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Superspace description of the homologous series $Ga_4Ti_{m-4}O_{2m-2}$ with the crystallographic shear structure based on that of rutile

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A generalized approach is proposed for the structure description of the homologous series $Ga_4Ti_{m-4}O_{2m-2}$ with crystallographic shear (CS) structures based on that of rutile. A (3 + 1)-dimensional model for an ideal CS structure is built up in connection with the CS operation in three-dimensional space. Its structural parameters are determined by m, the shear plane and the shear vector. The Rietveld fitting of the X-ray diffraction profile of $Ga_4Ti_{13}O_{32}$ (m = 17) was successfully carried out using the ideal CS structure as an initial model, where modulation functions of atomic positions are inherently discontinuous and sawtooth-like. The deviation of a real structure from the ideal one was described by a few additional Fourier terms. This method was confirmed to be efficient for reducing the number of structural parameters required in the refinement in comparison to the conventional three-dimensional description.

1. Introduction

The homologous series $Ga_4Ti_{m-4}O_{2m-2}$ ($15 \leq m \leq 23$, m odd) in the system TiO_2–Ga_2O_3 was first reported by Gibb & Anderson (1972). Later, the phases for up to m = 31 were observed by electron diffraction (Kamiya & Tilley, 1977). Lloyd *et al.* (1976) carried out the single-crystal X-ray diffraction analysis of $Ga_4Ti_{21}O_{48}$, that is, the phase with m = 25. According to their analysis, it is certain that the structure is a crystallographic shear (CS) structure based on that of rutile, despite the fact that a few problems are seen in the results. (For example, the isotropic displacement parameters of many O atoms were negative.) It is known that such long-period structures can be described as special modulated structures in a superspace formalism, in which the modulation functions are discontinuous (Elcoro *et al.*, 2000, 2001, 2004; Boullay *et al.*, 2002*a*,*b*, 2003). Most of those structures can be described as commensurately modulated structures, but an incommensurate CS structure was found recently (Michiue *et al.*, 2005). Owing to the discontinuity of the modulation functions, their diffraction patterns are quite different from those of the usual modulated structures.

In the latter, the deviation from a basic structure (represented by straight lines along the fourth direction in the superspace description) is usually small. In addition, in some commensurately modulated structures, higher-order satellite reflections are not observed. In many cases, we can recognize the hierarchy of the reflection intensity, that is, the higher the order, the weaker the intensity. It is known that the maximum order of Fourier coefficients required in refinements is generally equal to that of observed reflections. (Strictly, this is the case for occupational modulation but not for displacive modulation.) Therefore, the number of parameters necessary

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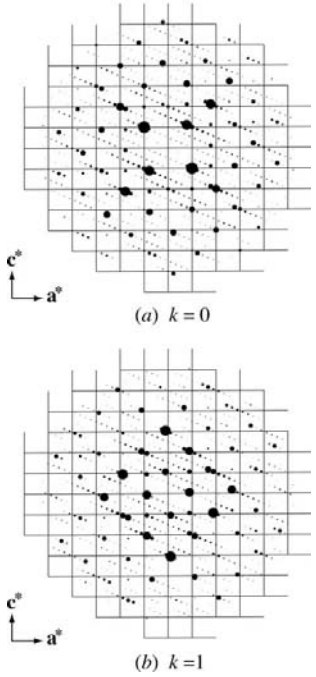
in (3 + 1)-dimensional refinements of commensurate structures can be less than that in three-dimensional refinements in such cases. On the other hand, the hierarchy of satellite reflection intensities is broken in CS structures, suggesting that it is difficult to reduce the number of parameters even in a superspace approach (see Fig. 1). Nevertheless, we can reduce the number of parameters by using an ideal CS structure in (3 + 1)-dimensional superspace, as shown in this paper.

In the CS structures, atoms are defined in limited ranges, which are called occupation domains. In particular, the modulation functions of ideal CS structures in (3 + 1)-dimensional superspace can be given by sawtooth-like functions (Michiue *et al.*, 2005). Appropriate sawtooth-like functions can minimize the deviation of real modulation functions from those of an initial model. The deviation is described by introducing additional Fourier terms. Therefore, when it is well expressed by a small number of Fourier terms, the number of parameters can be reduced. The purpose of this study is to establish a way of building such an ideal structure in (3 + 1)-dimensional superspace in connection with the CS operation in three-dimensional space, which is defined by the shear plane and the shear vector. As an example, a model building is shown for the CS structures of $Ga_4Ti_{m-4}O_{2m-2}$. First, a superspace model is built up in a manner applicable to all the phases with arbitrary m. Subsequently, the efficiency of the model is confirmed by the refinement for X-ray diffraction data of the phase with $m = 17$, $Ga_4Ti_{13}O_{32}$. The advantage of the superspace approach over the conventional three-dimensional refinement will be clearly demonstrated.



(*a*) $k = 0$

(*b*) $k = 1$

Figure 1
The simulated diffraction patterns of $Ga_4Ti_{13}O_{32}$ obtained from the results of the Rietveld refinement. (*a*) *h*0*lm* plane; (*b*) *h*1*lm* plane. The grids show the reciprocal lattice for the average structure.

