

Superspace description of the homologous series
 $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ Yuichi Michiue^{a*} and Noboru
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A unified description for the structures of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$, gallium zinc oxide, is presented using the superspace formalism. The structures were treated as a compositely modulated structure consisting of two subsystems. One is constructed with metal ions and the other with O ions. The ideal model is given, in which the displacive modulations of ions are well described by the zigzag function with large amplitudes. Alternative settings are also proposed which are analogous to the so-called modular structures. The validity of the model has been confirmed by refinements for phases with $m = 6$ and $m = 9$ in the homologous series. A few complex phenomena in real structures are taken into account by modifying the ideal model.

1. Introduction

Long-period structures are known in ZnO-based homologous series, $M_2\text{O}_3(\text{ZnO})_m$ ($M = \text{In}, \text{Fe}, \text{Ga}$; Kasper, 1967; Kimizuka *et al.*, 1995, 1993), where m is an integer. The homologous series $\text{In}_2\text{O}_3(\text{ZnO})_m$ has drawn attention as a candidate for photocatalysts (Kudo & Mikami, 1998), transparent conducting oxides (Moriga *et al.*, 1998) and thermoelectric materials (Ohta *et al.*, 1996). Structures of $\text{In}_2\text{O}_3(\text{ZnO})_m$ are basically isotypical to those of $\text{LuFeO}_3(\text{ZnO})_m$ (Isobe *et al.*, 1994). Structures of $\text{Fe}_2\text{O}_3(\text{ZnO})_m$ are also understood as superstructures of $\text{In}_2\text{O}_3(\text{ZnO})_m$ (Kimizuka *et al.*, 1993). Recently, the structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ has been determined (Michiue *et al.*, 2008), which is of a new type and is completely different from those in the homologous series $\text{In}_2\text{O}_3(\text{ZnO})_m$ and $\text{Fe}_2\text{O}_3(\text{ZnO})_m$. In systems $\text{In}_2\text{O}_3\text{--}M_2\text{O}_3\text{--ZnO}$ ($M = \text{Fe}, \text{Ga}, \text{Al}$), the homologous phases $\text{InMO}_3(\text{ZnO})_m$ are formed (Kimizuka *et al.*, 1989; Nakamura *et al.*, 1990, 1991, 1993), which are basically isostructural with $\text{In}_2\text{O}_3(\text{ZnO})_m$. Thus, only $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ forms a different type of structure series from that of the other ZnO-based homologous series.

A structure unit consisting of metal ions in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ resembles the arrangement of Zn ions in the wurtzite ZnO structure. A structure unit of oxygen ions in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ also resembles the arrangement of the O ions in ZnO. The structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ as a whole is, however, completely different from that of wurtzite. One of the most distinct differences is that the distance between the neighboring metal ions is longer than that between neighboring O ions in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$, while the two distances are equal in ZnO. That is, the density of the metal ions is lower than that of the O ions in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$, which coincides with the chemical composition of this compound. Structures of other phases in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ were predicted, in which the basic period of metal ions was shorter than that of O ions along *c*, analogous to $\text{Ga}_2\text{O}_3(\text{ZnO})_6$. Thus, it is expected that

Table 1

Crystallographic data and conditions for data collection and refinement for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_9$.

For all structures: $Z = 8$, $D_x = 5.68 \text{ Mg m}^{-3}$. Experiments were carried out at 298 K with Mo $K\alpha$ radiation using a Rigaku AFC-7R diffractometer. Data collection used ω scans. The weighting scheme based on measured s.u.s was $w = 1/[\sigma^2(I) + 0.0001F^2]$.

	$m = 6$	$m = 9$
Crystal data		
Chemical formula	$\text{Ga}_{0.25}\text{O}_{1.25}\text{Zn}_{0.75}$	$\text{Ga}_{0.1818}\text{O}_{1.0909}\text{Zn}_{0.8181}$
M_r	84.5	83.6
Crystal system, space group	Orthorhombic, $Cmmm(00\gamma)0s0$	Orthorhombic, $Cmcm(00\gamma)000$
Wave vectors	$\mathbf{q} = 9\mathbf{c}^*/8$	$\mathbf{q} = 12\mathbf{c}^*/11$
a, b (Å)	3.2465 (9), 19.640 (5)	3.2494 (14), 19.722 (6)
c_1 (Å)	3.0979 (8)	3.0513 (11)
c_2	2.7537 (7) = $c_1 \times 8/9$	2.7970 (10) = $c_1 \times 11/12$
V (Å ³)	197.53 (9)	195.54 (12)
No. of reflections for cell measurement	25	25
μ (mm ⁻¹)	24.6	24.7
Color	Colorless	Colorless
Crystal size (mm)	0.12 × 0.06 × 0.02	0.20 × 0.12 × 0.024
Data collection		
Radiation source	Rotating anode	Rotating anode
Absorption correction	φ scan	Analytical
T_{\min}, T_{\max}	0.18, 0.61	0.034, 0.417
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7287, 3699, 1349	3662, 1862, 993
R_{int}	0.122	0.048
θ values (°)	$\theta_{\max} = 45.0, \theta_{\min} = 2.7$	$\theta_{\max} = 30.1, \theta_{\min} = 2.8$
Range of h, k, l_1, l_2	$h = 0 \rightarrow 6, k = 0 \rightarrow 38, l_1 = -7 \rightarrow 7, l_2 = -6 \rightarrow 6$	$h = 0 \rightarrow 4, k = -27 \rightarrow 0, l_1 = -7 \rightarrow 7, l_2 = -7 \rightarrow 7$
No. and frequency of standard reflections	3 every 200	3 every 200
Intensity decay (%)	0.0	0.0
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.044, 0.099, 1.03	0.034, 0.068, 1.35
No. of reflections	3699	1862
No. of parameters	115	149
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	2.29, -2.27	1.60, -1.21
Extinction coefficient	404 (14)	590 (20)

