be described as layered structures with the sequence of layers along the $[110]_p$ direction changing with the value of n . The value of n introduces a certain proportion of vacant ABO layers along the sequence and these are distributed to form a so-called uniform sequence (Elcoro *et al.*, 2001).

The superspace formalism (de Wolf, 1974; Janner & Janssen, 1980*a,b*; Janssen *et al.*, 1992) has been proved to be a very useful tool to describe and analyze long-period commensurate crystal structures and, in particular, families of layered compounds with composition-dependent unit-cell sizes. The atomic positions in these compounds are coupled in a way that it is not easily modelled in a conventional three-dimensional

structure determination, while they are included naturally in the superspace description. If the deviations of the atomic sites with respect to their ideal layer position are small, it is convenient to use structural parameters rather than the absolute atomic coordinates and this is what the superspace description essentially does. The method involves describing the observed composition-dependent layer sequences as an occupational modulation with a wavevector related to composition. This usually leads to a single structural model in (3+1)-dimensional superspace with discontinuous atomic domains (crenel occupational functions). As the displacements from the ideal layer structure follow smooth patterns, the number of parameters required to reproduce the deviations from the ideal reference structure is usually small. As a consequence, for compounds with long unit-cell parameters along the stacking direction, the number of effective parameters required for the structure description is much smaller in (3+1)-dimensional superspace than in a conventional three-dimensional approach. As examples, see Evain *et al.* (1998), Perez-Mato *et al.* (1999), Gourdon *et al.* (2000), Elcoro *et al.* (2000, 2001), Boullay *et al.* (2002) and Darriet *et al.* (2002), and references therein.

A fundamental property of the superspace description of these families of layered compounds with composition-dependent unit-cell sizes is the empirical fact that usually a single superspace model and a single superspace group is valid for a whole family of compounds. Thus, for instance in the case of the series $\text{Sr}_n[\text{Nb,Ti}]_n\text{O}_{3n+2}$, the different three-dimensional symmetries observed for different compositions could be traced back to a single superspace group (Elcoro *et al.*, 2001). The superspace symmetry only changed when considering different phases as a function of temperature.

In the present work, we analyze the experimental three-dimensional structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ within the general superspace framework proposed by Elcoro *et al.* (2001) for compounds of the type $A_nB_n\text{O}_{3n+2}$. Although the general structural features of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ broadly correspond to this type of compound, its detailed structure, and in particular its symmetry, does not fit into the particular superspace model proposed for the series $\text{Sr}_n[\text{Nb,Ti}]_n\text{O}_{3n+2}$. This new compound clearly requires a superspace description with a symmetry constraint defined by a different superspace group. Through a systematic use of the (3+1)-dimensional embedding of the experimental structure, we identify the relevant superspace symmetry. The efficiency of the resulting superspace model has been checked by comparing its structure refinement with a three-dimensional conventional one. Assuming its general relevance, we then present the symmetry properties predicted for the whole series $[\text{Na,Ca}]_n\text{Nb}_n\text{O}_{3n+2}$ as a function of n .

The present analysis constitutes a striking example of the fundamental ambiguity that underlies the superspace description of a commensurate structure. This description is in principle not unique. In general, quite different superspace models with different symmetries can describe the same real commensurate structure. We will present here, for instance, a full refinement of the structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ under two different superspace groups with equivalent results. To choose

one specific superspace model may be in the end a matter of convenience or efficiency. In many cases the choice is fully guided by physical arguments and becomes obvious. For instance, in the case of a lock-in commensurate modulated phase, the obvious choice is the superspace group of the preceding incommensurate phase. In our case, however, the situation is quite different. We know a single experimental three-dimensional commensurate long-period structure and its essential modulation is given by the layer sequence. The deviations of the atoms from their ideal positions in the idealized perfect layer model are to be described by displacive modulation functions. The main question is if the possible superspace symmetries that one can force into this displacive distortion are more efficient for the description of the experimental structure. One in principle should look for the highest possible symmetry that yields smooth displacive atomic modulations and minimizes the number of parameters for the description. We will show that under this criterion one of the choices clearly surpasses all the other possible ones. This suggests that, as in other series of layered compounds, the choice of superspace symmetry transcends a mere practical issue and reflects some underlying physical constraint present in the whole series of analogous compounds.

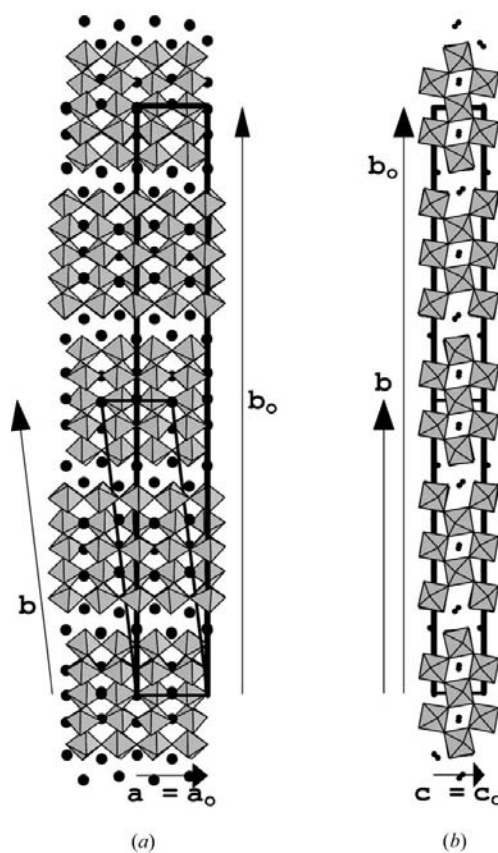


Figure 1

(a) (x, y) and (b) (y, z) projections of the structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ from Zúñiga & Darriet (2003). Monoclinic and pseudo-orthorhombic unit cells are outlined by thin and thick lines, respectively. Solid circles represent Ca/Na atoms, O atoms are located at the vertices of the octahedra and Nb cations occupy the centres of the octahedra.

Table 1

Experimental and crystal data for NaCa₄Nb₅O₁₇ in different settings.

(a) Crystal data for the *P* and *C* cells.

| | Primitive | <i>C</i> -centred |
|----------------------------|---|--|
| Space group | <i>P</i> 112 ₁ / <i>b</i> | <i>C</i> 112 ₁ / <i>d</i> |
| Symmetry | <i>x, y, z</i> | <i>x, y, z</i> |
| Operations | $-x, \frac{1}{2} - y, \frac{1}{2} + z$ $-x, -y, -z$ $x, \frac{1}{2} + y, \frac{1}{2} - z$ | $\frac{1}{4} + x, \frac{3}{4} + y, \frac{1}{2} - z$ $-x, -y, -z$ $\frac{3}{4} - x, \frac{1}{4} - y, \frac{1}{2} + z$ |
| <i>a</i> (Å) | 7.710 (2) | 7.710 (2) |
| <i>b</i> (Å) | 32.350 (5) | 64.24 (1) |
| <i>c</i> (Å) | 5.4838 (6) | 5.4838 (6) |
| γ (°) | 96.820 (13) | 89.98 (1) |
| <i>V</i> (Å ³) | 1358.0 (4) | 2716.0 (8) |
| <i>Z</i> | 4 | 8 |

(b) Data collection for three-dimensional and (3+1)-dimensional indexations. For the (3+1)-dimensional indexation the basis *a* = 7.710, *b* = 5.392, *c* = 5.4838 Å and modulation vector **q** = (0, $\gamma/2$, 0) have been used.