2. Ideal (3 + 1)-dimensional models of CS structures

All the CS structures of the homologous series $Ga_4Ti_{m-4}O_{2m-2}$ are derived from the rutile structure by the CS operation as shown in Fig. 2 for $m = 17$. The shear plane $(20\overline{1})_r$ and the shear vector $\mathbf{S} = [\frac{1}{2}\,\frac{1}{2}\,\frac{1}{4}]_r$ are independent of m, where the subscript r represents the parent rutile structure coordinate system. (For convenience we take **b** as a unique axis for the rutile structure in this paper despite the tetragonal unit cell of rutile.) An ideal CS structure can be obtained from the rutile structure by the following two steps. First, some atoms in the vicinity of shear planes are removed from the rutile structure in Fig. 2(*a*). Then the structure consists of separated blocks, as shown in Fig. 2(*b*). Next, each block is displaced by the shear vector to fill the gap between the blocks. This gives the CS structure in Fig. 2(*c*). This procedure can be described in (3 + 1)-dimensional superspace so as to generate all structures of the series in a unified form. In the following, we show how to build up the corresponding (3 + 1)-dimensional structures for $Ga_4Ti_{m-4}O_{2m-2}$. For convenience, the shear vector **S** is decomposed into the two components $\mathbf{S_b} = [0\,\frac{1}{2}\,0]_r$ and $\mathbf{S_{ac}} = [\frac{1}{2}\,0\,\frac{1}{4}]_r$. Using these vectors, the CS operation can be divided into three steps: step I: removal of

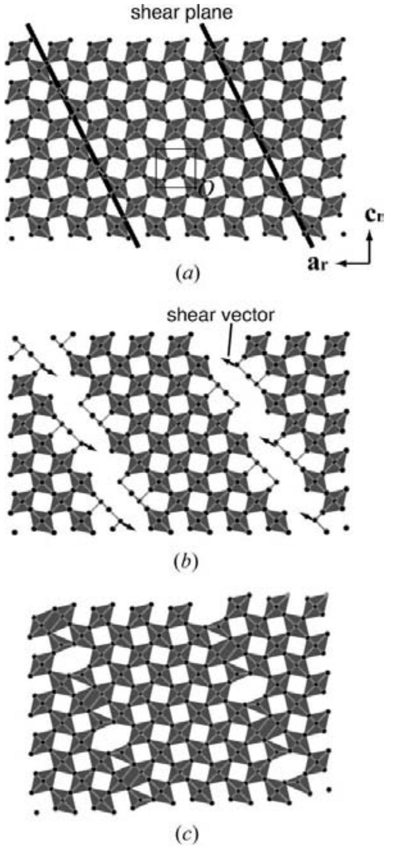
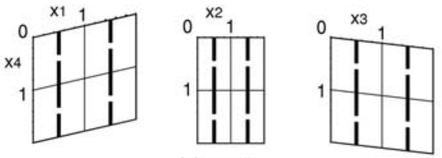


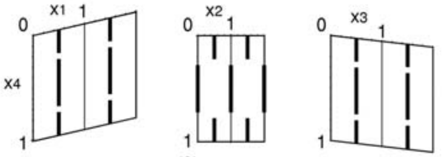
Figure 2
Projection along **b** of (*a*) a parent structure of rutile, (*b*) rutile blocks and (*c*) the CS structure of $Ga_4Ti_{m-4}O_{2m-2}$. Removal of atoms in the vicinity of the shear planes from the rutile structure of (*a*) gives rutile blocks in (*b*). The displacement of the rutile blocks by the shear vector completes the CS operation, resulting in the CS structure of (*c*).

atoms; step II: displacement of blocks by $\mathbf{S_b}$ or $-\mathbf{S_b}$; and step III: shifting of blocks by $\mathbf{S_{ac}}$.

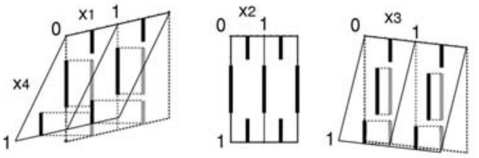
In step I, we consider the structure in Fig. 2(*b*) as a commensurately modulated structure. At this stage, a basic cell is still similar to the unit cell of rutile: $\mathbf{a} = \mathbf{a}_r$, $\mathbf{b} = \mathbf{b}_r$, $\mathbf{c} = \mathbf{c}_r$ and $\beta = 90^\circ$, where $\mathbf{a}_r$, $\mathbf{b}_r$ and $\mathbf{c}_r$ are the the unit vectors of the rutile structure. Since the direction of the wavevector is normal to the shear plane and its (inverse) magnitude corresponds to the interval of the shear planes in real (external) space, the modulation wavevector is given by $\mathbf{q}_0 = 4\mathbf{a}^*/(m + 1) - 2\mathbf{c}^*/(m + 1)$. Although the space group of the parent rutile structure is $P4_2/mmn$, the modulation introduced by the removal of atoms reduces the symmetry. In the present case the highest average structure symmetry becomes $P2/m$. Then the basic structure contains four non-equivalent atom sites, Ti1 $(0, 0, 0)$, Ti2 $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, O1 $(u, 0, u)$ and O2 $(\frac{1}{2} - u, \frac{1}{2}, u - \frac{1}{2})$, in the unit cell. Among them, Ti2, O1 and O2 atoms near the shear plane are removed. The ratio of removed atoms for each site is $2/(m + 1)$ in the present case. Corresponding to this operation, the modulation functions become discontinuous. Therefore crenel functions have to be applied to modulation functions for the occupancy of Ti2, O1 and O2 atoms. This approach is equivalent to the use of an occupation domain with length $\Delta = 1 - 2/(m + 1)$. Note that the length is less than 1, and therefore there is a gap with a width of $2/(m + 1)$ due to the removal of these atoms in the modulation function. As an example, a (3 + 1)-dimensional structure of the Ti2 site is shown in Fig. 3(*a*). The symmetry operations of this structure are given by x_1, x_2, x_3, x_4; $-x_1, x_2, -x_3, -x_4$; $-x_1, -x_2, -x_3, -x_4$; $x_1, -x_2, x_3, x_4$. The corresponding superspace group is $P2/m(\alpha 0 \gamma)$.



