

Superspace description of the crystal structures of  
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The crystal structures of two members of the homologous series  $\text{Ca}_n(\text{Nb,Ti})_n\text{O}_{3n+2}$ , with  $n = 5$  and  $6$ , are presented within the superspace formalism. A common  $(3 + 1)$ -dimensional superspace model is used to describe the crystal structures of both compositions within a particular homologous series, where the primary modulation wavevector and the width of the atomic domains vary systematically with composition. The two crystal structures are characterized as commensurately modulated structures consisting of discontinuous atomic domains described by occupational crenel functions. The displacive modulation functions for the two compounds exhibit similarities, but they also show that the idea of a unified superspace model does not extend toward the precise atomic positions. For  $n = 6$ , the centrosymmetric  $(3 + 1)$ -dimensional superspace symmetry provides a natural explanation for the pseudo-symmetries that are present in the non-centrosymmetric (three-dimensional) superstructure of this compound. The efficiency of the superspace approach is demonstrated by structure refinements in  $(3 + 1)$ -dimensional superspace and by comparing these results with the refinements in their three-dimensional superstructures.

## 1. Introduction

The crystal structures of  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  ( $n = 5$ ) and  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ ) at room temperature have recently been determined, employing different unit cells and different space groups for the two compounds (Guevarra *et al.*, 2005, 2007). These compounds belong to the homologous series  $A_nB_n\text{O}_{3n+2}$  with  $A = \text{Ca}$  and  $B = \text{Nb}$  or  $\text{Ti}$ . The crystal structures of these compounds can be described as layered structures comprising slabs of corner-sharing  $\text{ABO}_3$  octahedra, which are stacked along the  $[110]$  direction of the cubic perovskite structure. The width of the slabs is determined by the composition and it is given directly by the parameter  $n$ . Neighbouring slabs are separated by additional layers of O atoms and they are displaced with respect to each other by half the body diagonal of an octahedron along **a** (Fig. 1). This general packing scheme is described in more detail in Levin & Bendersky (1999; see Fig. 1 therein for a schematic projection of these structures), as well as in the presentations of the superstructures (Guevarra *et al.*, 2005, 2007).

Perez-Mato *et al.* (1999) have proposed that different compounds within a homologous series can be described by a unified structure model employing the superspace approach. The crystal structures of different compounds (different thickness of the perovskite slabs, *i.e.* different number  $n$  of stacked octahedra  $\text{BO}_6$  in the perovskite slabs) are obtained from a systematic variation of the modulation wavevectors

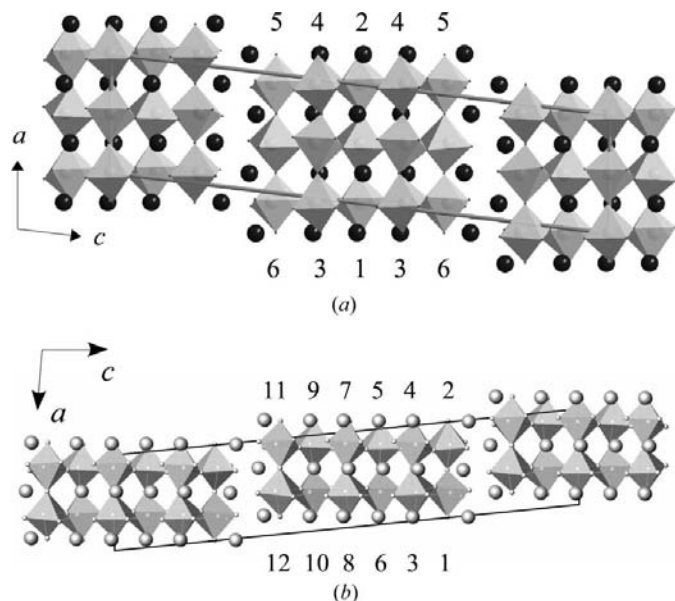
**Table 1**

Details of the three-dimensional superstructure refinements in the primitive (monoclinic) and C-centred (pseudo-orthorhombic) settings.

Diffraction data are from Guevarra *et al.* (2005) and Guevarra *et al.* (2007). Please note, that in the  $n = 6$  case the O atoms are refined with isotropic ADPs.