| | Three-dimensional indexation | (3+1)-Dimensional indexation |
|--|------------------------------|--------------------------------|
| No. of reflections | 17 947 | 17 947 |
| (<i>hklm</i>) range | $\pm 13, \pm 116, 0 - 9, 0$ | $\pm 13, \pm 10, 0 - 9, \pm 6$ |
| Independent reflections/observed (<i>I</i> > 3 σ) | 8692/6424 | 8692/6424 |
| <i>R</i> _{int} | 0.035 | 0.035 |
| Main reflections (<i>m</i> = 0) | | 690/535 |
| Satellites <i>m</i> = 1 | | 1507/1043 |
| Satellites <i>m</i> = 2 | | 1384/1126 |
| Satellites <i>m</i> = 3 | | 1518/983 |
| Satellites <i>m</i> = 4 | | 1392/1156 |
| Satellites <i>m</i> = 5 | | 1508/1023 |
| Satellites <i>m</i> = 6 | | 694/558 |

2. Structure of NaCa₄Nb₅O₁₇

The structure of NaCa₄Nb₅O₁₇ (Zúñiga & Darriet, 2003) consists of perovskite slabs with five consecutive corner-sharing NbO₆ octahedra stacked along the *y* direction. Among the Nb atoms, two (in the middle of the slabs) lie on inversion centres, while the Ca and Na atoms are located in the oxygen-coordinated cavities between the octahedra, with a preference to share the sites inside the slabs, while the inter-slab positions are fully occupied by Ca atoms. Projections of the structure along the [001] and [100] directions are shown in Figs. 1(a) and (b), where the outlined cells correspond to the standard primitive cell and to a new setting **a**_o = **a**, **b**_o = **a** + 2**b** and **c**_o = **c**, transforming the original primitive cell to a *C*-centred cell. The use of this second setting helps to understand the layer model (see §3) and its relation with the ideal prototype ABO₃ perovskite structure.

A comparison with the ideal perovskite evidences two main features: a doubling of the periodicity along the *a* axis and an **a**/4 shift between consecutive blocks. The doubled periodicity of the *a* axis is due to the tilt system of consecutive octahedra along the *a* axis, which are tilted around *b* in antiphase. As only O atoms are mainly affected by the tilts, Ca/Na and Nb atoms exhibit a pseudo-symmetry relating (*x, y, z*) and (*x* + $\frac{1}{2}$, *y, z*) site pairs. This gives a pseudo-translation of **a**/2 in the global structure. On the other hand, the relations between the tilt phases of the perovskite slabs along the stacking

Table 2

Symmetry elements of the (3+1)-dimensional superspace group of the parent structure for *a* = 7.710, *b* = 5.392, *c* = 5.4838 Å and modulation vector **q** = (0, $\gamma/2$, 0).

The 128 non-equivalent symmetry elements by unit-cell translations are obtained combining the 16 centring translations and the eight rotational elements. The generators of the 16 centring translations and of the eight rotational elements are given in two notations in the first and second columns, respectively.

| | | | |
|--|--|--------------------------|----------------------|
| $(\frac{1}{4} + x_1, x_2, \frac{1}{2} + x_3, \frac{1}{4} + x_4)$ | $\{E \frac{1}{4}, 0, \frac{1}{2}, \frac{1}{4}\}$ | $(-x_1, x_2, x_3, x_4)$ | $\{m_x 0, 0, 0, 0\}$ |
| $(\frac{1}{4} + x_1, x_2, \frac{1}{2} + x_3, \frac{3}{4} + x_4)$ | $\{E \frac{1}{4}, 0, \frac{1}{2}, \frac{3}{4}\}$ | $(x_1, -x_2, x_3, -x_4)$ | $\{m_y 0, 0, 0, 0\}$ |
| $(x_1, \frac{1}{2} + x_2, \frac{1}{2} + x_3, x_4)$ | $\{E 0, \frac{1}{2}, \frac{1}{2}, 0\}$ | $(x_1, x_2, -x_3, x_4)$ | $\{m_z 0, 0, 0, 0\}$ |

direction are such that an oblique primitive unit cell is formed. For the present analysis it is convenient to have the layer stacking direction as part of the main crystallographic axes. This is readily obtained using the new setting given above, rather than the standard cell used for the structural description. The vectors **a**_o and **b**_o are close to orthogonality, so that the *C*-centred unit cell is pseudo-orthorhombic. Within this setting the space group of the structure can be labelled as *C*112₁/*d*. All the calculations and an analysis of the NaCa₄Nb₅O₁₇ compound (see §4 and sections therein) are performed using this *C*-centred setting with crystal data summarized in Table 1(a).

3. Superspace description of the layered perovskite compounds A_nB_nO_{3n+2}

The structure of NaCa₄Nb₅O₁₇ follows, to a first approximation, the general pattern of the layered perovskite compounds A_{*n*}B_{*n*}O_{3*n*+2} (Elcoro *et al.*, 2001), formed by successive distinct perovskite slabs stacked along the [110]_{*p*} direction of the perovskite cubic reference axes. For a general composition, the ideal layer description of each perovskite slab consists of the equidistant stacking of layers of two kinds (say *N* and *M*) with the composition ABO, separated by intermediate O₂ layers. Consecutive slabs have their layers shifted by **a**_{*p*}/2 and are separated by what can be considered a 'vacant' ABO layer. We can label the **a**_{*p*}/2-shifted ABO layers *N'* and *M'*. Taking the *y* axis parallel to the stacking direction (the **b**₀ cell vector in Figs. 1a and b), the atomic positions on the *M* layer are (*x, z*) = (0,0), ($\frac{1}{2}, \frac{1}{2}$) and ($0, \frac{1}{2}$) for the A, B and O atoms, respectively. The layers *N, M'* and *N'* are obtained from the layer *M* by ($0, \frac{1}{2}$), ($\frac{1}{2}, 0$) and ($\frac{1}{2}, \frac{1}{2}$) shifts. The number and sequence of layers depend on the composition. For instance, for *n* = 5, which corresponds to our case, the ABO layer stacking sequence is MNMNMO₂N'M'N'Ø..., where Ø represents a 'vacant' ABO layer. The structure is completed by layers composed of O₂ sandwiched between the *M, N, M', N'* and Ø layers, with the O atoms located at (*x, z*) = ($\frac{1}{2}, \frac{1}{4}$) and ($\frac{1}{2}, \frac{3}{4}$) for layers close to *M* or *N* layers, and (*x, z*) = ($0, \frac{1}{4}$) and ($0, \frac{3}{4}$) for layers close to *M'* or *N'* layers. The *n* parameter of the general formula A_{*n*}B_{*n*}O_{3*n*+2} is in most cases an integer, but more general compositions with *n* being a fraction can also exist (Levin *et al.*, 2000). In this last case, the stacking sequence consists of the intergrowth of slabs with a different number of layers.

Due to the regularity and similarity between the sequences for different compositions, also evidenced in the diffraction patterns (Levin *et al.*, 2000), a common superspace group for the whole family can be assumed (Elcoro *et al.*, 2001). The superspace unit cell contains a set of atomic domains, which is the same for the whole range of compositions. The only composition-dependent parameters are the modulus of the modulation wavevector and the size of the atomic domains. Fig. 2 reproduces Fig. 3 of Elcoro *et al.* (2001), where the ideal superspace construction for $n = 5$ is represented. The (3+1)-dimensional superspace group of this construction can be labelled as $F'mmm(0\gamma 0)$, where $\gamma = 1/(n + 1)$ and F' represents a set of non-standard centring translations (0000), $(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2})$ and $(0, \frac{1}{2}, \frac{1}{2}, 0)$. In the standard setting (Janssen *et al.*, 1992) the space group is $Fmmm(1, \gamma, 0)$.