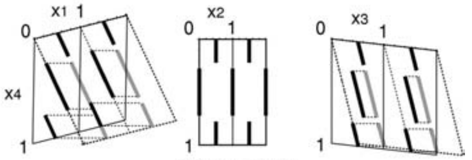
(*a*) step I



(*b*) step II



(*c*) step III (1)



(*d*) step III (2)

Figure 3

Modification of the (3 + 1)-dimensional structure for the Ti2 atom according to the process of the shear operation for (*a*) step I (removal of some of the atoms), (*b*) step II (displacement of the rutile blocks by the vector $[0\,\frac{1}{2}\,0]_r$) and (*c*) step III (displacement of the blocks by the vector $[\frac{1}{2}\,0\,\frac{1}{4}]_r$). The description in (*c*) is equivalent to (*d*) in the standard embedding for the modulated structures.

In step II, we consider the alternate shifts of consecutive blocks in Fig. 2(*b*) by $\mathbf{S_b}$ and $-\mathbf{S_b}$ relative to the previous block. Since the shift of blocks in Fig. 2 in three-dimensional space corresponds to the shift of atoms in Fig. 3 along the external space (horizontal line), this leads to the superspace structure shown in Fig. 3(*b*). Then the *b* axis of the average structure is halved. In this structure an atom on $x_2 = \frac{1}{2}$ is related to another atom on $x_2 = 0$ by the centering translation $(0, \frac{1}{2}, 0, \frac{1}{2})$. Thus, the fourth axis of the new unit cell is doubled. Consequently, the modulation wavevector becomes $\mathbf{q} = \mathbf{q}_0/2 = 2\mathbf{a}^*/(m + 1) - \mathbf{c}^*/(m + 1)$. This leads to the symmetry operations $(0, 0, 0, 0; 0, \frac{1}{2}, 0, \frac{1}{2}) + x_1, x_2, x_3, x_4$; $-x_1, x_2, -x_3, -x_4$; $-x_1, -x_2, -x_3, -x_4$; $x_1, -x_2, x_3, x_4$. They give the superspace group $P2/m(\alpha 1/2 \gamma)$ which is equivalent to $P2/m(\alpha\beta 1/2)$ listed in *International Tables for Crystallography* (1999, Vol. C, pp. 899–947, Table 10.3).

In step III, we consider the remaining shift by $\mathbf{S_{ac}}$. Similarly to step II, this operation shifts the consecutive atoms along the external space. In contrast to step II, the shift is not alternate in this case. As a result, the fourth axis becomes oblique relative to that in step II (Fig. 3*c*). This is similar to the description of quasicrystals, where the unit vectors in a higher-dimensional space are parallel to neither the external nor the internal space. In the standard embedding of the modulated structure, however, the fourth axis is taken to be parallel to the internal space. Such an expression can be obtained by introducing the shear strain, which leaves the external space invariant (Yamamoto, 1996; Fig. 3*d*). Accordingly, we have a sawtooth-like function in the final description. Since the rotation of atoms in Fig. 3(*d*) is obtained by the shear strain and the strength of the shear strain is determined by the shear vector $\mathbf{S_{ac}}$, the rotation angle of the atoms in Fig. 3(*d*) is uniquely determined. However, the superspace group of the resulting structure is unchanged.

The cell parameters for the ideal CS structures of any *m* are given as functions of cell dimensions of rutile. Fractional coordinates of atoms in three-dimensional space based on the new cell deviate from those based on the old one. They can also determine the parameters for sawtooth-like modulation functions by lifting these into the four-dimensional unit cell. The periods **A** and **C** along **a** and **c** (after the shear operation) are shown in Fig. 4. They are given by $\mathbf{A} = (m + 1)\mathbf{a}_r/2 - 2\mathbf{S_{ac}}$ and $\mathbf{C} = (m + 1)\mathbf{c}_r + 2\mathbf{S_{ac}}$ since they cross the boundary twice. (Note that *m* is an odd number in the present case.) Then the unit vectors of the average structure are defined by $\mathbf{a} = 2\mathbf{A}/(m + 1)$, $\mathbf{b} = \mathbf{b}_r$ and $\mathbf{c} = \mathbf{C}/(m + 1)$. Therefore we have $\mathbf{a} = \mathbf{a}_r - 2\alpha\mathbf{S_{ac}} = (1 - 2\alpha S_a)\mathbf{a}_r - 2\alpha S_c\mathbf{c}_r$, $\mathbf{c} = \mathbf{c}_r - 2\gamma\mathbf{S_{ac}} = -2\gamma S_a\mathbf{a}_r + (1 - 2\gamma S_c)\mathbf{c}_r$, where S_a and S_c are components of the shear vector, **S**

Table 1
Crystallographic data and structural parameters for the ideal CS structure of $Ga_4Ti_{m-4}O_{2m-2}$.