Computer programs: JANA2006 (Petříček *et al.*, 2006).

the structures of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ can be treated as commensurate phases of the compositely modulated structures (Yamamoto, 1996; van Smaalen, 1995). Many studies (van Smaalen, 1987; Yamamoto *et al.*, 1985; Perez-Mato *et al.*, 1987) have proved that the superspace formalism, which was originally developed for the analysis of incommensurate structures (de Wolff, 1974; Janner & Janssen, 1980*a,b*), is useful for the description of commensurate structures.

In the usual modulated structures, an initial model for the refinement in (3 + 1)-dimensional superspace is a so-called basic structure, in which each atom is expressed by a straight line extending along the fourth direction. In compositely modulated structures, an initial model is usually obtained by combining basic structures of the two subsystems. Although the structures of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ are considered as composite crystals, we were unable to use such an initial model because a basic structure was not available for either of the two subsystems. Similar situations often happen

when a structure model in superspace is established for the unified description of long-period structures in a homologous series such as layered perovskites of Arivillius phases (Boullay *et al.*, 2002) and Ruddlesden-Popper phases (Elcoro *et al.*, 2001, 2004), hexagonal perovskites (Evain *et al.*, 1998; Perez-Mato *et al.*, 1999), metal-deficient perovskites (Elcoro *et al.*, 2000; Boullay *et al.*, 2003), shear structures (Michiue *et al.*, 2005, 2006, 2007) and hexagonal ferrites (Orlov *et al.*, 2007). In order to treat these structures as a kind of (compositely) modulated structure, we need to introduce discontinuous modulation functions, such as the crenel function and the sawtooth function. In other words, the modulations in these structures are too strong to define a conventional basic structure. During the process of the (3 + 1)-dimensional description for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$, it has been proven that displacive modulations of ions in the structures are properly defined by the zigzag function with large amplitudes. This originated from a unique structural character in this homologous series. The structures are constructed by stacking of the slab-like structure unit. Two consecutive slabs are related to each other by mirror symmetry. The mirror plane acts like a twinning operation. In other words, the twinning in this case is considered to be a structure-building operation,

that is a kind of unit-cell twinning that is classified by Hyde *et al.* (1979). This kind of twinning has been described for some minerals with a so-called modular structure, for which a unified description based on the superspace formalism was recently presented (Elcoro *et al.*, 2008).

In this study, a unified description for structures in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ is presented using the superspace formalism. In §3 an ideal structure model is presented. First, the ideal structure is defined in three-dimensional space. Next, the model is treated as a compositely modulated structure and expressed in (3 + 1)-dimensional space. It is shown that there are several possible ways for the setting of subsystems. In §4 the validity of the model is confirmed by the refinements of real structures in the homologous series. Predicted structures of even m are constructed by simply extending the structure units seen in $\text{Ga}_2\text{O}_3(\text{ZnO})_6$, while those of odd m consist of structure units which are of different types from those used for even m . Therefore, the structure refinement is necessary for both even and odd m .

The structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ is refined using the $(3+1)$ -dimensional model for even m . Intensity data collected in our previous study (Michiue *et al.*, 2008) are used. In addition, single crystals of $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ were newly grown for intensity data collection (as mentioned in §2), and the structure is refined using the model proposed for odd m . A few complex phenomena in real structures, which are ignored in §3, are taken into account by modifying the ideal model.

2. Experimental

Single crystals of $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ were grown by heating a mixture of metal oxides. Ga_2O_3 (Rare Metallic Co. Ltd, 99.99%) and ZnO (High Purity Chemicals, 99.99%), in a molar ratio of $\text{Ga}_2\text{O}_3:\text{ZnO} = 1:9$, were mixed in an agate mortar with ethanol. The sample was dried and heated at 1723 K for 4 d in an unsealed Pt tube, then taken out of the furnace. Intensity data were collected for a single-crystal mounted on a four-circle diffractometer (Rigaku AFC 7R). X-ray diffraction data collected for a single crystal of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ in our previous study (Michiue *et al.*, 2008) were again used for the $(3+1)$ -dimensional refinement in this work. Crystallographic data and the conditions for data collection of

$\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ are listed in Table 1.¹ Programs used were *JANA2006* (Petříček *et al.*, 2006) for calculations, and *VESTA* (Momma & Izumi, 2008) and *ATOMS* (Dowty, 2005) for graphics.