Compound	Ca <sub>5</sub> Nb <sub>4</sub> TiO <sub>17</sub>		Ca <sub>6</sub> (Nb,Ti) <sub>6</sub> O <sub>20</sub>	
	Primitive	C-centred	Primitive	C-centred
Space group	<i>P</i> 112 <sub>1</sub> / <i>b</i>	<i>C</i> 112 <sub>1</sub> / <i>d</i>	<i>P</i> 112 <sub>1</sub>	<i>C</i> 112 <sub>1</sub>
<i>a</i> (Å)	7.6889 (3)	7.6889 (3)	7.681 (2)	7.681 (2)
<i>b</i> (Å)	32.253 (1)	64.057 (2)	37.747 (6)	75.09 (1)
<i>c</i> (Å)	5.4763 (1)	5.4763 (1)	5.465 (1)	5.465 (1)
$\gamma$ (°)	96.767 (7)	89.921 (7)	95.87 (1)	90.04 (1)
<i>V</i> (Å <sup>3</sup> )	1348.6 (1)	2697.2 (2)	1576.1 (1)	3152.3 (2)
<i>Z</i>	4	8	4	8
No. of reflections	54 795	54 795	24 459	24 459
No. of unique reflections {obs[ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]/all}	2731/3231	2731/3231	5577/7800	5577/7800
<i>hkl</i> range	-9 $\rightarrow$ <i>h</i> $\rightarrow$ 9 -41 $\rightarrow$ <i>k</i> $\rightarrow$ 41 -7 $\rightarrow$ <i>l</i> $\rightarrow$ 7	-9 $\rightarrow$ <i>h</i> $\rightarrow$ 9 -82 $\rightarrow$ <i>k</i> $\rightarrow$ 82 -7 $\rightarrow$ <i>l</i> $\rightarrow$ 7	-10 $\rightarrow$ <i>h</i> $\rightarrow$ 10 -50 $\rightarrow$ <i>k</i> $\rightarrow$ 50 -7 $\rightarrow$ <i>l</i> $\rightarrow$ 7	-10 $\rightarrow$ <i>h</i> $\rightarrow$ 10 -100 $\rightarrow$ <i>k</i> $\rightarrow$ 100 -7 $\rightarrow$ <i>l</i> $\rightarrow$ 7
<i>R</i> <sub>int</sub> (obs/all)	0.020/0.021	0.020/0.021	0.031/0.033	0.031/0.033
<i>R</i> (obs/all)	0.050/0.058	0.050/0.058	0.055/0.076	0.055/0.076
<i>wR</i> (obs/all)	0.058/0.060	0.058/0.060	0.061/0.064	0.061/0.064
<i>S</i> (obs/all)	2.78/2.60	2.78/2.60	2.45/2.17	2.45/2.17
No. of parameters	254	254	292	292

and of the widths of the block-wavefunctions that are used to describe the occupational modulations of the atoms. The basic structure and the symmetry – as specified by a superspace group – are common to all compounds of a homologous series. The efficiency of the superspace approach has been demon-



**Figure 1**  
Projections of the structures along **b** of (a) Ca<sub>5</sub>Nb<sub>4</sub>TiO<sub>17</sub> ( $n = 5$ ) and (b) Ca<sub>6</sub>(Nb,Ti)<sub>6</sub>O<sub>20</sub> ( $n = 6$ ) in the monoclinic *b*-unique setting. The circles represent Ca atoms while (Nb,Ti)O<sub>6</sub> octahedra are outlined. The slabs consisting of five and six layers of octahedra, respectively, are stacked along the **c** axis. The numbers give the numbering of the Nb/Ti cations in the respective superstructures. The top line in each figure refers to the octahedra at the border of the unit cell ( $x = 0$ ), the bottom line to those in the middle of the cell ( $x = 1/2$ ).

strated for several compounds belonging to different homologous series (Zakhour-Nakhl *et al.*, 2000; Boullay *et al.*, 2002; Darriet *et al.*, 2002).

A superspace model for the homologous series  $A_nB_nO_{3n+2}$  has been proposed by Elcoro *et al.* (2001). It was successfully applied to the structure refinement of the  $n = 5$  member NaCa<sub>4</sub>Nb<sub>5</sub>O<sub>17</sub> of the series (Na,Ca)<sub>*n*</sub>Nb<sub>*n*</sub>O<sub>3*n*+2</sub> (Elcoro *et al.*, 2004). In the present work we have applied the superspace model of Elcoro *et al.* (2004) to the  $n = 5$  and  $n = 6$  members of the homologous series Ca<sub>*n*</sub>(Nb,Ti)<sub>*n*</sub>O<sub>3*n*+2</sub>. It is shown that the unified superspace approach also applies to these two compounds. Their structures are described by a unique superspace group and a common basic structure. The different stoichiometry is introduced *via* the modulation wavevectors and

occupational modulation functions, which systematically depend on  $n$ . However, it is found that the unified description is not valid for the displacive modulations that define the precise atomic positions in the supercells. For the  $n = 6$  compound, the (3 + 1)-dimensional superspace approach provides a natural explanation for the pseudo-symmetries as they were previously noticed in the three-dimensional superstructure of Ca<sub>6</sub>(Nb,Ti)<sub>6</sub>O<sub>20</sub> (Guevarra *et al.*, 2005).

## 2. Superspace description of $A_nB_nO_{3n+2}$

As introduced by Elcoro *et al.* (2001), the crystal structures of the perovskite-related homologous series  $A_nB_nO_{3n+2}$  can be described to a first approximation in terms of a stacking of two kinds of layers with the composition *ABO* and layers of pure oxygen. The stacking sequence is interrupted regularly by an empty *ABO* layer. The layer stacking sequence can be described by a common superspace group which is valid for the whole homologous series  $A_nB_nO_{3n+2}$ . For this homologous series, the unique (3 + 1)-dimensional superspace group to describe the parent, non-distorted orthorhombic structure is given by  $F'mmm(0 \sigma'_2 0)$ , where  $\sigma'_2 = 1/(n + 1)$  and  $F'$  represent a set of non-standard centring translations (0, 0, 0, 0), ( $\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2}$ ), ( $\frac{1}{2}, 0, \frac{1}{2}, \frac{1}{2}$ ), and (0,  $\frac{1}{2}, \frac{1}{2}, 0$ ) (Elcoro *et al.*, 2001). However, the actual atomic positions deviate from this ideal atomic layer-stacking (Elcoro *et al.*, 2001), which is constrained by symmetry. In a further development of their model, Elcoro *et al.* (2004) introduced a splitting of the atomic domain for the *A* cations (in the present case the Ca ion) into three domains. This was necessary due to the fact that the *A* cations at the border of the slab are shifted along the **b** axis towards the O2 layer and therefore have different average positions than those in the centre of the slab.