Monoclinic, $P2/m(\alpha 1/2 \gamma)$
$a = [(1-2\alpha S_a)^2 + (2\alpha S_c)^2]^{1/2} a_r = [(m^2-2m+2)^{1/2}/(m+1)] a_r$
$b = b_r$
$c = [(2\gamma S_a)^2 + (1-2\gamma S_c)^2]^{1/2} c_r = [(4m^2+12m+13)^{1/2}/2(m+1)] c_r$
$\beta = \cos^{-1}(\mathbf{a}\cdot\mathbf{c}/ac) = \cos^{-1}[-5/(m^2-2m+2)^{1/2}(4m^2+12m+13)^{1/2}]$
$\mathbf{q} = \alpha\mathbf{a}^* + \gamma\mathbf{c}^* = [P_a/(m+1)]\mathbf{a}^* + [P_c/(m+1)]\mathbf{c}^*$

	x_1^0	x_2^0	x_3^0	x_4^0	Δ
$M1$ (Ti/Ga)	0	0	0	0	1/2
$M2$ (Ti/Ga)	0.5	0.5	0.5	0	$1/2 - 1/(m+1)$
O1	u_1	0	u_3	$\alpha x_1^0 + \gamma x_3^0 - (1/2 - \Delta)/2$	$1/2 - 1/(m+1)$
O2	v_1	0.5	v_3	$\alpha x_1^0 + \gamma x_3^0 - (1/2 - \Delta)/2$	$1/2 - 1/(m+1)$

For all atoms
$V_{x1} = \Delta S_a/D$
$V_{x2} = 0$
$V_{x3} = \Delta S_c/D$

a_r, b_r, c_r: cell dimensions of rutile. P_a, P_c: components of the shear plane $(P_a\ 0\ P_c) = (20\overline{1})_r$, which are correlated to the modulation wavevector $\mathbf{q} = (\alpha\ 0\ \gamma)$ by $(m+1)\mathbf{q} = (P_a\ 0\ P_c)$, or $\alpha = P_a/(m+1) = 2/(m+1)$, $\gamma = P_c/(m+1) = -1/(m+1)$. S_a, S_c: components of the shear vector, $[S_a\ \frac{1}{2}\ S_c] = [\frac{1}{2}\ \frac{1}{2}\ \frac{1}{4}]_r$. The sawtooth-like function is defined by $u_{xi} = (2V_{xi}/\Delta)(x_4 - x_4^0)$. $D = 1 - 2\alpha S_a - 2\gamma S_c$. $u_1 = \{[1 + 2(S_a - S_c)\gamma]u - S_a(\frac{1}{2} - \Delta)\}/D = [(2m+1)u - 1]/(2m-1)$. $u_3 = \{[1 + 2(S_a - S_c)\alpha]u - S_c(\frac{1}{2} - \Delta)\}/D = (4mu - 1)/2(2m-1)$. $v_1 = \{[1 - 2(S_a + S_c)\gamma](\frac{1}{2} - u) - S_a(\frac{1}{2} - \Delta)\}/D = [(2m+3)(\frac{1}{2} - u) - 1]/(2m-1)$. $v_3 = \{[1 - 2(S_a + S_c)\alpha](u - \frac{1}{2}) - S_c(\frac{1}{2} - \Delta)\}/D = [4m(u - \frac{1}{2}) - 1]/2(2m-1)$. u (= 0.305): fractional coordinate for x and z of an O atom in the rutile structure.

$= [S_a\ S_b\ S_c]_r = [\frac{1}{2}\frac{1}{2}\frac{1}{4}]_r$, and α and γ are the $\mathbf{a}_r^*$ and $\mathbf{c}_r^*$ components of the modulation wavevector $\mathbf{q}$; $\alpha = 2/(m+1)$, $\gamma = -1/(m+1)$. The shear operation distorts the unit cell, so that the unit vectors in the corresponding reciprocal lattice, $\mathbf{a}^*$, $\mathbf{c}^*$, are also changed. The modulation wavevector is, however, given by $\mathbf{q} = \alpha\mathbf{a}^* + \gamma\mathbf{c}^*$ with the same α and γ.

All the three-dimensional atom positions in the block including the origin are given by $(x + l_x)\mathbf{a}_r$, $(y + l_y)\mathbf{b}_r$, $(z + l_z)\mathbf{c}_r$, where l_x, l_y and l_z are integers. When these positions are written as $(x_1 + l_x)\mathbf{a}$, $(x_2 + l_y)\mathbf{b}$, $(x_3 + l_z)\mathbf{c}$ in terms of $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$, x_1 and x_3 change depending on l_x and l_z, while x_2 does not change. Then $x_1 = x + 2S_a t$, $x_2 = y$, $x_3 = z + 2S_c t$, where $t = \alpha(x_1 + l_x) + \gamma(x_3 + l_z)$. Therefore, at $t = 0$, $x_1 = x$ and $x_3 = z$. These positions are written as x_1^0, x_2^0 and x_3^0, that is, $x_1^0 = x$, $x_2^0 = y$ and $x_3^0 = z$. In the superspace description of modulated structures, t modulo 1 is regarded as the fourth coordinate. Note that $(x_1^0, x_2^0, x_3^0, 0)$ may not correspond to a real atom position of a commensurately modulated structure as in the present case, since t may not be equal to zero modulo 1 for any integers l_x and l_z. We can, however, use $(x_1^0, x_2^0, x_3^0, 0)$ to specify the position of the occupation domain. As shown in Appendix A, the above relations led us to conclude that the deviations from x_1^0 and x_3^0 depend linearly on $x_4' = \alpha(x_1^0 + l_x) + \gamma(x_3^0 + l_z)$ with the coefficients given by the shear vector components: $x_1 - x_1^0 = 2S_a x_4'/D$ and $x_3 - x_3^0 = 2S_c x_4'/D$ $(D = 1 - 2\alpha S_a - 2\gamma S_c)$. This is the origin of the amplitude of the sawtooth-like modulation functions.