3. Structure model

3.1. Ideal structures in three-dimensional space

For the unified description of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ structures first we define an ideal structure model in three-dimensional space, which is then expressed in $(3+1)$ -dimensional superspace. The ideal model here is not an absolute one but is tentative, and is used as an initial model in the refinement. The ideal model should ideally be transformed into a $(3+1)$ -dimensional model as simply as possible. We need to consider two cases of even and odd m separately.

Structural relationships between $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ and wurtzite ZnO have been described in our previous study (Michiue *et al.*, 2008). The arrangement of metal ions (*i.e.* Ga and Zn ions, which are represented by M hereafter) in part of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ resembles that of the Zn ions in the wurtzite ZnO structure. Also, the arrangement of O ions in part of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ resembles that of O ions in the wurtzite structure. In the $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ structure, however, the two structure units (one consisting of M ions and the other of O ions) are combined in a different mode from that seen in the wurtzite structure, resulting in a centrosymmetric structure in contrast to the noncentrosymmetric structure of wurtzite. Therefore, it is not easy to build up an ideal model for $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ in connection with the wurtzite structure. Instead, the structure in Fig. 1 is used as an ideal model, which is obtained by modifying a real (*i.e.* refined) structure of phase $m = 6$ as follows. First, grid points $(y, z) = (i/8, j/16)$ are drawn on planes $x = 0$ and $x = \frac{1}{2}$ in the real structure, where i and j are integers. It is found that each M ion on the planes is close to one of these grid points, as shown in Fig. 2(a). Next, every M ion is displaced so as to locate on the nearest grid point. The arrangement of O ions in the real structure is also modified by a similar manner to that used for M ions, so that all O ions are put on the grid points $(y, z) = (1/16 + i/8, 1/36 + j/18)$ on planes $x = 0$ and $x = 1/2$ (Fig. 2b). Thus, the structure model in Fig. 1 is obtained, which has the same symmetry as that of the real structure for $m = 6$ with the space group $Cmcm$. Considering the predicted structures for other phases (Michiue *et al.*, 2008), the ideal model for even m are generally given as that consisting of M ions at $(y, z) = (i/8, j/2(m+2))$ and O ions at $(y, z) = (1/16 + i/8, 1/4(m+3) + j/2(m+3))$. To establish an ideal model for odd m , a predicted model in our previous study is used instead of a refined structure. In this case M ions are on the grid points $(y, z) = (1/16 + i/8, 1/4(m+2) + j/2(m+2))$, while O ions are on $(y, z) = (i/8, j/2(m+3))$.

Strictly, the ideal model in Fig. 1 needs a few more modifications before being used in the refinement of real structures.

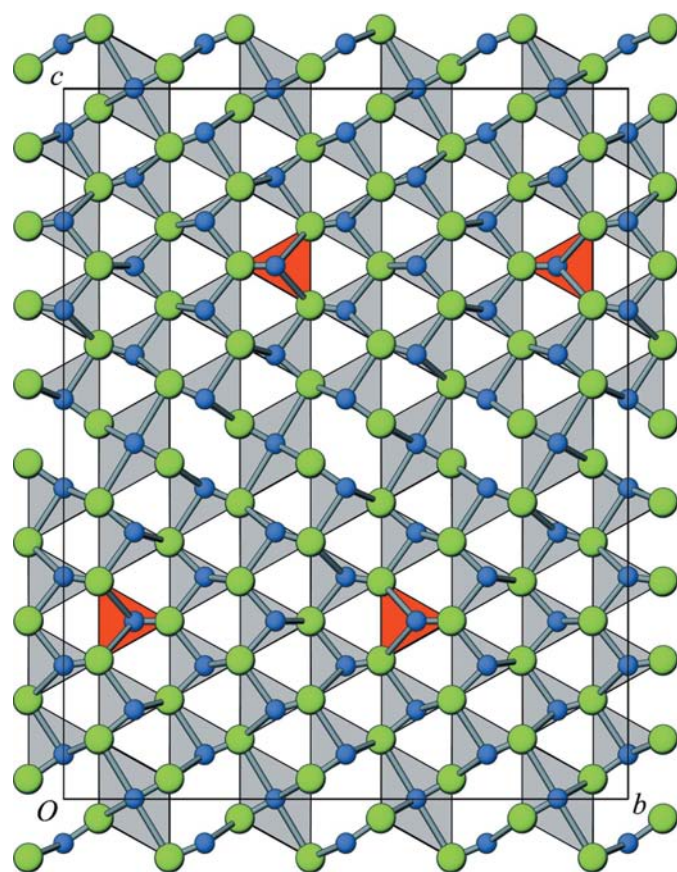


Figure 1
Ideal structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ projected along a . Smaller and larger spheres are metal (Zn/Ga) and O ions, respectively. Metal–oxygen distances less than 2.5 Å are indicated by bonds. Square-pyramidal coordination sites are in red.

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: SN5090). Services for accessing these data are described at the back of the journal.