The basic idea underlying this construction and similar ones in other series of layered compounds (Evain *et al.*, 1998; Perez-Mato *et al.*, 1999; Gourdon *et al.*, 2000; Elcoro *et al.*, 2000; Boullay *et al.*, 2002; Darriet *et al.*, 2002) is the fact that one can

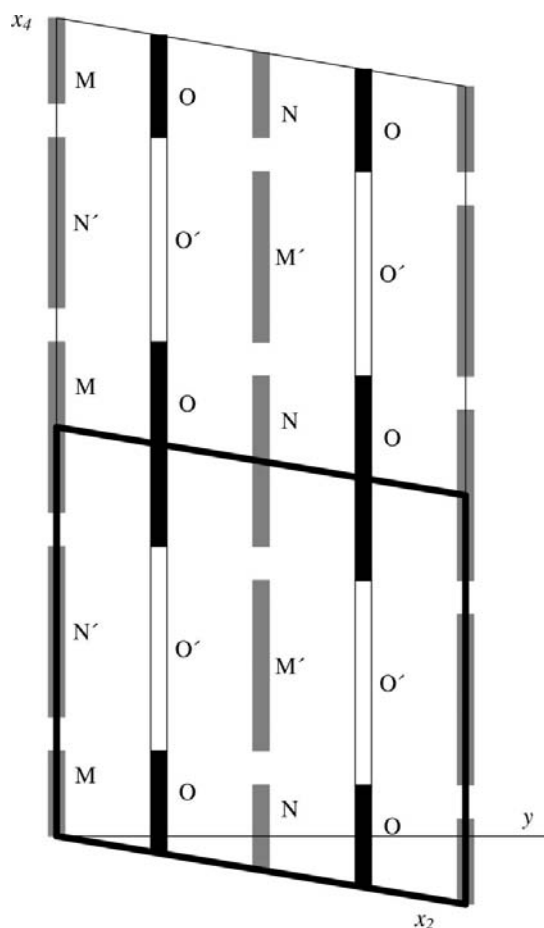


Figure 2

Superspace construction for the $A_n B_n O_{3n+2}$ general compound series (see Elcoro *et al.*, 2001). The superspace unit cell for the $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ compound has been doubled along x_4 with respect to the superspace unit cell of the $\text{Sr}_n[\text{Nb},\text{Ti}]_n\text{O}_{3n+2}$ compound series, represented by thick lines. The modulation parameter is $\gamma = 1/(n + 1)$ for the small cell and $\gamma/2$ for the doubled cell.

describe the layer sequences in terms of step-like (0 or 1) atomic occupational modulations, with respect to the underlying average period, resulting from the interlayer distance. In this case, for instance, the average period is taken as the distance between two layers of the same type ($M-M$ or $N-N$), and the presence of either a vacant ABO layer or shifted layers (M',N') along the sequence is realised through the limitation of the corresponding atomic occupation functions along the internal space to discontinuous intervals, the so-called crenel functions (Petricek & Dusek, 2000). In this sense, one can talk of atomic domains, as in the superspace description of quasicrystals.

The fact that a single superspace model is valid for any composition is directly related to an additional property common to these families of layered compounds. Namely that the layer sequence realised for each composition is the so-called *uniform* sequence, where the composition-dependent *minority motif* (in this case the vacant ABO layer) is distributed along the sequence as uniformly as possible (Elcoro *et al.*, 2003). This condition fully determines the relation between the modulation wavevector and the composition.

The superspace group $F'mmm(0\gamma 0)$ is common for the whole $A_n B_n O_{3n+2}$ family of compounds and yields directly, depending on the value of n , the possible maximal three-dimensional space groups associated with each composition. For instance, for the case where $n = 5$, the possible space groups are $Immm$, $Imcm$ and $Im2m$. However, this superspace symmetry is maximal, as obtained from the idealized layer model, and is usually realised only at high temperature. Most of the compounds exhibit successive phase transitions as temperature is lowered and they lose some symmetry elements, which remain in the structure as pseudo-symmetry operations (Levin & Bendersky, 1999). Even at the lowest temperatures, after several phase transitions the structures can be interpreted as relatively small distortions of the idealized layer model of high temperature. The latter may be considered as the common *parent* structure from which the other phases are obtained by successive distortions.

In principle, once the parent structure is distorted and the maximal symmetry broken, one could expect that the possibility of using a unique superspace framework common to all compositions would disappear. There is at least no obvious reason for the distortions taking place in the different structures (with different n) to comply with a common unique superspace symmetry description. However, in Elcoro *et al.* (2001), it was shown that for the family of compounds $\text{Sr}_n[\text{Nb},\text{Ti}]_n\text{O}_{3n+2}$, the observed successive symmetry breakings could also be described in superspace using superspace symmetry considerations independent of the composition. In particular, these compounds exhibit a first phase transition that can be described by the symmetry breaking in superspace $F'mmm(0\gamma 0) \rightarrow C'mcb(0\gamma 0)$, where C' represents the centring translations (0000) and $(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$. The symmetry change is induced by the antiphase tilts around the a axis of the octahedra in successive layers along the stacking direction. Upon further lowering of the temperature a second phase transition occurs and an extra incommensurate modulation parallel to

Table 3

(3+1)-Dimensional subgroups of the superspace group of Table 2, which give rise to the experimental $C112_1/d$ space group after a three-dimensional cut, with a Nb atom at the inversion center.

In the first row the eight elements of the G_1 group are included. G_2, G_3, G_4 and G_5 superspace groups are the combination of G_1 and the centring translation given in each case. G_1, G_4 and G_5 are equivalent to $P2_1/b(\alpha\beta 0)$, and G_2 and G_3 are equivalent to $B2/b(\alpha\beta 0)$, No. 141 and No. 151, respectively (*International Tables for Crystallography*, 1992, Vol. C, p. 797).

| | | | | |
|-------|--|--|---|--|
| G_1 | (x_1, x_2, x_3, x_4) | $\{E 0, 0, 0\}$ | $(\frac{1}{4} - x_1, -x_2, \frac{1}{2} + x_3, \frac{1}{4} - x_4)$ | $\{2_z \frac{1}{4}, 0, \frac{1}{2}, \frac{1}{4}\}$ |
| | $(\frac{1}{2} + x_1, x_2, x_3, \frac{1}{2} + x_4)$ | $\{E \frac{1}{2}, 0, 0, \frac{1}{2}\}$ | $(\frac{3}{4} - x_1, -x_2, \frac{1}{2} + x_3, \frac{3}{4} - x_4)$ | $\{2_z \frac{3}{4}, 0, \frac{1}{2}, \frac{3}{4}\}$ |
| | $(\frac{1}{2} - x_1, -x_2, -x_3, -x_4)$ | $\{I \frac{1}{2}, 0, 0, 0\}$ | $(4 + x_1, x_2, \frac{1}{2} - x_3, \frac{1}{4} + x_4)$ | $\{m_z \frac{1}{4}, 0, \frac{1}{2}, \frac{1}{4}\}$ |
| | $(-x_1, -x_2, -x_3, \frac{1}{2} - x_4)$ | $\{I 0, 0, 0, \frac{1}{2}\}$ | $(\frac{1}{4} + x_1, x_2, \frac{1}{2} - x_3, \frac{3}{4} + x_4)$ | $\{m_z \frac{1}{4}, 0, \frac{1}{2}, \frac{3}{4}\}$ |
| G_2 | $(\frac{1}{2} + x_1, \frac{1}{2} + x_2, \frac{1}{2} + x_3, x_4)$ | $\{E \frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0\}$ | | |
| G_3 | $(x_1, \frac{1}{2} + x_2, \frac{1}{2} + x_3, x_4)$ | $\{E 0, \frac{1}{2}, \frac{1}{2}, 0\}$ | | |
| G_4 | $(\frac{3}{4} + x_1, \frac{1}{2} + x_2, x_3, \frac{1}{4} + x_4)$ | $\{E \frac{3}{4}, \frac{1}{2}, 0, \frac{1}{4}\}$ | | |
| G_5 | $(\frac{3}{4} + x_1, \frac{1}{2} + x_2, x_3, \frac{3}{4} + x_4)$ | $\{E \frac{3}{4}, \frac{1}{2}, 0, \frac{3}{4}\}$ | | |

Table 4

General structural parameters in the (3+1)-dimensional superspace description of the $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ compound with superspace group G_4 (see Table 3).