All the parameters including the modulation functions are listed in Table 1. The definition of each parameter is similar to the corresponding definition in our previous work (Michiue *et al.*, 2005). (Since the ratio of Ti^{4+} to O^{2-} ions removed from the parent structure in step I is Ti:O = 1:4, negative charges of TiO_4^{4-} should be compensated by the substitution of Ga^{3+} ions for some of the Ti^{4+} ions. Therefore, the metal sites Ti1 and Ti2 were renamed $M1$ and $M2$ in the table.) Atoms $M1$, $M2$, O1 and O2 pass through (0, 0, 0, 0), $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}, 0)$, $(u, 0, u, 0)$, and $(\frac{1}{2} - u, \frac{1}{2}, u - \frac{1}{2}, 0)$, respectively. From their site symmetry, the length of the occupation domain from these points should be the same for both sides in $M1$ and $M2$, while it can be different from one side to the other in O1 and O2. The length for each side is chosen so that the external space passes through the center of the gap. This criterion requires asymmetric occupation domains around $(u, 0, u, 0)$ for O1 and $(\frac{1}{2} - u, \frac{1}{2}, u - \frac{1}{2}, 0)$ for O2. When we specify the center of the occupation domain, x_4^0 deviates from zero for O1 and O2. Consequently, the first and third coordinates of O1 and O2 in Table 1 also deviate a little from $(u, 0, u)$ and $(\frac{1}{2} - u, \frac{1}{2}, u - \frac{1}{2})$, respectively. Obviously, when m is large enough, u_1, u_3, v_1 and v_3 in the table approximate to u, u, $\frac{1}{2} - u$, and $u - \frac{1}{2}$, respectively. Thus, the basic cell and sawtooth parameters for the ideal CS structures in the present homologous series are unambiguously given by the shear plane and the shear vector. It should be noted that the structure of commensurately modulated structures depends on the choice of three-dimensional hyperplane. The three-dimensional section should be switched

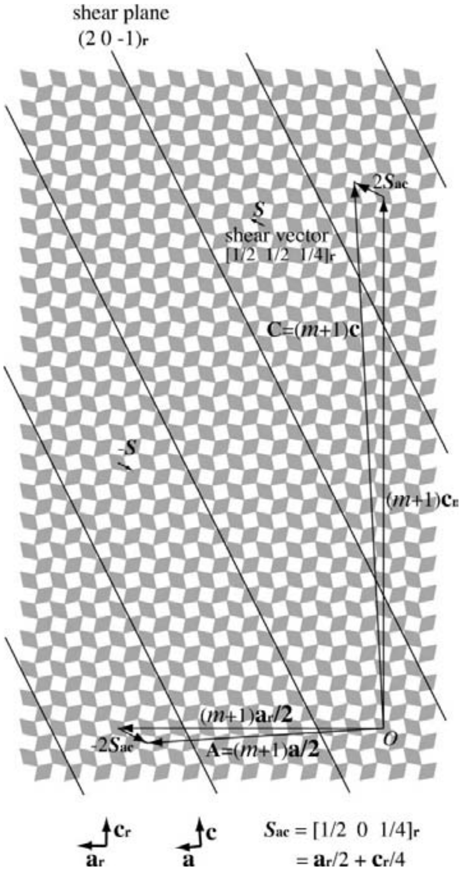


Figure 4
Relations between the basic cell of the ideal CS structure and the unit cell of rutile. **a** and **c** are axes for the ideal CS structure, while $\mathbf{a}_r$ and $\mathbf{c}_r$ are those for rutile.

according to m; $t' = 0$ for $m = 4n + 1$ [modulo $1/(m + 1)$] (n= integer) and $t' = 1/2(m + 1)$ [modulo $1/(m + 1)$] for $m = 4n + 3$ as is usually seen in the superspace description of homologous series. It is remarkable that Table 1 is applicable to incommensurate structures when m becomes an irrational number, because the closeness condition (Cornier-Quiquandon *et al.*, 1992) is fulfilled even in this case, as mentioned by Elcoro *et al.* (2003).

3. Structure refinement of $Ga_4Ti_{13}O_{32}$

As an example of the application of the above theory, the structure refinement of $Ga_4Ti_{13}O_{32}$ has been performed, thus demonstrating that the structure can be well determined by parameters less than those in conventional refinements.

3.1. Experimental

We were unable to obtain single crystals suitable for the intensity measurement. (Actually, a single crystal used by Lloyd *et al.*, 1976, contained the adjacent phase of $m = 23$, and all the reflections from the second phase were removed in their refinement.) Therefore, we prepared powder samples and employed the Rietveld method. Powder samples of $Ga_4Ti_{13}O_{32}$ were prepared by a solid-state reaction. TiO_2 and Ga_2O_3 heated at 1273 K for 1 d were mixed in a molar ratio of TiO_2:Ga_2O_3 = 13:2 using an agate mortar in ethanol. The mixture was heated in a platinum tube at 1723 K for 4 d and then cooled to room temperature. After grinding, the sample was reheated at 1723 K for 5 d. X-ray diffraction data were collected using a high-resolution diffractometer with Debye–Scherer geometry installed at the BL-15XU beamline at SPring-8. The specimen was sealed into a quartz capillary tube with an inner diameter of 0.5 mm. The measurement was carried out with a wavelength of 0.8 Å in a 2θ range between 4 and 80°, with a step interval of 0.004°. The structure was refined by Rietveld profile fitting using *JANA2000* (Petricek *et al.*, 2000). Crystallographic data and conditions for the refinement are summarized in Table 2.[1]

3.2. Results

According to previous studies for rutile summarized by Howard *et al.* (1991), cell dimensions of $a_r = c_r = 4.594$, $b_r = 2.959$ Å were used to calculate a basic cell for an ideal CS structure of a phase with $m = 17$, $Ga_4Ti_{13}O_{32}$; $a = 4.092$, $b = 2.959$, $c = 4.729$ Å, $\beta = 90.48°$. Parameters for ideal modulation functions were obtained from Table 1. In an initial stage, all structural parameters except for cell parameters and the scale factor were fixed at initial values, and the remaining parameters (the background, peak profile *etc.*) were refined. The modulation for the occupation factor of metal ions, representing the replacement of Ti and Ga, was not considered yet. Namely, occupation ratios were fixed at Ga/Ti = 4/13 for all the metal sites. At this stage, the reliability factors were $R_p = 0.142$ and $R_{\rm wp} = 0.209$. The deviations of refined cell parameters from the ideal values were −0.05, 0.56, 0.14 and 0.21% for a, b, c and β, respectively.