One of the non-equivalent metal sites on the mirror plane $z = 1/4$ is in a square-pyramidal coordination (colored in red in Fig. 1); a metal ion at $(0, 1/8, 1/4)$ is coordinated by five O ions at $(\pm 1/2, 1/16, 7/36)$, $(\pm 1/2, 1/16, 11/36)$ and $(0, 3/16, 1/4)$. As the square-pyramidal coordination is a rather peculiar and unstable environment for Ga and Zn ions, complex

phenomena were observed around this site in the structure refinement of a phase $m = 6$ (Michiue *et al.*, 2008). It is expected that a similar situation is also found in other phases. These are carefully treated in structure refinements in §4, but ignored in this section for simplicity.

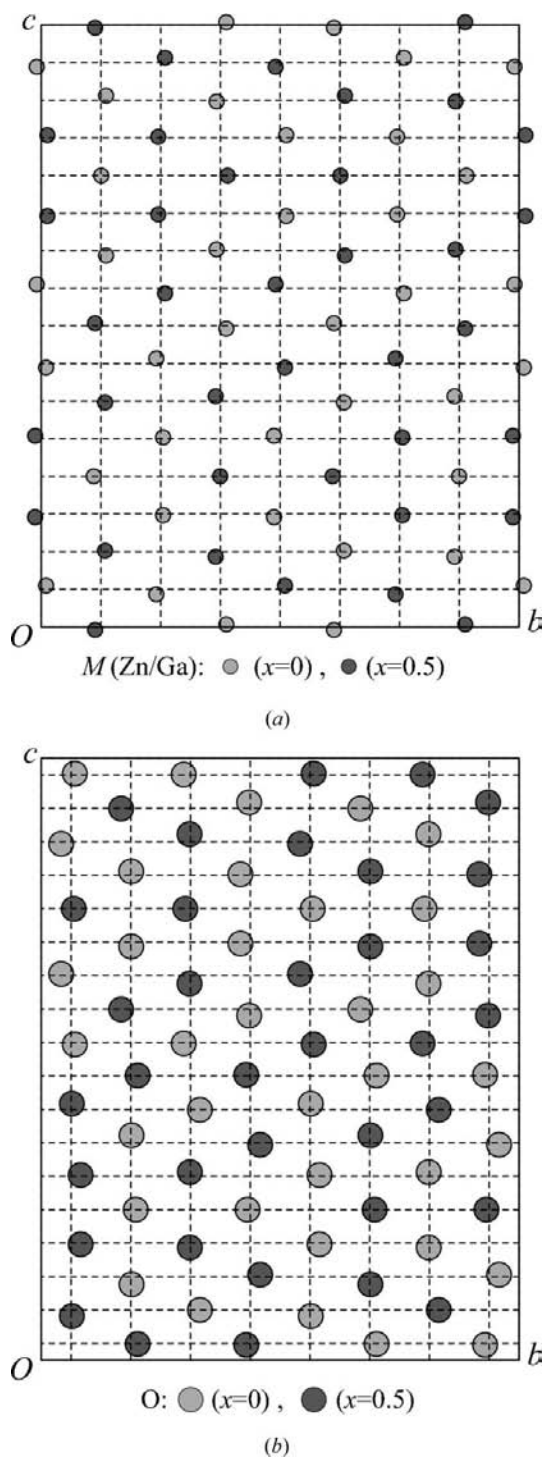


Figure 2
Deviation of (a) metal (Zn/Ga) ions from the grid points $(y, z) = (i/8, j/16)$ and (b) O ions from the grid points $(y, z) = (1/16 + i/8, 1/36 + j/18)$ in the structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_6$.

3.2. Composite crystal model in (3 + 1)-dimensional superspace

Here the structures presented in §3.1 are treated as composite crystals consisting of two subsystems. However, as mentioned in §1, the problem is that a conventional basic structure is not available for either of the two subsystems. Therefore, we are unable to establish an initial model by combining the basic structures of the two subsystems. Instead, an ideal structure model is expressed in (3 + 1)-dimensional superspace and used as an initial model, in which an atom extends in the fourth direction as a zigzag rather than a straight line with respect to x_2 .

3.2.1. Phases of even m . The arrangement of M and O ions on the $x = 0$ plane for the $m = 6$ phase is shown in Fig. 3. The