**Table 2**  
Details of the (3 + 1)-dimensional superspace refinements.

Compound	Ca <sub>5</sub> Nb <sub>4</sub> TiO <sub>17</sub>	Ca <sub>6</sub> (Nb,Ti) <sub>6</sub> O <sub>20</sub>
Superspace group	$C'2_1/d (\sigma_1 \sigma_2 0) \bar{1} 0$	$C'2_1/d (\sigma_1 \sigma_2 0) \bar{1} 0$
Superspace centring	(0, 0, 0, 0) $(\frac{1}{2}, 0, 0, \frac{1}{2})$ $(\frac{3}{4}, \frac{1}{2}, 0, \frac{1}{4})$ $(\frac{1}{4}, \frac{1}{2}, 0, \frac{3}{4})$	(0, 0, 0, 0) $(\frac{1}{2}, 0, 0, \frac{1}{2})$ $(\frac{3}{4}, \frac{1}{2}, 0, \frac{1}{4})$ $(\frac{1}{4}, \frac{1}{2}, 0, \frac{3}{4})$
Superspace Symmetry Operators	$(x_1 x_2 x_3 x_4)$ $(-x_1 -x_2 -x_3 \frac{1}{2} -x_4)$ $(-x_1 \frac{1}{2} -x_2 \frac{1}{2} +x_3 \frac{1}{2} -x_4)$ $(x_1 \frac{1}{2} +x_2 \frac{1}{2} -x_3 x_4)$	$(x_1 x_2 x_3 x_4)$ $(-x_1 -x_2 -x_3 \frac{1}{2} -x_4)$ $(-x_1 \frac{1}{2} -x_2 \frac{1}{2} +x_3 \frac{1}{2} -x_4)$ $(x_1 \frac{1}{2} +x_2 \frac{1}{2} -x_3 x_4)$
Basic structure unit cell		
<i>a</i> (Å)	7.6889 (3)	7.6805 (3)
<i>b</i> (Å)	5.3381 (3)	5.3641 (3)
<i>c</i> (Å)	5.4763 (1)	5.4653 (1)
$\gamma$ (°)	89.921 (4)	90.036 (4)
<i>V</i> (Å <sup>3</sup> )	224.77 (2)	225.17 (2)
<b>q</b>	(0 1/12 0)	(0 1/14 0)
No. of unique reflections (obs[ <i>I</i> > 3σ( <i>I</i> )]/all)	2731/3231	5186/5863
<i>HKLM</i> range	-9 → <i>H</i> → 9 -7 → <i>K</i> → 7 -7 → <i>L</i> → 7 -6 → <i>M</i> → 6	-8 → <i>H</i> → 10 -6 → <i>K</i> → 7 -7 → <i>L</i> → 7 -7 → <i>M</i> → 7
<i>R</i> <sub>int</sub> (obs/all)	0.021/0.021	0.030/0.031
<i>R</i> (obs/all)	0.051/0.058	0.058/0.065
<i>wR</i> (obs/all)	0.060/0.061	0.065/0.067
No. of reflections (obs/all)		
Main reflections <i>M</i> = 0	212/246	262/271
Satellites <i>M</i> = 1	465/565	1012/1124
Satellites <i>M</i> = 2	463/499	539/542
Satellites <i>M</i> = 3	448/578	909/1130
Satellites <i>M</i> = 4	479/509	554/556
Satellites <i>M</i> = 5	431/578	896/1138
Satellites <i>M</i> = 6	233/256	533/538
Satellites <i>M</i> = 7	-	481/564
No. of parameters	146	162

To appropriately describe the experimentally observed distorted structures, which in many cases exhibit double periodicity along the *a* axis as in the modulated structure of NaCa<sub>4</sub>Nb<sub>5</sub>O<sub>17</sub> (an *n* = 5 member of the homologous series), the valid superspace group is  $Xmmm(0 \sigma_2 0)$ , where  $\sigma_2 = \sigma_2'/2$  and *X* represents a set of non-standard centring translations (0, 0, 0, 0),  $(\frac{1}{4}, 0, \frac{1}{2}, \frac{1}{4})$ ,  $(\frac{1}{4}, 0, \frac{1}{2}, \frac{3}{4})$  and  $(0, \frac{1}{2}, \frac{1}{2}, 0)$  (Elcoro *et al.*, 2004). The extra centring contained in *X* compensates for the larger unit cell in this compound. The superspace group, which has been used in the present investigations (see below), is a subgroup of this superspace group  $Xmmm(0 \sigma_2 0)$  and can reduce to the three-dimensional space groups  $C112_1/d$  for *n* = 5 and  $C112_1$  for *n* = 6, respectively.