Table 2
Crystallographic data and conditions for refinement of $Ga_4Ti_{13}O_{32}$.

Crystal data	
Chemical formula	$Ga_{0.444}O_{3.556}Ti_{1.444}$
M_r	157
Cell setting, superspace group	Monoclinic, $P2/m(\alpha\,1/2\,\gamma)$
Temperature (K)	295
a, b, c (Å)	4.09045 (2), 2.97554 (1), 4.73593 (2)
β (°)	90.2935 (2)
$\mathbf{q}$ (= $\alpha\mathbf{a}^* + \gamma\mathbf{c}^*$)	$\mathbf{a}^*/9 - \mathbf{c}^*/18$
Z	1
D_x (Mg m^{-3})	4.52
Radiation type	Synchrotron
Refinement	
R factors	$R_p = 0.065$, $R_{\rm wp} = 0.094$, $R_{\rm obs} = 0.040$, $wR_{\rm obs} = 0.039$
Profile function	Pseudo-Voigt
No. of parameters	78
No. of structural parameters	45

In the next step this model was modified. The local structure in the vicinity of the boundary (shear plane) is basically identical to that seen in the β-Ga_2O_3 structure (Geller, 1960). In the course of the refinement, it has been proved that metal sites in this part should be treated as independent sites rather than those included in the $M1$ and $M2$ sites; otherwise, modulation functions were locally perturbed near the edges of the occupation domains and required higher-order additional Fourier terms. A part of the $M1$ site is a tetrahedral site, which is to be fully occupied by the Ga ion. Therefore, the occupation domain of $M1$ was divided into two parts to give two non-equivalent sites in the basic structure; one is the tetrahedral site allotted to the Ga ion, and the other forms an octahedral coordination. Thus, a part of the occupation domain, with the length $2/(m + 1) = 1/9$, of the $M1$ site was removed, and instead a new metal site, $M1'$, with a width $1/(m + 1) = 1/18$ was added. The parameter x_4^0 of the $M1'$ site is chosen at $x_4^0 = \alpha x_1^0 + \gamma x_3^0 + (\Delta_{M1} + \Delta_{M1'})/2 = x_1^0/9 - x_3^0/18 + 2/9$, so that the occupation domains of the two sites are just connected to each other in the projection on to the fourth axis. Similarly, parts of the occupation domain of the $M2$, O1, and O2 sites were separated and treated as new non-equivalent sites $M2'$, O1′, O1″, O2′ and O2″. The Ga ions are expected to be more concentrated at the $M2'$ site than at $M2$. Fourier terms were then introduced for modulation functions of the atomic positions for the $M1$, $M2$, O1 and O2 sites. Sawtooth parameters were fixed at the ideal values in order to prevent correlations between the sawtooth-like function and Fourier terms. The orthogonization was unnecessary in the refinement applying Fourier terms up to the second order for atoms $M1$ and $M2$, and the first order for atoms O1 and O2. The occupation ratios for the metal sites were refined imposing the constraint condition so as to keep the Ga/Ti ratio of the whole structure at 4/13. The modulations for displacement parameters were not taken into account for all the sites. The final structural parameters are listed in Table 3. Metal–oxygen distances and bond-valence sums at

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: CK5017). Services for accessing these data are described at the back of the journal.

Table 3
Structural parameters for $Ga_4Ti_{13}O_{32}$.

	x_1^0	x_2^0	x_3^0	x_4^0	Δ	U^{iso}
*M*1	0	0	0	0	7/18	0.0093 (4)
*M*1′	0.1363 (5)	0	0.1050 (4)	0.23153 (6)	1/18	0.0118 (6)
*M*2	0.5	0.5	0.5	0	1/3	0.0095 (4)
*M*2′	0.6738 (6)	0.5	0.5838 (5)	0.20910 (7)	1/18	0.0045 (7)
O1	0.301 (7)	0	0.311 (5)	−0.0116 (8)	1/3	0.0041 (6)
O1′	0.055 (2)	0	0.267 (2)	−0.2309 (3)	1/18	0.002 (2)
O1″	0.456 (3)	0	0.390 (2)	0.1957 (3)	1/18	0.013 (3)
O2	0.219 (7)	0.5	−0.178 (5)	0.0064 (8)	1/3	0.0080 (7)
O2′	0.003 (3)	0.5	−0.291 (2)	−0.2057 (3)	1/18	0.009 (3)
O2″	0.415 (3)	0.5	−0.076 (2)	0.2170 (3)	1/18	0.019 (3)

		x_1	x_2	x_3
*M*1	V	7/33	0	7/66
	U_1^s	−0.050 (3)	0	−0.018 (3)
	U_2^s	0.025 (2)	0	0.006 (2)
*M*2	V	2/11	0	1/11
	U_1^s	−0.025 (6)	0	0.028 (5)
	U_2^s	0.004 (4)	0	−0.018 (3)
O1	V	2/11	0	1/11
	U_1^s	−0.0102 (18)	0	−0.0104 (15)
	U_1^c	−0.020 (7)	0	−0.010 (6)
O2	V	2/11	0	1/11
	U_1^s	−0.0087 (18)	0	−0.0131 (14)
	U_1^c	−0.017 (7)	0	−0.010 (6)