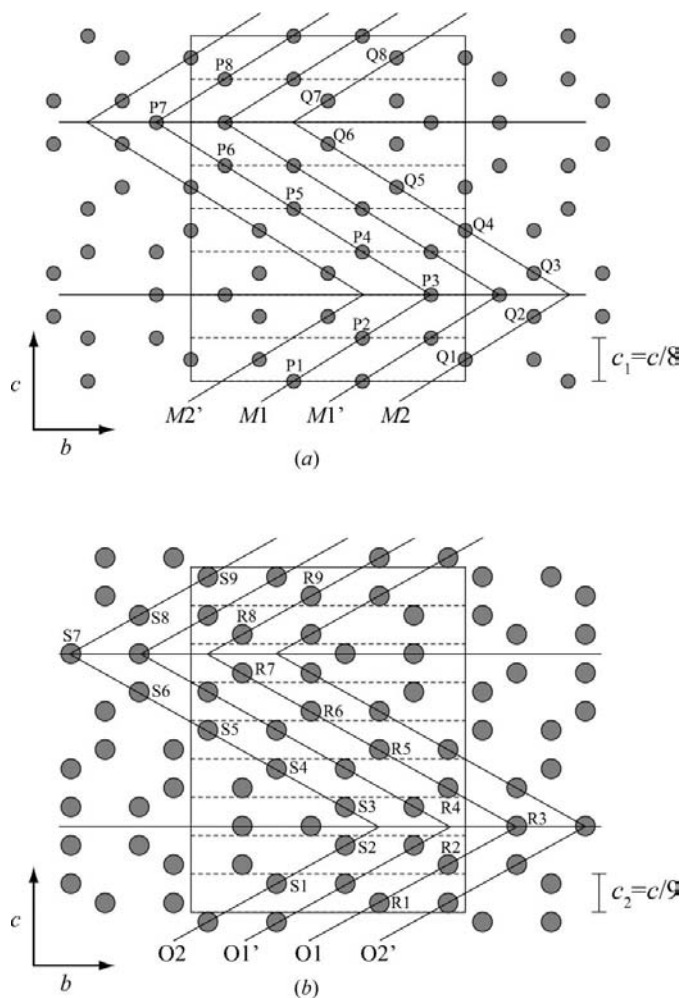


Figure 3
Arrangement of (a) metal and (b) oxygen ions on the $x = 0$ plane in the ideal model for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$.

Table 2

Symmetry operations and space groups at three-dimensional sections of superspace groups.

M is the denominator in γ ; $\gamma = N/M$.

	Symmetry operations (0, 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, 0, 0$) +		$t_0 = 0$ (modulo $1/2M$)	$t_0 = 1/4M$ (modulo $1/2M$)	$t_0 = \text{general}$
<i>Cmmm</i> (00 γ)0s0	$x_1, x_2, x_3, x_4; -x_1, x_2, x_3, x_4;$	$\gamma = \text{odd/even}$	<i>Cmcm</i>	<i>Cmc2</i> ₁	<i>Cmc2</i> ₁
	$x_1, -x_2, x_3, \frac{1}{2} + x_4;$ $-x_1, -x_2, x_3, \frac{1}{2} + x_4;$	$\gamma = \text{even/odd}$	<i>C2/m</i>	(as $t_0 = \text{general}$) <i>Cm2m</i>	<i>Cm</i>
	$-x_1, -x_2, -x_3, -x_4; x_1, -x_2, -x_3, -x_4;$ $-x_1, x_2, -x_3, \frac{1}{2} - x_4;$ $x_1, x_2, -x_3, \frac{1}{2} - x_4$	$\gamma = \text{odd/odd}$	<i>C2/m</i>	<i>Cm2m</i>	<i>Cm</i>
<i>Cmcm</i> (00 γ)000	$x_1, x_2, x_3, x_4; -x_1, x_2, x_3, x_4;$	$\gamma = \text{odd/even}$	<i>C2/m</i>	<i>Cm2m</i>	<i>Cm</i>
	$x_1, -x_2, \frac{1}{2} + x_3, x_4;$ $-x_1, -x_2, \frac{1}{2} + x_3, x_4;$	$\gamma = \text{even/odd}$	<i>Cmcm</i>	(as $t_0 = \text{general}$) <i>Cmc2</i> ₁	<i>Cmc2</i> ₁
	$-x_1, -x_2, -x_3, -x_4; x_1, -x_2, -x_3, -x_4;$ $-x_1, x_2, \frac{1}{2} - x_3, -x_4;$ $x_1, x_2, \frac{1}{2} - x_3, -x_4$	$\gamma = \text{odd/odd}$	<i>C2/m</i>	<i>Cm2m</i>	<i>Cm</i>
<i>Cmcm</i> (00 γ)0s0	$x_1, x_2, x_3, x_4; -x_1, x_2, x_3, x_4;$	$\gamma = \text{odd/even}$	<i>C2/m</i>	<i>Cm2m</i>	<i>Cm</i>
	$x_1, -x_2, \frac{1}{2} + x_3, \frac{1}{2} + x_4;$ $-x_1, -x_2, \frac{1}{2} + x_3, \frac{1}{2} + x_4;$	$\gamma = \text{even/odd}$	<i>C2/m</i>	<i>Cm2m</i>	<i>Cm</i>
	$-x_1, -x_2, -x_3, -x_4; x_1, -x_2, -x_3, -x_4;$ $-x_1, x_2, \frac{1}{2} - x_3, \frac{1}{2} - x_4;$ $x_1, x_2, \frac{1}{2} - x_3, \frac{1}{2} - x_4$	$\gamma = \text{odd/odd}$	<i>Cmcm</i>	(as $t_0 = \text{general}$) <i>Cmc2</i> ₁	<i>Cmc2</i> ₁