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 modulation wavevector and width of the atomic domains. The atomic domains are described in terms of step-like atomic occupational modulations with respect to the underlying average period. The presence of either a vacant *ABO* layer or shifted layers along the stacking sequence is thus realised through the limitation of the corresponding atomic occupation functions

along the internal subspace *x*<sub>4</sub> to discontinuous intervals, as characteristic of the step-like functions (Petricek *et al.*, 2000). The crystal structures of the two compounds investigated here may be described as commensurate modulations of the underlying basic structure. Thus, the initial phase of the modulation, *t*<sub>0</sub>, must be properly chosen to yield the appropriate three-dimensional structure (superstructure) since different values of *t*<sub>0</sub> yield different structures in real space (van Smaalen, 1987). For the two compounds investigated, *t*<sub>0</sub> = 0 for *n* = 5 and *t*<sub>0</sub> =  $\frac{1}{56}$  for *n* = 6 yield the correct space groups for the superstructures, as presented in Table 1.

### 3. Structure refinements in three- and in (3 + 1)-dimensional space

#### 3.1. Superstructure refinements

The crystal structures of Ca<sub>5</sub>Nb<sub>4</sub>TiO<sub>17</sub> (*n* = 5) and Ca<sub>6</sub>(Nb,Ti)<sub>6</sub>O<sub>20</sub> (*n* = 6) have been described with monoclinic unit cells with nearly equal *a* and *b* lattice parameters and long *c* axes of different length in a *b*-unique setting (Guevarra *et al.*, 2005, 2007). In order to be consistent with the setting of Elcoro *et al.* (2004), the unit cells have been transformed into a *c*-unique setting. In addition, the primitive (monoclinic) unit cells have been transformed into non-standard *C*-centred (pseudo-orthorhombic) unit cells according to **a**<sub>0</sub> = **a**<sub>*m*</sub>, **b**<sub>0</sub> = **a**<sub>*m*</sub> + 2**b**<sub>*m*</sub>, **c**<sub>0</sub> = **c**<sub>*m*</sub> (Table 1). Finally, the origins of the unit cells have been shifted by  $-\frac{1}{4}\mathbf{a}_0 - \frac{1}{2}\mathbf{c}_0$ , in order to conform to the superspace model of Elcoro *et al.* (2004). The *C*-centred settings are related to the layer model through the axes **b**<sub>0</sub> being the stacking axes.

Structure refinements have been performed for both compounds in their *C*-centred settings, employing the computer program *JANA2000* (Petricek *et al.*, 2000). Nb and Ti atoms are disordered over the same sites. Therefore, equal atomic coordinates and atomic displacement parameters (ADPs) were assigned to Nb and Ti on each of the independent sites in agreement with the previous refinements (Guevarra *et al.*, 2005, 2007).

For the centrosymmetric Ca<sub>5</sub>Nb<sub>4</sub>TiO<sub>17</sub> (*n* = 5), the structural model contains six independent (Nb,Ti) atoms, five independent Ca atoms and 17 independent O atoms, requiring a total of 84 positional parameters. The refinement, including anisotropic atomic displacement parameters for all atoms, the twin volume fraction and occupation fraction of Ti for each (Nb,Ti) site required a total of 254 parameters. In the case of the non-centrosymmetric Ca<sub>6</sub>(Nb,Ti)<sub>6</sub>O<sub>20</sub> (*n* = 6), the structure model consists of 12 independent (Nb,Ti) atoms, 12 independent Ca atoms and 40 independent O atoms resulting in a total of 192 positional parameters. Additional constraints, defined by a pseudo-inversion centre, were imposed on the anisotropic ADPs and occupancies of (Nb,Ti) sites that are related by a pseudo-inversion centre. The refinement with

**Table 3**

Definition of the occupational modulation functions (crenel functions) for  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  ( $n = 5$ ) and  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ ).

Atomic coordinates highlighted in bold are refinable (Elcoro *et al.*, 2004).  $x_4$  denotes the centre of the atomic domain while  $\Delta$  refers to its width. Nb domains, which have site symmetry  $\bar{1}$ , are described by antisymmetric displacive modulation functions. All other domains have no restriction on the type of symmetry-allowed displacive modulation functions.

	$\text{Ca}_n(\text{Nb,Ti})_n\text{O}_{3n+2}$			$\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$		$\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$	
	$x_1$	$x_2$	$x_3$	$x_4$	$\Delta$	$x_4$	$\Delta$
Nb1	1/4	0	1/2	0	5/24	0	3/14
Nb2	3/4	0	1/2	0	5/24	0	3/14
Ca1	<b>0</b>	<b>0</b>	<b>0</b>	0	1/8	0	1/7
Ca2	<b>0</b>	<b>1/4</b>	<b>0</b>	5/48†	1/24	3/28†	1/28
Ca3	<b>0</b>	<b>-1/4</b>	<b>0</b>	-5/48†	1/24	-3/28†	1/28
O1	<b>0</b>	<b>0</b>	<b>1/2</b>	0	5/24	0	3/14
O2	<b>1/4</b>	<b>1/4</b>	<b>1/4</b>	0	1/4	0	1/4
O3	<b>3/4</b>	<b>1/4</b>	<b>1/4</b>	0	1/4	0	1/4

† These numbers are starting values for the refinement for the case where  $x_2 = 1/4$ , respectively  $x_2 = -1/4$ . They will change with a change in  $x_2$ . An explanation is given in the text.

isotropic ADPs for O atoms, the twin volume fraction and occupation fractions required a total of 292 parameters.

The structure refinements in the C-centred setting converged to identical  $R$  values and identical structures as those reported for refinements in the primitive settings (Table 1 and Guevarra *et al.*, 2005, 2007).