Atomic coordinates highlighted in bold are refineable. In the last column, ‘antisym’ indicates an antisymmetric function for the displacive modulation with respect to its centre.

| | x_1 | x_2 | x_3 | x_4 | Width | Point symmetry | Displacive modulation |
|------------|------------|-------------|------------|-------|-------|----------------|-----------------------|
| Nb1 | 1/4 | 0 | 1/2 | 0 | 5/24 | $\bar{1}$ | Antisym |
| Nb2 | 3/4 | 0 | 1/2 | 0 | 5/24 | $\bar{1}$ | Antisym |
| Ca/Na(Ca1) | 0 | 0 | 0 | 0 | 1/8 | 1 | No restriction |
| Ca2 | 0 | 1/4 | 0 | 5/48 | 1/24 | 1 | No restriction |
| Ca3 | 0 | -1/4 | 0 | -5/48 | 1/24 | 1 | No restriction |
| O1 | 0 | 0 | 1/2 | 0 | 5/24 | 1 | No restriction |
| O2 | 1/4 | 1/4 | 1/4 | 0 | 1/4 | 1 | No restriction |
| O3 | 3/4 | 1/4 | 1/4 | 0 | 1/4 | 1 | No restriction |

the a axis appears. A description of these incommensurate structures, common for all compositions, therefore requires a (3+2)-dimensional superspace. The superspace group of this incommensurate phase, common to all the members of the family series, was identified in Elcoro *et al.* (2001) as $C'mcb(0\gamma 0)000(\gamma'00)0s0$, where C' represents the centring translations (0000) and $(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}, 0)$, $\gamma = 1/(n + 1)$ is the composition-dependent modulation parameter and γ' the incommensurate modulation parameter. From this unique (3+2)-dimensional superspace group, the different (3+1)-dimensional superspace groups to be used to describe the displacive modulated phases, depending on the composition n , could be predicted and were in agreement with those reported in the literature. Finally, at lower temperatures, there is a lock-in phase transition where the γ' modulation parameter takes the commensurate value 1/2 (Levin *et al.*, 2000, and references therein), *i.e.* the parameter a is doubled. The common (3+1)-dimensional superspace group relevant for the description of this lock-in phase in the whole series can then be derived from the (3+2)-dimensional superspace group $C'mcb(0\gamma 0)000(\gamma'00)0s0$ particularizing for $\gamma' = 1/2$. Depending on the section taken along the internal coordinate x_5 , three (3+1)-dimensional superspace groups are possible, namely $Pmnb(0\gamma 0)$, $Pbnb(0\gamma 0)ss0$ or $P2_1nb(0\gamma 0)$. For the case where $n = 5$ ($\gamma = 1/6$) this yields for this phase, with the parameter a doubled, the following possible three-dimensional space groups: $Pmn2_1$, $Pm11$, $P12_11$, $P1b1$, $P1$ and

$P12_1/b1$. $P12_1/b1$ is the experimentally observed space group for the lock-in phase of $\text{Sr}_5\text{TiNb}_4\text{O}_{17}$ (Levin *et al.*, 2000).

4. Superspace description of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$

The structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ agrees with the general features of the family $\text{Sr}_n[\text{Nb}, \text{Ti}]_n\text{O}_{3n+2}$ as the refined atomic positions differ only slightly from the ideal layer model with the symmetry $F'mmm(0\gamma 0)$, but the distortion of the true structure with respect to this reference parent structure follows quite a different pattern from that observed in the $\text{Sr}_n(\text{Nb}, \text{Ti})_n\text{O}_{3n+2}$ series. The doubling of the a parameter of the primitive unit cells could suggest that the structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ at room temperature corresponds to a lock-in phase with a displacive modulation of wavevector $\mathbf{a}^*/2$, similarly as observed in the $\text{Sr}_n(\text{Nb}, \text{Ti})_n\text{O}_{3n+2}$ compounds. However, the experimental space group is different from those relevant for this lock-in phase in the $\text{Sr}_n(\text{Nb}, \text{Ti})_n\text{O}_{3n+2}$ series (see §3).

Therefore, we can conclude that a different superspace group [but also the subgroup of the parent symmetry $F'mmm(0\gamma 0)$] must be considered for this system.

The usual way to determine the superspace group of a structure is by careful analysis of the diffraction pattern, determining the point-group symmetry and the systematic extinctions. However, in commensurate structures, as reflections with different indices superpose at the same position on the diffraction pattern, a rigorous determination of the set of systematic extinctions for a (3+1)-dimensional indexation is, in general, not possible. This problem is particularly severe if the modulation is large and anharmonic, as it is in the present case, owing to the fundamental step-like occupational atomic modulations, which are intrinsic in the model. In fact, this situation is just the consequence of the fundamental ambiguity of both the (3+1)-dimensional indexation and the superspace description in the case of a commensurate structure. The superspace description and superspace symmetry of a commensurate structure is in principle not unique (even after the modulation wavevector has been chosen). In general, quite different superspace models can describe the same real commensurate structure. To choose one of them is in the end a matter of convenience or efficiency. In our case, we know a single experimental three-dimensional commensurate structure and its essential modulation is given by the layer sequence. The deviations of the atoms from their ideal positions in the idealized perfect layer model are described by

displacive modulation functions of the atomic domains representing in superspace the ideal parent layer model. The use of a superspace approach will be justified if the resulting modulations are sufficiently smooth, so that there is a significant reduction in the number of parameters necessary for describing the structure. Therefore, the searched superspace model should minimize the number of structural parameters by means of the highest possible symmetry compatible with smooth displacive modulations.

We have some information which helps in this search:

(i) the required superspace group must be a subgroup of the superspace group of the parent structure and, for $\gamma = 1/6$ ($n = 5$), one of the possible resulting three-dimensional groups must be the experimental one;

(ii) since the three-dimensional structure has been determined, the experimental atomic positions can be embedded in superspace and be used to observe discrete points of the atomic domains for each of the possible superspace symmetries.

The first condition determines the set of superspace groups which can be used to describe the structure. The second

information will help us to choose the most adequate among them for describing the actual experimental structure.

As stated in §2, when expressed in a pseudo-orthorhombic unit cell, $a = 7.710$, $b = 64.24$, $c = 5.4838$ Å, consistent with the layer description, the experimental space group is $C112_1/d$. The superspace group of the parent (non-distorted) structure in the average orthorhombic unit cell defined by $a = 3.855$, $b = 5.392$ and $c = 5.4838$ Å is $F'mmm(0\gamma 0)$, where $\gamma = 1/6$ for the present composition. To identify the subgroups of $F'mmm(0\gamma 0)$, which could be relevant for describing the experimental distorted structure $C112_1/d$, it is convenient to express the symmetry elements of the group $F'mmm(0\gamma 0)$ in a supercell describing the superspace lattice of the distorted experimental structure. This would double both the a parameter and the lattice parameter along the internal x_4 axis of the average unit cell. In this way, the modulation vector becomes $\mathbf{q} = (0, \gamma/2, 0)$ rather than $(0, \gamma, 0)$, leading to a period of 12 double layers along the b axis, as observed. In this new setting, the space group $F'mmm(0\gamma 0)$ can be denoted as $Xmmm(0, \gamma/2, 0)$, where the larger unit cell is compensated for by additional centring translations. Table 2 lists the

generators of the group in this setting.

It contains 128 non-trivial elements as coset representatives with respect to the sublattice defined by the supercell.