$2(m + 2)$ layers of M ions are seen in a unit cell along \mathbf{c} , while $2(m + 3)$ O layers are contained in a unit cell. The structure is considered to be a composite crystal, in which M ions construct the first subsystem and the second subsystem consists of O ions. Both subsystems are obviously different from the conventional basic structure as shown below. The ratio of basic periods for the two subsystems along \mathbf{c} is $c_1/c_2 = (m + 3)/(m + 2)$. The two subsystems have the same periodicity along \mathbf{a} and \mathbf{b} . Therefore, a unit basis set for a composite crystal model is defined by $\mathbf{a}, \mathbf{b}, \mathbf{c}_1 = \mathbf{C}_m/(m + 2)$, and $\mathbf{c}_2 = \mathbf{C}_m/(m + 3)$, where \mathbf{C}_m is the c axis for a superstructure of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$. The modulation wavevector of the first subsystem is $\mathbf{q}_1 = \mathbf{c}_2^* = (m + 3)\mathbf{c}^*/(m + 2)$, or $\gamma = (m + 3)/(m + 2)$. A superspace group *Cmmm*(00 γ)0s0 is taken because the space group at the three-dimensional section $t_0 = 0$ [modulo $1/2(m + 2)$] of this superspace group is *Cmcm* for even m (that is, $\gamma = \text{odd/even}$) as listed in Table 2.

A zigzag arrangement of M ions is seen as indicated in Fig. 3(a), which is considered to be a type of unit-cell twinning (Hyde *et al.*, 1979). M ions indicated by P1–P8 on the zigzag line $M1$ in Fig. 3 are at $z = 0, 1, 2, \dots$ in the sublattice based on \mathbf{c}_1 . These ions are allotted for the $M1$ ion in the $(3 + 1)$ -dimensional model as projected on the x_3 – x_4 plane (Fig. 4a), which are at $x_3 = 0, 1, 2, \dots$ and extend along x_4 . A three-dimensional section defined by $t_0 (= x_4 - \gamma x_3) = 0$ is expressed by a horizontal line in the figure. As indicated in the figure, the fractional coordinate x_4 for Pn ($n = 1, 2, 3, \dots$) on the three-dimensional section is simply given by $(n - 1)\gamma = 9(n - 1)/8$. These positions are translated in a unit cell, as shown in Fig. 4(b). The fractional coordinates y of P1–P8 varies from $-1/8$ to $7/8$, as seen in Fig. 3(a). Considering Fig. 3(a) and Fig. 4(b), the positions of P1–P8 are plotted on the x_2 – x_4 plane in Fig. 5(a). It seems that the sawtooth function is suitable to describe such an arrangement. An occupation domain with a sawtooth function defined by the center $(x_1^0, x_2^0, x_3^0, x_4^0) = (0, 3/8, 0, 0)$,

the width of an occupation domain $\Delta = \frac{1}{2}$, and the amplitude $V_{x_2} = 1/2$ corresponds to ions P7, P8, P1, P2 and P3 in three-dimensional space. Applying the symmetry operation $-x_1, x_2, -x_3, \frac{1}{2} - x_4$ to this occupation domain, another occupation domain is generated, giving ions P3–P7 in three-dimensional space. However, the problem is that occupation domains overlap at the edge positions $(x_1, x_2, x_3, x_4) = (0, x_2, 0, 1/4 + n/2)$, causing double multiplicities for P3 and P7 ions. Therefore, occupation domains corresponding to these ions should be separated from the original one and treated as independent sites with the crenel function, for which occupation factors are reduced so as to have the proper multiplicity. We can settle this problem in an alternative way. That is the use of the zigzag function, which was recently implemented in *JANA2006* to describe modular structures (Elcoro *et al.*, 2008). In a continuous zigzag function with $\Delta = \frac{1}{2}$, the multiplicity is properly treated including the edge positions. Thus, a zigzag function for $M1$ is defined by $(x_1^0, x_2^0, x_3^0, x_4^0) = (0, 3/8, 0, 0)$, $\Delta = \frac{1}{2}$, and $V_{x_2} = \frac{1}{2}[V_{x_2} = (m + 2)/16$ in general], as in Table 3.

M ions indicated by Q1–Q8 on the zigzag line $M2$ (Fig. 3a) are at $z = 1/2, 3/2, 5/2, \dots$ in a sublattice based on \mathbf{c}_1 . These ions are allotted for the $M2$ ion in the $(3 + 1)$ -dimensional model as projected on the x_3 – x_4 plane (Fig. 4c), which ions are at $x_3 = 1/2, 3/2, 5/2, \dots$ and extend along x_4 . The atomic coordinate x_4 for Qn ($n = 1, 2, 3, \dots$) on the three-dimensional section $t_0 = 0$ is given by $(n - \frac{1}{2})\gamma = 9(2n - 1)/16$. These positions are translated in a unit cell as shown in Fig. 4(d). Considering Fig. 3(a) and Fig. 4(d), the positions of Q1–Q8 are plotted on the x_2 – x_4 plane in Fig. 5(a). Parameters for a zigzag function of $M2$ are obtained from the figure, as given in Table 3. M ions on the zigzag line $M1'$ and $M2'$ in Fig. 3(a) are generated from those on the zigzag line $M1$ and $M2$ by symmetry operations.