### 3.2. Superspace refinements

Structure refinements in the  $(3 + 1)$ -dimensional superspace were carried out with JANA2000 (Petricek *et al.*, 2000). Reflection indices ( $hkl$ ) with respect to the supercells were transformed toward four-integer indexing ( $HKLM$ ) with respect to the basic structure unit cells and modulation wavevectors. The main reflections correspond to the reflections ( $hkl$ ) with  $k = 12K$  for  $n = 5$  and  $k = 14K$  for  $n = 6$ . Satellite reflections are those reflections with  $k = 12K + M$  ( $M = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6$ ) and  $k = 14K + M$  ( $M = \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6, \pm 7$ ) for  $n = 5$  and  $n = 6$ , respectively. The distribution of reflections among the different categories is given in Table 2.

The superspace model for  $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$  ( $n = 5$ ) of Elcoro *et al.* (2004) was employed as a starting model for the present refinements. Crenel functions for the occupational modulations in  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  were identical to those in Elcoro *et al.* (2004), while the crenel functions for  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  were adapted to the different composition and supercell period of this compound (Table 3). Displacement modulations and modulations of the anisotropic ADPs were described by orthogonalized functions according to the procedure of Petricek *et al.* (1995). Displacement parameters were determined by refinements starting with arbitrary but small values for those parameters. To retain the superspace construct, *i.e.* to keep the centres of the atomic domains for the split Ca positions at constant distances with respect to the  $t$  parameter

( $t = x_4 - \mathbf{qr}$ ), it was necessary to apply the following constraints during refinement:

$$x_4(\text{Ca2}) = [\Delta(\text{Ca1}) + \Delta(\text{Ca2})]/2 + \sigma_2 \cdot y(\text{Ca2})$$

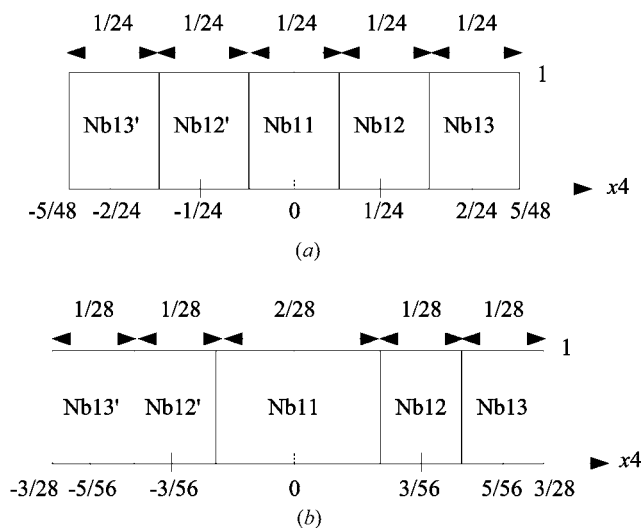
and

$$x_4(\text{Ca3}) = -[\Delta(\text{Ca1}) + \Delta(\text{Ca3})]/2 + \sigma_2 \cdot y(\text{Ca3}).$$

In these equations,  $x_4$  denotes the centre of the atomic domain and  $\Delta$  refers to its width,  $\sigma_2$  is the component of the modulation wavevector.

Initial refinements including variations of the fraction of Ti on the two crystallographically independent (Nb,Ti) sites were not entirely satisfactory, resulting in  $R_F(\text{obs}) = 0.058$  for  $n = 5$  and  $R_F(\text{obs}) = 0.071$  for  $n = 6$ . The reason is that the two refined occupancy parameters are insufficient to describe the variations of Nb/Ti ratios, as observed in the superstructure refinements. Modulation functions for the Ti occupancy would be necessary, combined with the Crenel functions. However, then the orthogonalization in the JANA2000 software is no longer automatic and has to be introduced by hand. Rather than doing so, the domains of the occupancies of each of the two (Nb,Ti) sites were split into five subdomains as shown in Fig. 2. Each  $\text{Nbi}$  ( $i = 1, 2$ ) site was split into three crystallographically independent  $\text{Nbi}1$ ,  $\text{Nbi}2$  and  $\text{Nbi}3$  sites. The Nb/Ti ratio was then independently refined for each of the six independent sites. The model occupancies correspond exactly to the variations in the occupancies, as observed in the three-dimensional superstructure approach.

Orthogonalized functions for the displacement modulations were determined for the full domains of Nb1 and Nb2. They appeared to be well approximated by the first and sixth harmonics of the sine functions for  $n = 5$  and an additional



**Figure 2**

Subdomains comprising the atomic domains of Nb1 in (a)  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  ( $n = 5$ ) and (b)  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ ). The widths and centres of the subdomains along  $x_4$  are indicated. The occupancy probability of a subdomain is equal to 1 within the indicated interval and zero outside this interval (and similarly for corresponding sets of sub-domains centred at  $x_4 = \text{integer}$ ). An equivalent definition of subdomains Nb21, Nb22 and Nb23 applies to the site Nb2.

**Table 4**

Summary of partial  $R$  values of the three-dimensional superstructure and the  $(3 + 1)$ -dimensional superspace refinements.