The systematic search of all the possible subgroups of $Xmmm(0, \gamma/2, 0)$, which can reduce to the experimental three-dimensional space group $C112_1/d$ for $\gamma = 1/6$ yields 10 different possible (3+1)-dimensional superspace groups. However, five of them can be discarded as they would locate Na/Ca atoms on inversion centres, while in the experimental structure only Nb atoms lie on centrosymmetric sites. This is compatible with the remaining five subgroups, which are listed in Table 3. The first group, G_1 , contains the minimal set of symmetry operations necessary to produce the three-dimensional symmetry $C112_1/d$. The other four superspace groups, G_i , $i = 2, \dots, 5$, are obtained by 'adding' additional superspace operations that do not produce any additional symmetry when the real space section is considered. These operations are generated by multiplying all the elements of the first group G_1 by the centring translation indicated in Table 3. Thus, G_2 can be decomposed in cosets with respect to G_1 in the form $G_2 = G_1 + \{E|1/2, 1/2, 1/2, 0\}G_1$.

In principle, any of these five different superspace groups are valid

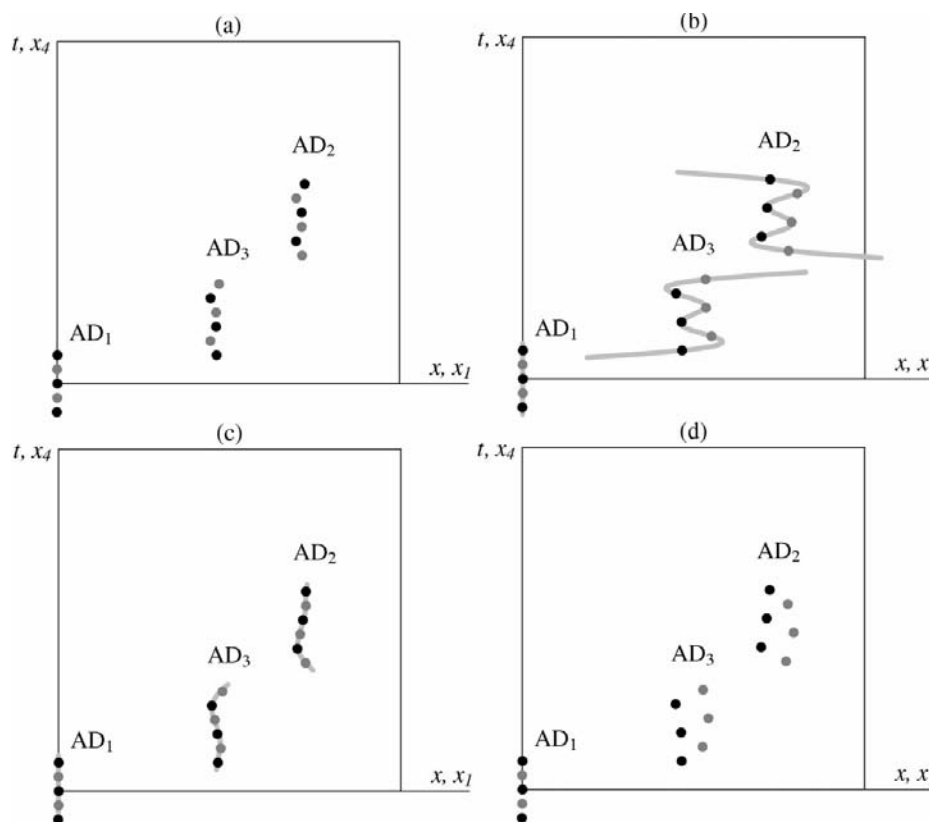


Figure 3

Black dots represent the atomic positions from Zúñiga & Darriet (2003) (or Table S1 of the supplementary material) embedded into the superspace construction [projection onto (x, x_4) subspace]. Only oxygen atomic domains AD1, AD2 and AD3 (see text), located at $(0, 0, \frac{1}{2}, 0)$, $(\frac{3}{4}, \frac{1}{4}, \frac{1}{4}, 0)$ and $(\frac{1}{2}, \frac{3}{4}, \frac{3}{4}, \frac{1}{4})$ superspace positions, respectively, are represented for clarity. Grey dots are obtained from the complete set of atomic domains assuming (a) G_2 , (b) G_3 , (c) G_4 and (d) G_5 superspace groups, respectively. The set of black points (common for the four figures) has G_1 superspace-group symmetry. In (b) and (c) the resulting atomic domains from the structure refinements under G_3 and G_4 are outlined.

Table 5

Results of the three-dimensional structure refinement (in the pseudo-orthorhombic *C*-centred setting) and the (3+1)-dimensional structure refinements under G_4 and G_3 superspace groups.

R factors in the second line refer to the complete set of reflections. The following lines correspond to partial *R* factors for main ($m = 0$) and satellite reflections of the order m in the superspace refinements.

| | Three-dimensional | G_4 | G_3 |
|-----------------------|-------------------|-------------|-------------|
| Parameters | 249 | 111 | 140 |
| $R(F)/wR(\text{obs})$ | 0.034/0.070 | 0.035/0.081 | 0.036/0.079 |
| $m = 0$ | | 3.33/4.59 | 3.20/3.85 |
| $m = 1$ | | 4.72/4.53 | 4.71/4.34 |
| $m = 2$ | | 3.12/4.61 | 3.15/3.93 |
| $m = 3$ | | 6.03/6.56 | 6.01/6.41 |
| $m = 4$ | | 2.39/13.89 | 2.71/13.76 |
| $m = 5$ | | 6.21/6.23 | 6.22/6.35 |
| $m = 6$ | | 2.81/4.14 | 2.81/4.11 |

for the description of the structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ and could be used in a (3+1)-dimensional refinement of the structure. In each case, the independent set of atomic domains, their symmetry and their parameterization would be different. The first superspace group, G_1 , contains the minimum set of the (3+1)-dimensional set of symmetry operations fulfilled by the set of atomic domains which are compatible with the experimental three-dimensional space group. The other four superspace groups contain extra symmetry operations which either relate the shape of the atomic domains which are independent under the group G_1 and/or introduce extra restrictions to the shape of the atomic domains which are independent under G_1 . These extra symmetry restrictions are different for the four superspace groups G_2, \dots, G_5 . The question is then whether one of these four groups results in smooth modulation functions and, as a consequence, in a more efficient and physically consistent description of the experimental structure. The reason for the validity of the five superspace groups to describe the structure and the advantages or disadvantages of taking one group from another will be clearly seen in the following when looking at the experimental atomic positions of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ embedded in superspace according to the different possible groups.

5. Three-dimensional refinement in the $C112_1/d$ setting

The experimental data used is the same as that employed for the conventional three-dimensional study (Zúñiga & Darriet, 2003). Reflection indices and lattice constants were transformed to the *C*-centred setting for the three-dimensional description, while for the superspace analysis a four-integer indexation was introduced using the average unit cell and wavevector mentioned above. Experimental and crystal data are summarized in Table 1. All the transforming cell calculations and refinements were performed using the software package *JANA2000* (Petricek & Dusek, 2000).

To make possible a direct comparison between the performance of the superspace and the conventional three-dimensional methods, the structure was first refined anew with conventional three-dimensional methods using the *C*-centred

Table 6

(3+1)-Dimensional superspace groups for the incommensurate phases of the compounds with rational composition $\gamma/2 = r/s$ and different values of the height of the section, t .