O ions indicated by R1–R9 on the zigzag line O1 in Fig. 3(b) are at $z = 1/4, 5/4, 9/4, \dots$ in a sublattice based on \mathbf{c}_2 , that is $z =$

$2/9, 10/9, 18/9 (= 2), \dots$ in a sublattice based on \mathbf{c}_1 . These ions are allotted for the O1 ion in the second subsystem, and projected on the x_3 - x_4 plane (Fig. 4e), which are at $x_4 = 1/4, 5/4, 9/4, \dots$ extending along x_3 . The atomic coordinate x_3 for R_n ($n = 1, 2, 3, \dots$) on the three-dimensional section $t_0 = 0$ is given by

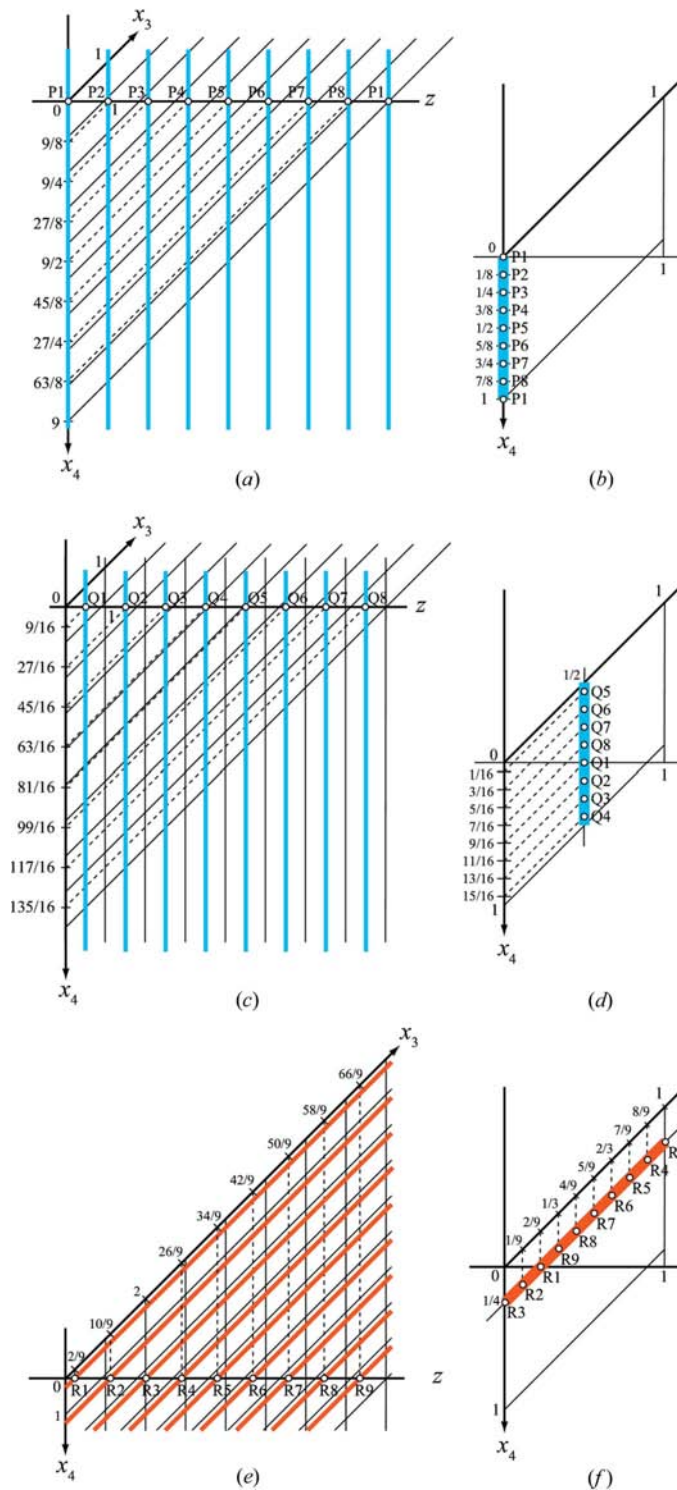


Figure 4 Occupation domains for (a), (b) M1, (c), (d) M2, and (e), (f) O1 in the ideal (3 + 1)-dimensional model for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ projected on the x_3 - x_4 plane. Atoms P1–P8, Q1–Q8, and R1–R9 correspond to those in Fig. 3.

$(n - 3/4)/\gamma = 2(4n - 3)/9$. These positions are translated in a unit cell, as shown in Fig. 4(f). Considering Fig. 3(b) and Fig. 4(f), the positions of R1–R8 are plotted on the x_2 - x_4 plane in the setting of the second subsystem (Fig. 5b), which clarifies the parameters for a zigzag function of O1 as given in Table 3. O ions indicated by S1–S9 on the zigzag line O2 (Fig. 3b) are allotted for the O2 ion. Parameters for O2 are determined in the same manner as that used for O1, and listed in Table 3. O ions on the zigzag line O1' and O2' in Fig. 3(b) are generated from those on a zigzag line O1 and O2 by a symmetry operation.