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

	Three-dimensional	(3 + 1)-dimensional	Three-dimensional	(3 + 1)-dimensional
Compound	$\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$		$\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$	
No. of parameters	254	146	292	162
$R(\text{obs})/wR(\text{obs})$	0.050/0.058	0.051/0.060	0.055/0.061	0.058/0.065
$M = 0$		0.047/0.059		0.044/0.058
$M = 1$		0.044/0.054		0.071/0.069
$M = 2$		0.047/0.060		0.045/0.055
$M = 3$		0.046/0.054		0.085/0.078
$M = 4$		0.056/0.066		0.041/0.049
$M = 5$		0.057/0.060		0.110/0.097
$M = 6$		0.061/0.064		0.044/0.057
$M = 7$		–		0.094/0.096

12th harmonic sine function for the  $n = 6$  compound. This particular selection of sine functions was used for the displacement modulations of the (Nb,Ti) sites with split domains, because orthogonalized functions could not be generated in this approach. All six Nb11, Nb12, Nb13, Ti11, Ti12 and Ti13 atoms were constrained to have identical parameters for the basic position, ADPs and displacement modulations, with a similar set of constraints for Nb21, Nb22, Nb23, Ti21, Ti22 and Ti23. Final refinements converged to  $R$  values almost equal to the  $R$  values of the superstructure refinements, while employing about half as many parameters (Table 4).

## 4. Discussion

### 4.1. Validation of the superspace refinements

Structure refinements applying the superspace approach have resulted in fits to the data of nearly equal quality as the superstructure refinements, while employing many fewer parameters (Tables 1 and 2). For  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  equal numbers of parameters have been used for the atomic positions in both three-dimensional superstructure and  $(3 + 1)$ -dimensional superspace refinements. The slightly higher  $R$  values of the superspace refinements are thus due to a large reduction in the number of ADPs. However, the introduction of additional harmonic waves for the modulation of the ADPs in the superspace model does not lead to significant non-zero values for them. Therefore, it is concluded that the slightly better fit of the superstructure model mainly represents a fit to the noise rather than a true structural effect. Compared with the structural model of  $\text{NaCa}_4\text{Nb}_5\text{O}_{17}$  ( $n = 5$ ) (Elcoro *et al.*, 2004), the present model of  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  contains one additional modulation function each for the displacement modulations of O2 and O3. These additional functions were necessary to obtain a good fit to the data, and their values are comparable to the values of other modulation functions.

In the refinement of  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  the atomic positions have been described by a smaller number of parameters in the superspace model than have been used in the superstructure refinement. This reduction of parameters has led to less

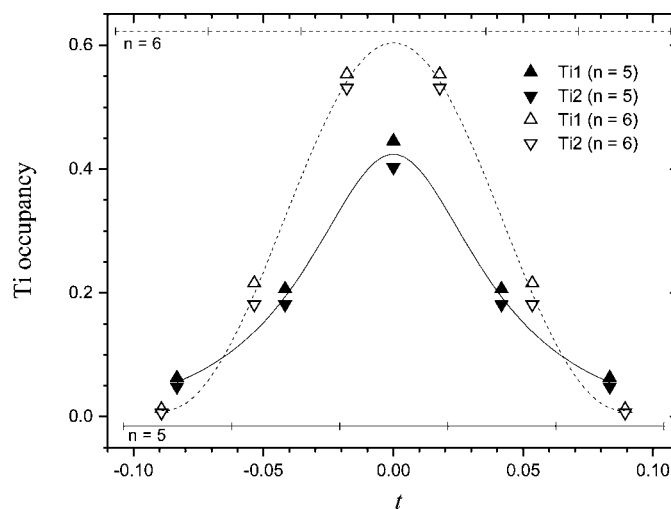
correlation and resulted in improved interatomic distances (see the discussion below).

As proposed by Perez-Mato *et al.* (1999) and Elcoro *et al.* (2001), the same superspace model should apply to all members of the series  $\text{Ca}_n(\text{Nb,Ti})_n\text{O}_{3n+2}$ . In the case of  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$ , we have noticed that 1937 reflections of the type  $(HKLM) : H + 2K - M \neq 4i$  ( $i = \text{integer}$ ) are classified as extinct. Intensities of these reflections range up to  $11\sigma$ , with 394 observed reflections and 105 reflections with  $I > 5\sigma$ . Obviously this class of reflections is weak, but some significant intensity

has been observed. This intensity could possibly be explained if the centring translations  $(\frac{1}{4}, \frac{1}{2}, 0, \frac{3}{4})$  and  $(\frac{3}{4}, \frac{1}{2}, 0, \frac{1}{4})$  are dropped. However, refinements without this lattice centring are unstable and suffer from high correlations between parameters. Alternatively, intensity at these points may be explained by stacking faults. Therefore, we conclude that the unified superspace structure model is applicable to the  $n = 6$  compound to a very good approximation.

### 4.2. Modulation functions

The three-dimensional superstructures follow from the  $(3 + 1)$ -dimensional superspace structure model by the values of the modulation functions at  $n$  equidistant values of their arguments  $\bar{x}_4$ . For the Nb/Ti occupational modulation, a one-to-one match is thus obtained between superstructure and



**Figure 3**

Site occupancy factors of Ti at the different Ti subdomains in  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  ( $n = 5$ , filled triangles and the solid line) and  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ , open triangles and the dotted line). The curves are obtained by fits of pseudo-Voigt functions centred at  $t = 0$  to the data points. For the sake of clarity the subdomains as defined in Fig. 2 are also indicated at the bottom ( $n = 5$ ) and the top ( $n = 6$ ) of the graph.