B' represents the (0000) , $(0, \frac{1}{2}, 0, \frac{1}{2})$ set of centring translations and X for (0000) , $(0, \frac{1}{2}, 0, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{4}, 0, \frac{3}{4})$ and $(\frac{1}{2}, \frac{3}{4}, 0, \frac{1}{4})$. The number of the equivalent standard superspace group in the *International Tables for Crystallography* (1992, Vol. C, p. 797) is given in parentheses.

| | | | |
|---------------------|---|--|--|
| $s = 4N$ | $t = 0(\text{mod. } 1/2s)$ $B'112_1/d(\gamma'00)00q$ (No. 14.1) | $t = 1/4s(\text{mod. } 1/2s)$ $B'112_1/d(\gamma'00)00q$ (No. 14.1) | $t = \text{arbitrary}$ $B'11d(\gamma'00)00q$ (No. 7.1) |
| $s = 4N + 2$ | $t = 0(\text{mod. } 1/2s)$ $X\bar{1}(\gamma'00)$ (No. 2.1) | $t = 1/8(\text{mod. } 1/2s)$ $X112_1(\gamma'00)$ (No. 4.1) | $t = \text{arbitrary}$ $X1(\gamma'00)$ (No. 1.1) |
| $r = \text{even}$ | $t = 0(\text{mod. } 1/2s)$ $P112_1/b(\gamma'00)$ (No. 14.1) | $t = 1/8(\text{mod. } 1/2s)$ $P112_1/b(\gamma'00)$ (No. 14.1) | $t = \text{arbitrary}$ $P11b(\gamma'00)$ (No. 7.1) |
| $r, s = \text{odd}$ | $t = 0(\text{mod. } 1/2s)$ $P112_1/b(\gamma'00)00s$ (No. 14.1) | $t = 1/8(\text{mod. } 1/2s)$ $P112_1/b(\gamma'00)00s$ (No. 14.1) | $t = \text{arbitrary}$ $P11b(\gamma'00)00s$ (No. 7.1) |

orthogonal setting. The structural model contains six Nb (two on inversion centers), five Ca (three on shared Ca/Na sites) and 17 O independent atoms, requiring a total of 84 positional parameters. The starting values for the atomic parameters were those previously reported in Zúñiga & Darriet (2003) (after application of the corresponding matrix transformation to change the setting). This refinement converged without significant changes in the parameters to $R = 0.034$, including a population parameter for the twin (the twin law is given by a binary axis about the [100] direct lattice direction), anisotropic thermal displacements for all atoms and an occupation fraction of Na atoms on the three Ca/Na mixed sites which was fixed to 1/3. There were 249 parameters refined in the last cycle. Structural parameters can be found in Table S1 of the supplementary material.¹ The origin of the unit cell has been translated $-\frac{1}{4}\mathbf{a}_o - 1/2\mathbf{c}_o$ to compare the structural model with the (3+1)-dimensional construction in Elcoro *et al.* (2001). These coordinates have been chosen for the embedding into the superspace. Note that in this setting the inversion centre is located at $1/4\mathbf{a}_o$.

6. Superspace refinement of the structure

6.1. Assignment of the superspace group

In the superspace framework, once the shapes of all the atomic surfaces have been determined, the atomic positions in real space are easily obtained as a three-dimensional section of the superspace construction. Conversely, when the atomic positions are known, one can reconstruct (at least partially) the shape of the atomic domains, moving (*embedding*) the known atomic positions onto the superspace unit cell, by means of superspace unit-cell translations. Figs. 3, 4 and 5 show the result of this process. For simplicity, we have included the atomic positions corresponding to only a few independent atomic domains associated with O atoms: the so-

¹Supplementary data for this paper are available from the IUCr electronic archives (Reference: CK5002). Services for accessing these data are described at the back of the journal.

called AD1, AD2 and AD3 located in the superspace unit cell at $(0,0,\frac{1}{2},0)$, $(\frac{3}{4},\frac{1}{4},\frac{1}{4},\frac{1}{2})$ and $(\frac{1}{2},\frac{3}{4},\frac{3}{4},\frac{1}{4})$, respectively. The three atomic domains chosen are independent under all the G_i superspace groups except for G_2 . Under G_2 , AD2 and AD3 are symmetry related. The translated atomic positions are represented by black dots. The three atomic domains contain three independent atomic positions after the embedding. They crudely outline the shape of the atomic surfaces. The superspace group symmetry of the construction is G_1 . However, if we assume that one of the other four superspace groups of Table 3 is the correct one, the extra centring translation associated to each specific superspace group generates extra equivalent positions in the superspace unit cell. Fig. 3 depicts the (x, x_4) projection of the atomic positions associated with these atomic domains considered assuming each of these additional possible symmetries, *i.e.* superspace groups G_2 , G_3 , G_4 and G_5 . Black dots, corresponding to the minimal group G_1 , are common and present in all cases. Extra equivalent positions resulting from the assumption of the additional centring are represented by grey dots. Figs. 4 and 5 depict in the same form the corresponding (y, x_4) and (z, x_4) projections. The extra atomic sites in superspace represented by the grey dots do not give rise to additional atoms in real space with respect to those already represented by the black dots. However, once the corresponding superspace group is assumed the atomic sites constitute *real* points of the atomic domains defining the

corresponding superspace construction under this symmetry. It is important to note that this additional symmetry does not imply a formal reduction of the number of structural parameters, as the domain AD2 represents in this case six real space atomic positions, rather than three, and this in general will mathematically allow a double number of parameters when describing its displacive modulation. However, if these modulations are smooth enough, the number of effective parameters will reduce in practice and the corresponding superspace description will be an efficient method to take into account these hidden correlations. From Figs. 3, 4 and 5 it can be clearly seen that the resulting atomic domains for the superspace group G_4 are very much smoother compared with the atomic domains in the other cases.

From this result one can assume that a refinement of the structure under the superspace group G_4 will require fewer parameters than the refinement under any of the other possible superspace groups ones. Because of the commensurability of the structure, it is in principle possible to perform the analysis taking any of the other groups listed in Table 3. In all cases, one can always find an adequate atomic domain containing all the (finite) atomic sites associated with it. However, from the figures it seems clear that G_4 is the most adequate and best adapted to describe the full correlations among the atomic positions. In the next subsections we present the results of such refinements.

6.2. Structure refinement under superspace group G_4

The refinement of the superspace model was carried out with *JANA2000* (Petricek & Dusek, 2000). The dataset, transformed into a four-index indexation, contains two categories of reflections, main and commensurate satellites. The main reflections are those reflections of the conventional dataset in the C-centred basis with $k = 12n$, whereas those with $k = 12n + 1$, $12n + 2$, $12n + 3$, $12n + 4$, $12n + 5$ and $12n + 6$ transform to satellite reflections of the order 1, 2, 3, 4, 5 and 6, respectively. The distribution of the reflections among different categories is given in Table 1(b). The superspace refinement is based on the assumption that a long period structure can be described as a basic or reference structure (basic unit cell), plus a set of modulation functions with the modulation wavevector \mathbf{q} , which take into account the difference between the actual structure and the basic one. The modulation functions refer to atomic displacements and/or popula-

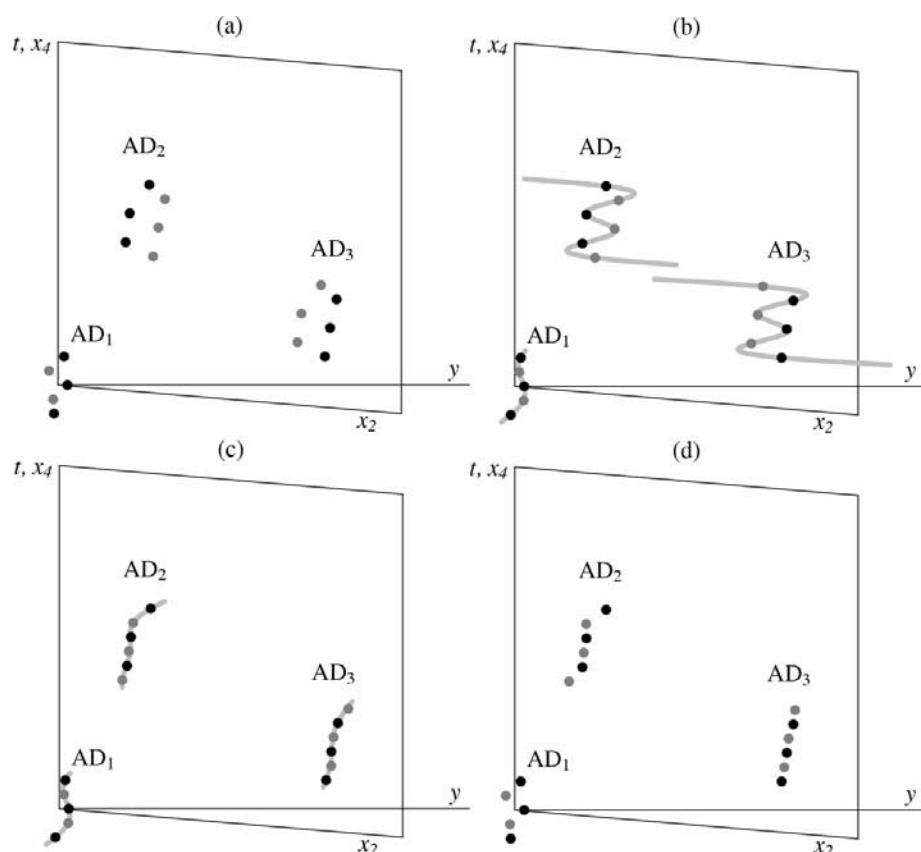


Figure 4
 (y, x_4) superspace projection of the same construction of Fig. 3.