The Ti/Ga ratio is 0.965 (5)/0.035 (5), 0.919 (6)/0.081 (6) and 0.63 (2)/0.37 (2) at *M*1, *M*2 and *M*2′, respectively. *M*1′ is fully occupied by Ga. V is 0 for x_1, x_2, x_3 at *M*1′, *M*2′, O1′, O1″, O2′ and O2″. Constraint conditions between x_1^o, x_3^0 and x_4^0 were imposed as follows: *M*1′: $x_4^0 = \Delta x_4^0 + 2/9$; *M*2′: $x_4^0 = \Delta x_4^0 + 1/6$; O1: $x_4^0 = \Delta x_4^0 - 1/36$; O1′: $x_4^0 = \Delta x_4^0 - 2/9$; O1″: $x_4^0 = \Delta x_4^0 + 1/6$; O2: $x_4^0 = \Delta x_4^0 - 1/36$; O2′: $x_4^0 = \Delta x_4^0 - 2/9$; O2″: $x_4^0 = \Delta x_4^0 + 1/6$; $\Delta x_4^0 = x_1^0/9 - x_3^0/18$.

metal sites were within normal ranges. (The projection of the refined three-dimensional structure is quite similar to Fig. 2*c*, so the figures of the refined structure were omitted.) Final modulation functions for the *x* and *z* coordinates are shown in Fig. 5. As is clear from the figure, the modulation functions are almost straight, indicating that their deviation from the sawtooth-like functions assumed in the ideal model is very small. This ensures the smooth convergence of the least-squares refinement.

In order to confirm the validity of the above refinement, we performed the refinement with the same data by the conventional technique. In this method, nine metal sites and 16 O atoms are non-equivalent in a unit cell of a' = 34.113, b' = 2.976, c' = 10.298 Å, β' = 96.989 ° under the space group *C*2/*m*. ($\mathbf{a}' = -8\mathbf{a} + 2\mathbf{c}$, $\mathbf{b}' = -\mathbf{b}$, $\mathbf{c}' = \mathbf{a} + 2\mathbf{c}$.) As one metal site is at the origin and others are on the mirror plane (x, 0, z), 48 parameters are necessary for fractional coordinates. In addition, isotropic displacement parameters for all sites (25 parameters) and occupation factors of metal sites (seven parameters), except for a tetrahedral site fully occupied by the Ga ion, were refined with a constraint condition so that the Ga/Ti ratio in the whole structure is kept at 4/13. Thus, in total, 81 structural parameters including the scale factor were used in the refinements. The reliability factors R_p = 0.064 and R_{wp} = 0.094 were almost the same as those of the superspace description using 45 structural parameters.

4. Discussion

We consider another possibility in the modeling, since a detailed model has several possibilities. If *M*1′, *M*2′, O1′, O1″, O2′ and O2″ are included in the *M*1, *M*2, O1 and O2 sites of the rutile-like domain, the perturbation of modulation functions is expected to be locally prominent near the edges of occupation domains, because the deviation from the ideal structure is remarkable near the boundary. Such functions require higher-order coefficients of additional Fourier terms. On the other hand, the removal of the edge parts reduces the order of coefficients required for the modulation functions of the domain parts. In this treatment, however, additional parameters are necessary since the separated parts are considered as independent atoms. Therefore, the number of parameters to be refined is roughly equal in the two cases, and the choice of each model may be possible in general. It is obvious that the larger the thickness of the domain (*i.e.* the larger *m*), the better the latter model is. In the present case of *m* = 17, better results were obtained by separating the metal sites. This is partly because the Ga ions are concentrated at the boundary regions.

In addition to the embedding employed in the present analysis, the description in Fig. 3(*c*) suggests an alternative description for the same CS structure. This situation is similar to that for quasicrystals, where the occupation domain is parallel to the internal space, and suggests that the CS structures are rather similar to quasicrystals in the higher-dimensional description. This description gives an equivalent embedding for the same structure but a non-standard one for the modulated structures. Since this is not familiar as a

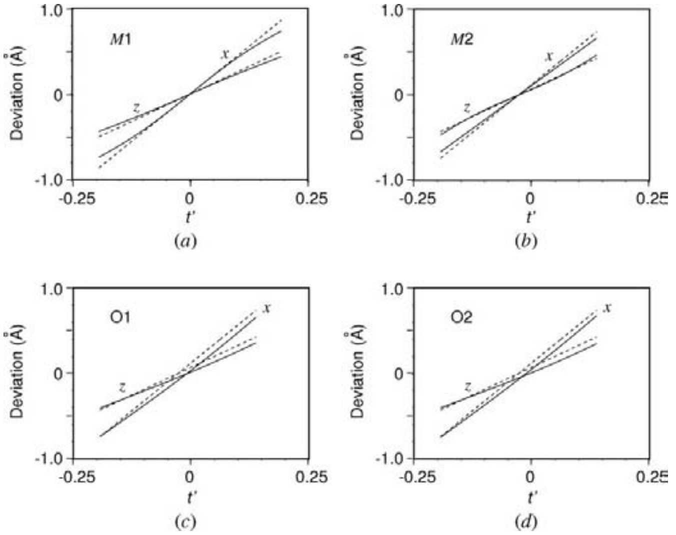

Figure 5
Deviations for x and z coordinates as a function of t' (= $x_4 - \mathbf{q}\cdot\mathbf{r}_j$). The solid and dotted lines show the modulation functions with and without the Fourier terms, respectively.

description of aperiodic crystals with crystallographic symmetry, we briefly discuss the relation between the standard embedding and the non-standard one.