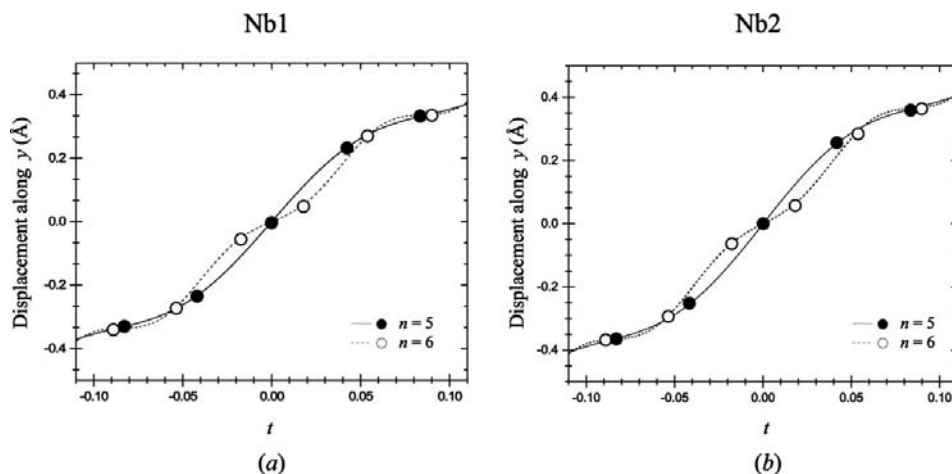
superspace refinements. The values of the latter are graphically shown in Fig. 3 (compare Fig. 3 with Fig. 6 of Guevarra *et al.*, 2005, and with Fig. 3 of Guevarra *et al.*, 2007). Minor differences in occupancies between the two approaches can be

explained by correlations that always exist between occupational parameters and ADPs.

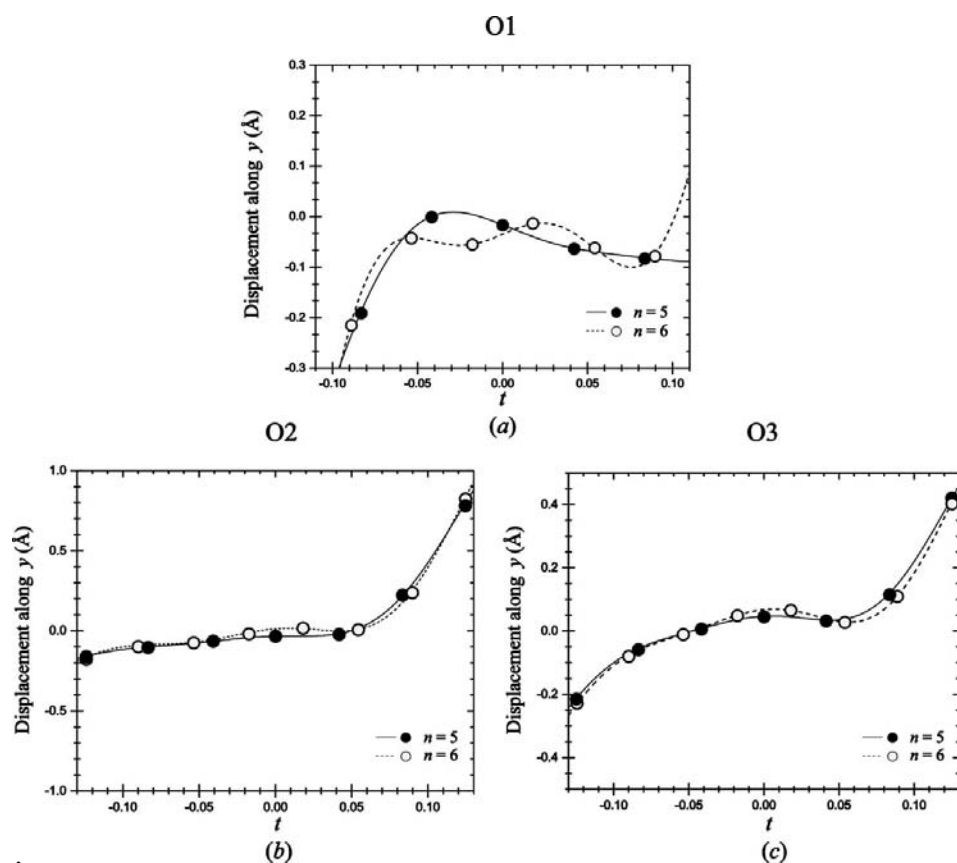
It has been proposed that the superspace approach should provide a unified model for all compounds of the homologous series  $\text{Ca}_n(\text{Nb,Ti})_n\text{O}_{3n+2}$ .

With accurate structure models for the two compounds this proposal can now be tested. First, it is noticed that a unified superspace model according to Table 3 applies to a good approximation indeed. However, displacement modulation functions are not identical between the two refinements (Figs. 4 and 5). In particular, the refined functions for displacement modulations of atoms incorporate more parameters in the case of  $n = 6$  than they possess for  $n = 5$ . Nevertheless, the refined functions of  $n = 6$  do not describe exactly the positions of the atoms of  $n = 5$ . However, a rough match between the two modulations might be inferred from Figs. 4 and 5. It is thus concluded that the superspace models of the  $n = 5$  and  $n = 6$  compounds are slightly different so that they can accommodate the different superstructure models of these two compounds.