tion factors and can be expressed by means of harmonic, saw-tooth, crenel functions or a combination of them. In our case, the application of crenel functions on the basic prototype structure is used to generate the vacancies between octahedral blocks. However, additional atomic displacements have to be considered to take into account the structural distortion of the real three-dimensional structure with respect to the ideal layered model. The widths of the crenels are determined by the composition and structural model and have fixed values (not refined), but the shape of the atomic domains are described by a series of displacive modulation functions whose amplitudes are refineable parameters. Table 4 lists the parameters for the starting point of the structure refinement under the symmetry G_4 with the displacive modulations set to zero: the first three columns include the reference three-dimensional coordinates for each independent atomic domain in the ideal layer description; the fourth and fifth columns list the center and width of the atomic domains along x_4 ; the last two columns contain the point symmetry of the atomic domain and the corresponding type of symmetry-allowed displacive modulation functions. The refinement parameters are:

(i) the three-dimensional coordinates of the atomic domains not restricted by symmetry (underlined coordinates in Table 4),

(ii) the amplitudes of the series describing the atomic displacive modulations and the modulation of the atomic thermal coefficients.

For each independent crenel function or atomic domain in Table 4 a series of functions, orthonormalized within its existence interval along x_4 , has been used as introduced in Petricek *et al.* (1995). These functions are also listed in Table S2 of the supplementary material. The number of significant terms in these series cannot be fixed *a priori*, but has to be determined during the refinement process. In any case, for each atomic domain the maximum number of positional parameters cannot exceed the number of parameters necessary for describing in conventional three dimensions the atomic sites represented by the atomic domain (Perez-Mato *et al.*, 1987). Some of the centers along x_4 of the crenel functions not fixed by symmetry were fixed by hand in order to keep the model consistent.

The main difference in this starting model for the refinement compared with the model in Elcoro *et al.* (2001), apart from the lower symmetry and the doubling of the unit cell, is the partition of the atomic domain which represents the Ca/Na cations in three pieces. The results for the $\text{Sr}_n(\text{Nb},\text{Ti})_n\text{O}_{3n+2}$ series in Elcoro *et al.* (2001) and the refined atomic positions for the $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ compound (Zúñiga & Darriet, 2003) indicate that the superspace positions of the two atoms at the extremes of the atomic domain corresponding to the *A* cations have a large displacement along the *y* direction. These atoms are those located in the *M*, *N*, *M'* or *N'* layers at the interface between perovskite slabs, with a neighbouring *ABO* vacant layer, whereas the other three atoms closer to the center of the atomic domain correspond to the internal layers of the slab. The rather different coordination of both groups of cations is the reason for their quite different displacements along *y*.

Therefore, it is convenient to divide the Ca/Na atomic domain into three pieces, so as not to force the use of a single displacive modulation to outline the clearly different displacement of internal and external cations.

The refinement was conducted through a very long number of refinement cycles, using the parameters of the structural model given in Table 4 as the starting parameters with non-modulated isotropic thermal parameters. During the first cycles, using unit weights and a damping factor of 0.4, only the positional parameters were refined including the maximum allowed number of displacive orthogonalized functions (2 for Nb, 2 for Ca1, 0 for Ca2 and Ca3, and 4 for O atoms). Then the weights were changed to $1/\sigma$ and all the parameters were free to vary over a long convergence process, which stopped when the largest shifts were similar to the sigma values. At this point, the Ca1 atom was partially replaced by Na in the ratio 2/3:1/3, according to the stoichiometry, and identical parameters were assigned for both species; isotropic thermal displacements were changed to anisotropic thermal displacements for all the atoms; and the first terms in the expansion series were added to the thermal tensors of Ca1 and O1 atoms. Finally, all the amplitudes whose value was lower than its standard deviation were set to zero and were not included in the following refinement cycles. Fraction volumes of the twin and isotropic extinction were also included in the last cycles, refining a total of 111 parameters. The relative occupancy modulation parameters were not included for the Ca/Na(Ca1) atomic domain. Final *R* factors for the main satellites of the order 1–6 and the whole set of reflections are given in Table 5. Final values of the atomic coordinates of the reference structure and amplitudes of the orthogonalized functions describing the displacive and thermal modulations can be found in Table S2 of the supplementary material. The shapes of some atomic domains are outlined in Figs. 3(c), 4(c) and 5(c), together with the specific points on them (in black) which give rise to atomic positions in the three-dimensional cut corresponding to the real three-dimensional structure. These positions coincide with the superspace atomic positions generated from the structure derived from the three-dimensional refinement and cannot be distinguished in the figures.

6.3. Structure refinement under the superspace group G_3

6.3.1. Example of a bad choice of the superspace group. A superspace alternative refinement was performed taking G_3 of Table 3 as the superspace group. The refinement process was performed following the same steps as in the refinement under G_4 , but the parameterization of the atomic domains is different. In fact, even the number of independent atomic domains is different; this is shown in Table S3 of the supplementary material, where the sets of parameters which define the structure are indicated. There are five independent atomic domains representing O atoms rather than three. Two oxygen atomic domains without symmetry restrictions in the G_4 description are split into four atomic domains with an inversion symmetry when the group G_3 is considered. The refinement was conducted following the same pattern as that carried

out under G_4 . After the removal of those amplitudes whose standard deviation was greater than the value of the parameter in the final steps of the refinement, the final model required 140 parameters (including the fraction volume of the twin and the extinction parameter) to achieve R factors similar to those obtained in the three-dimensional refinement and the (3+1)-dimensional refinement under G_4 . The final R factors for the main satellites of the order 1–6 and the whole set of reflections are given in Table 5. The shapes of some atomic domains are outlined in Figs. 3(b), 4(b) and 5(b), together with the specific points (in black) which give rise to the atomic positions in the three-dimensional section corresponding to the real three-dimensional structure. These positions also coincide with the atomic positions embedded in superspace generated from the three-dimensional coordinates calculated in the three-dimensional refinement.

6.4. Comparison between the two (3+1)-dimensional and the three-dimensional refinements

The first aspect concerns the efficiency of the (3+1)-dimensional refinement as opposed to the conventional one. It is noticeable that whereas the superspace refinements involve 111 and 140 parameters under the G_4 and G_3 superspace groups, respectively, the three-dimensional refinement deals with 249 variables. This economy is mainly due to the lack of

modulation of the (thermal) displacement parameters of most atomic domains. In the case of the refinement with the most adequate group, only the atomic domains of Ca/Na (Ca1) and O1 require some modulation, restricted to the first terms of the expansion and limited to the y component in the case of O1. It can be noticed in Table 5 that the R factors are systematically larger for odd satellites in both four-dimensional refinements. Odd satellites correspond to the superstructure reflections associated with the doubling of the unit cell along the x axis with respect to the reference perovskite. These reflections are systematically much weaker and this explains their larger R factors.