In Fig. 3(*c*), the fourth axis is not parallel to the internal space but has **a** and **c** components. As mentioned in §2, these are related to the shear strain, which leaves the external space invariant. In the reciprocal space, the corresponding shear strain leaves the internal space invariant. As a result, in the non-standard embedding, the diffraction vector moves in parallel to the internal space by the shear strain. Therefore, the first three unit vectors in the four-dimensional reciprocal lattice, which were taken on the external space in the standard embedding, have internal space components. These two different descriptions give the same structure factor for the same reflection for the following simple reason. Since this is given by the Fourier integral of the electron density within the four-dimensional unit cell, and the inner product of the diffraction vector and the positional vector in four-dimensional space is invariant under such shear strain, the structure factor gives the same value (Yamamoto, 1996).

It is noted that even in this non-standard embedding we can choose a fourth vector that has no **a** component, as is clear from Fig. 3(*c*). When we take the fourth axis parallel to the internal space, the *a* axis of the average structure is halved and we have a *C*-centered lattice. As a result, the (3 + 1)-dimensional superspace group has the centering translations (0, 0, 0, 0), $(\frac{1}{2}, \frac{1}{2}, 0, \frac{1}{2})$, leading to the superspace group $C2/m(\alpha 1 \gamma)$. [This is equivalent to $B2/m(\alpha\beta 0)$ in *International Tables for Crystallography* (1999, Vol. C, pp. 899–947, No. 12.1). In this setting, the wavevector $\mathbf{q}' = \mathbf{q} - \mathbf{a}^*$ is used.] This corresponds to the choice of an alternating shear vector $\mathbf{S_a}$ and $-\mathbf{S_a}$, similar to the case of the shear vector along **b** in the method discussed in §2. The consideration analogous to that in §2 leads to the corresponding embedding with this superspace group. It should be noted that this description is applicable only when $S_a = 1/2$. The superspace group $C2/m(\alpha 1 \gamma)$ is not equivalent to $P2/m(\alpha 1/2 \gamma)$ as the superspace group, but they are equivalent as the four-dimensional space group. This suggests that the superspace group is inappropriate to specify the symmetry of CS structures as in the composite crystals, where the symmetry can be specified by a combination of several (usually two) superspace groups (Yamamoto, 1993) or simply by an *n*-dimensional ($n > 3$) space group.

5. Concluding remarks

It was shown that the CS structures in the homologous series $Ga_4Ti_{m-4}O_{2m-2}$ are well described as modulated structures. A (3 + 1)-dimensional model for the ideal CS structures is unambiguously built up in connection with the shear operation in three-dimensional space. A basic cell for each phase is related to the unit cell of rutile. The shear operation leads to discontinuous and sawtooth-like modulation functions of atomic positions. It was also shown that their modulation wavevectors and sawtooth parameters are determined by *m*, together with the shear plane and the shear vector. The structure refinement can be carried out using this ideal CS model as an initial structure. Therefore, all the ideal structures in the series can be determined by the three-dimensional structure of one example and lattice parameters and chemical composition of the others. The deviation of a real structure from an ideal one can be considered by a small number of additional Fourier terms, giving the possibility of the structure analyses with a smaller number of parameters. The present method provides, therefore, a systematic and convenient method of structure determination in the series of compounds. Its efficiency has been demonstrated by the Rietveld analysis of $Ga_4Ti_{13}O_{32}$ ($m = 17$). Although the results from the conventional three-dimensional refinement give essentially the same results as those of the present method, the number of parameters used in the present method is much smaller than that in the conventional one. This suggests that in the conventional method, many parameters are highly correlated and redundant parameters are included. Obviously, the advantage of the superspace approach is more important for the phases with a larger *m*. We confirmed the efficiency of the present method only for $Ga_4Ti_{m-4}O_{2m-2}$, but the approach will be applicable to any homologous series of other CS structures after minor modifications and will be equally efficient for those series.

APPENDIX *A*

For the deviation of the first and third coordinates from those of the parent structure, the expressions $(x_1 - x_1^0) = 2S_a(\Delta x_4 + x_4')$ and $(x_3 - x_3^0) = 2S_c(\Delta x_4 + x_4')$, where $\Delta x_4 = \alpha(x_1 - x_1^0) + \gamma(x_3 - x_3^0)$ and $x_4' = \alpha(x_1^0 + l_x) + \gamma(x_3^0 + l_z)$ apply. These are written as

$$\begin{pmatrix} 1 - 2\alpha S_a & -2\gamma S_a \\ -2\alpha S_c & 1 - 2\gamma S_c \end{pmatrix} \begin{pmatrix} x_1 - x_1^0 \\ x_3 - x_3^0 \end{pmatrix} = \begin{pmatrix} 2S_a x_4' \\ 2S_c x_4' \end{pmatrix}. \quad (1)$$

This leads to

$$\begin{pmatrix} x_1 - x_1^0 \\ x_3 - x_3^0 \end{pmatrix} = \frac{1}{D} \begin{pmatrix} 1 - 2\gamma S_c & 2\gamma S_a \\ 2\alpha S_c & 1 - 2\alpha S_a \end{pmatrix} \begin{pmatrix} 2S_a x_4' \\ 2S_c x_4' \end{pmatrix}, \quad (2)$$

where $D = 1 - 2\alpha S_a - 2\gamma S_c$. Therefore, we have $x_1 - x_1^0 = 2S_a x_4'/D$ and $x_3 - x_3^0 = 2S_c x_4'/D$.

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