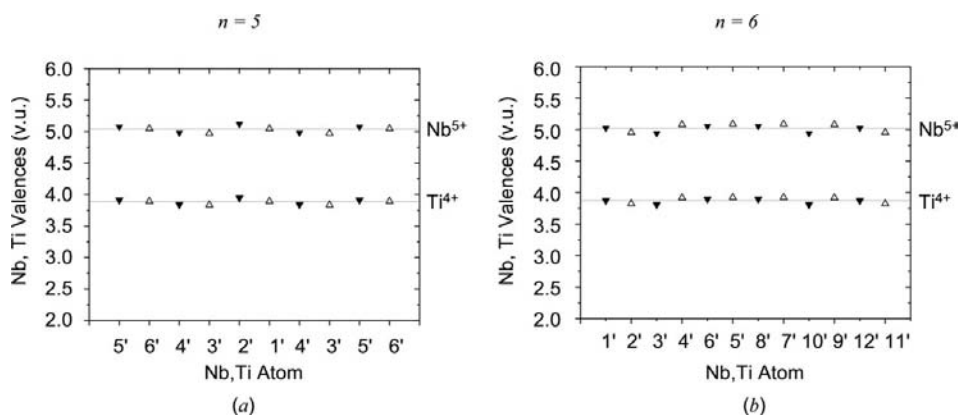
For  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ ), the superspace approach employs many fewer parameters than the superstructure refinement, unlike in  $n = 5$  for which the same number of occupational and positional parameters have been used. This difference reflects the different symmetries  $P2_1$  and  $P2_1/b$  (respectively  $C2_1$  and  $C2_1/d$  in the  $C$ -centred pseudo-orthorhombic setting) of the superstructures of the two compounds. The superspace approach for  $n = 6$  employs a centrosymmetric superspace group, and thus leads to equal Nb/Ti ratios on sites that are related by superspace inversion (Fig. 3), but that are independent sites in the non-centrosymmetric supercell. In this way the superspace approach gives a natural explanation for the pseudo-symmetries as they have been



**Figure 4**  
*t*-Plots of the *y* components of the displacive modulation functions of (a) Nb1 and (b) Nb2 atoms in  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  ( $n = 5$ , filled circles and solid lines) and  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ , open circles and dotted lines). Circles correspond to atomic displacements in three-dimensional space obtained by commensurate cuts of superspace.



**Figure 5**  
*t*-Plots of the *y* components of the displacive modulation functions of (a) O1, (b) O2 and (c) O3. Filled circles and solid lines correspond to  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  ( $n = 5$ ), open circles and dotted lines to  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ ). Circles correspond to atomic displacements in three-dimensional space obtained by commensurate cuts of superspace.



**Figure 6**

Nb and Ti valences for the different (Nb,Ti) sites in  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  ( $n = 5$ ) and  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ ). The horizontal axes refer to the (Nb,Ti) sites in the three-dimensional superstructure obtained from the superspace structure model. The (Nb,Ti) atoms are arranged such that the centre of the horizontal axis corresponds to the centre of the slabs, in agreement with Guevarra *et al.* (2005) and Guevarra *et al.* (2006). BVS parameters have been obtained from Brese & Keeffe (1991) as  $R_0(\text{Nb}-\text{O}) = 1.911$ ,  $R_0(\text{Ti}-\text{O}) = 1.815$  and  $R_0(\text{Ca}-\text{O}) = 1.967$  Å.

observed in the superstructure (Guevarra *et al.*, 2005), while removing interdependencies between parameters.

The higher quality of the structure model obtained from the superspace refinement is illustrated by the computed valences (Fig. 6). Especially in the case of  $n = 6$ , computed valences are much closer to their formal values of 5+ for Nb and 4+ for Ti for all sites in the structure (again, compare Fig. 6 with Fig. 7 of Guevarra *et al.*, 2005, and Fig. 4 of Guevarra *et al.*, 2007). Please note that the BVS in each case ( $n = 5$  and  $n = 6$ ) were calculated based on the atomic distances of the superstructures obtained by transforming with JANA2000 the refined superspace model to the corresponding superstructure. In the BVS computation it was assumed that each independent Nb/Ti site is fully occupied by either Nb or Ti since the compounds have exclusively Nb or Ti in each site.

## 5. Conclusions

The crystal structures of  $\text{Ca}_5\text{Nb}_4\text{TiO}_{17}$  ( $n = 5$ ) and  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ ) have been described within the superspace approach. The structures can be interpreted as commensurately modulated structures with discontinuous atomic domains given by occupational crenel functions. The modulation wavevector and the width of the atomic domains systematically depend on  $n$ . Refinements in superspace demonstrate the efficiency of the superspace approach. The

economy of parameters used in the refinements and application of a unified superspace model to both  $n = 5$  and 6 compounds show that the superspace approach is indeed effective in the structural description of these perovskite-related compounds. While a unified superspace model is valid for  $n = 5$  and 6, the displacement modulations of (Nb,Ti) and O atoms are described by different functions in the two compounds, thus a unified superspace model does not extend toward the fine details of the structure models. For  $\text{Ca}_6(\text{Nb,Ti})_6\text{O}_{20}$  ( $n = 6$ ) the superspace model offers a natural explanation for the pseudo-inversion symmetry, as it has been previously noticed in the

superstructure (Guevarra *et al.*, 2005).

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