A second relevant aspect is the difference between the two refinements performed in the superspace. It highlights several features of the superspace formalism applied to commensurate structures. As stressed above, the assignment of the superspace group is not unique. The results of the refinements performed confirm this assertion and similar R parameters are attained with the two superspace groups. If the three-dimensional atomic coordinates were not known *a priori*, we would not have had any hint about the existing extra correlation given by the centring operations of G_4 and the superspace refinement under these circumstances could have been tried blindly with any of the four possible groups with extra centring, or using G_1 assuming no extra superspace correlations. The refinement under the G_3 superspace group confirms

what one could expect from Fig. 3. More parameters are required to reach similar R factors, but finally the same three-dimensional atomic structure is obtained.

7. Predictions for other compounds of the type $[\text{Ca},\text{Na}]_n\text{Nb}_n\text{O}_{3n+2}$

An important advantage of the (3+1)-dimensional analysis above is that it can be used to predict the space group of other compounds of the same family with different compositions. The extra centring operations of superspace groups G_2 , G_3 , G_4 and G_5 do not yield additional space-group operations in three dimensions for the $n = 5$ composition ($\gamma/2 = 1/12$ modulation parameter) or any other $n = \text{odd/odd}$ ($\gamma/2 = \text{odd}/4 \times \text{integer}$) composition. The resulting space group is always $C112_1/d$, *i.e.* the experimental one. However, for other compositions the resulting space groups would be different for G_1 , G_2 , G_3 , G_4 or G_5 . Therefore, the choice of G_4 as the relevant superspace group of the lock-in phase at room temperature for the case where $n = 5$

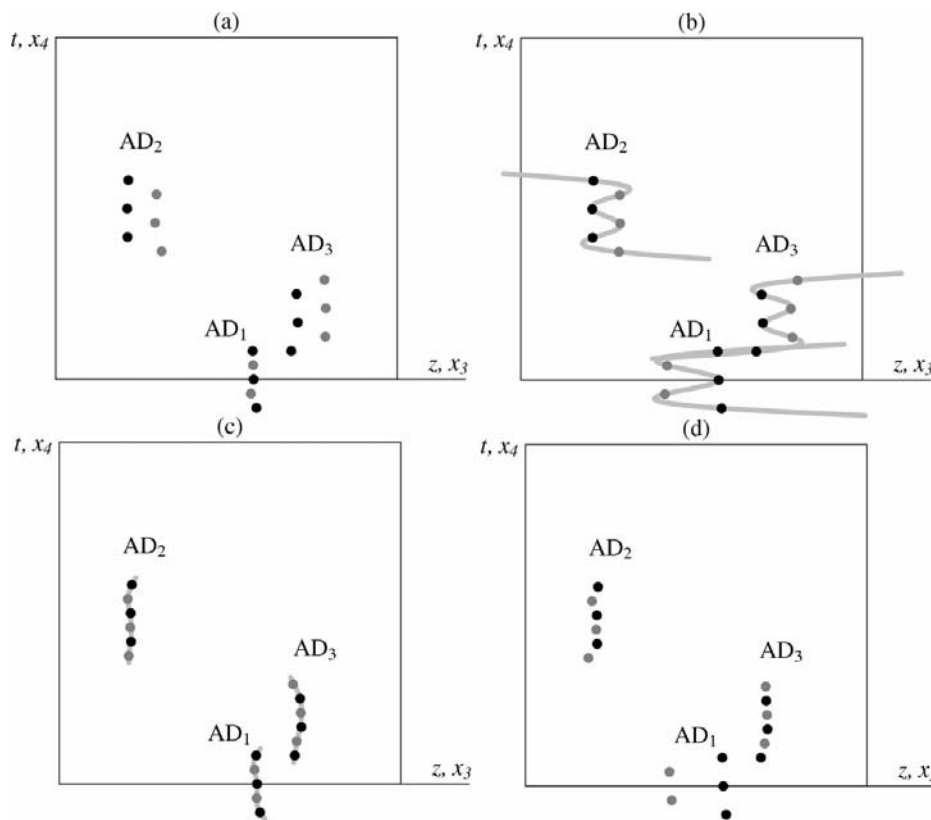


Figure 5
(z, x_4) superspace projection of the same construction of Fig. 3.

allows the prediction of the space group of the lock-in phases for other compositions, if we assume that the distortion is going to be described by the same superspace group in all cases for the whole series $[\text{Ca},\text{Na}]_n\text{Nb}_n\text{O}_{3n+2}$. The basis for this assumption is purely empirical and is confirmed in other families of layered compounds (Elcoro *et al.*, 2001; Boullay *et al.*, 2002). In this way we can postulate that for $n = \text{even/odd}$ ($\gamma/2 = 1/(4*\text{integer} + 2)$) the corresponding space group is either $P112_1$ or $P1$; for $n = \text{odd}/4*\text{integer}$ ($\gamma/2 = \text{even/odd}$), $P112_1/b$ or $P11b$; and for $n = \text{odd}/(4*\text{integer} + 2)$ ($\gamma/2 = \text{odd/odd}$), $P112_1/b$ or $P11b$. In order to obtain this listing of possible space groups, we have taken into account the fact that certain space groups, which are possible for the continuous atomic domains along the internal space, cannot be realised when the atomic domains are discontinuous and the corresponding real space section passes through the limits of some of the corresponding crenel domains. Out of the three cases and also from experience in other families (see, for example, Elcoro *et al.*, 2001; Darriet *et al.*, 2002), the most likely space group of the two is the most symmetric one.

As discussed above, the room-temperature structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ is most probably the lock-in phase of an incommensurate modulated phase stable at higher temperatures. This behaviour would be similar to that observed in the $\text{Sr}_n(\text{Nb},\text{Ti})_n\text{O}_{3n+2}$ series. The common description of these hypothetical high-temperature incommensurate modulated structures requires a (3+2)-dimensional analysis as in Elcoro *et al.* (2001). To calculate the superspace group of the incommensurate phases we must take into consideration that it is reduced to the G_4 superspace group of Table 3 when the modulation takes the rational value (1/2,0,0). Moreover, it must be compatible with the superspace group of the parent structure. These conditions fully determine the (3+2)-dimensional superspace group, whose complete set of symmetry operations is included in Table S4 of the supplementary material. Once the common (3+2)-dimensional superspace group has been determined, it is possible to predict the possible (3+1)-dimensional superspace groups for the incommensurate phases for any compositions. The complete set of possibilities is presented in Table 6.

8. Conclusions

We have shown that the recently reported structure of $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ (Zúñiga & Darriet, 2003) can be very efficiently described within the superspace model with discontinuous atomic domains proposed for other compounds of the general composition $A_nB_n\text{O}_{3n+2}$ (Elcoro *et al.*, 2001). The structure, however, does not fit into the superspace model and symmetry considered in the same reference for the specific series $\text{Sr}_n[\text{Nb},\text{Ti}]_n\text{O}_{3n+2}$. A different superspace symmetry, which is a subgroup of that associated with the ideal layered structure,

underlies this new structure. The analysis above demonstrates that despite the formal ambiguity of the superspace description of a commensurate structure, a unique superspace group is clearly much more advantageous to describe the displacements of the atoms in $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$ as smooth modulations, with respect to their positions in the idealized layered structure. A refinement of the structure under the resulting superspace model has confirmed its efficiency. One can expect that this superspace description will also be valid for other compositions (*i.e.* different layer sequence periods) within the series $[\text{Ca},\text{Na}]_n\text{Nb}_n\text{O}_{3n+2}$, including those compounds where the size of the unit cell and the correlations of the atomic positions would make a conventional structural analysis problematic. From this common superspace symmetry and model, the three-dimensional symmetry properties of these compounds, as a function of composition, have been predicted, including those of a hypothetical high-temperature incommensurate phase.

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