3.2.2. Phases of odd m . It was suggested from a previous study (Kimizuka *et al.*, 1995) that the space group of phases in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ is $Cmcm$ for odd m as well as even m . In our three-dimensional analyses for the phase $m = 9$ the space group $Cmcm$ was also confirmed. If M ions were taken as the first subsystem and O ions are allotted for the second subsystem, as for even m , the space group $Cmcm$ is impossible for any three-dimensional section of the superspace group $Cmmm(00\gamma)0s0$ for odd m , as a wavevector component is $\gamma = (m + 3)/(m+2) = \text{even}/\text{odd}$ (see Table 2). Instead, if O ions are taken as the first subsystem and M ions are as the second subsystem with the superspace group $Cmmm(00\gamma)0s0$, the space group at the three-dimensional section $t_0 = 0$ is $Cmcm$ for odd m (i.e. $\gamma = (m+2)/(m+3) = \text{odd}/\text{even}$). Therefore, this setting can be taken for phases of odd m . Successively, we can exchange x_3 and x_4 in symmetry

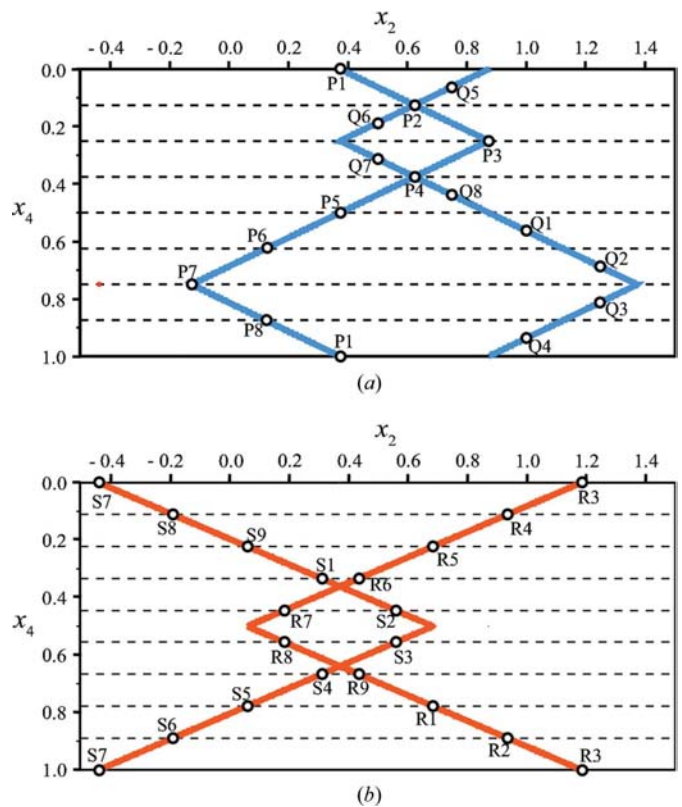


Figure 5 Projection of (a) metal and (b) oxygen ions in the ideal (3 + 1)-dimensional model for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ on the x_2 - x_4 plane. Atoms P1–P8, Q1–Q8, R1–R9 and S1–S9 correspond to those in Fig. 3.

Table 3
Crystallographic data and structural parameters for the ideal structure of $\text{Ga}_2\text{O}_3(\text{ZnO})_m$.

<i>m</i> : even	Orthorhombic, $Cmmm(00\gamma)0s0$ $a \approx 3.25, b \approx 19.7, c_1 \approx 3.05 \text{ \AA}, c_2 = (m+2)c_1/(m+3), \mathbf{q}_1 = (m+3)\mathbf{c}_1^*/(m+2)$					
	x_1^0	x_2^0	x_3^0	x_4^0	Δ	V_{x2}
Subsystem 1						
M1 (Zn/Ga)	0	3/8	0	0	$\frac{1}{2(m+2)}$	$(m+2)/16$
M2 (Zn/Ga)	0	7/8	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2(m+2)}$	$(m+2)/16$
Subsystem 2						
O1	0	5/8	1/4	3/4	$\frac{1}{2(m+3)}$	$(m+3)/16$
O2	0	1/8	3/4	1/4	$\frac{1}{2(m+3)}$	$(m+3)/16$
$V_{x1} = V_{x3} = 0$ for all sites.						

<i>m</i> : odd	Orthorhombic, $Cmcm(00\gamma)000$ $a \approx 3.25, b \approx 19.7, c_1 \approx 3.05 \text{ \AA}, c_2 = (m+2)c_1/(m+3), \mathbf{q}_1 = (m+3)\mathbf{c}_1^*/(m+2)$					
	x_1^0	x_2^0	x_3^0	x_4^0	Δ	V_{x2}
Subsystem 1						
M1 (Zn/Ga)	0	5/8	1/4	3/4	$\frac{1}{2(m+2)}$	$-(m+2)/16$
M2 (Zn/Ga)	0	1/8	3/4	1/4	$\frac{1}{2(m+2)}$	$-(m+2)/16$
Subsystem 2						
O1	0	3/8	0	0	$\frac{1}{2(m+3)}$	$-(m+3)/16$
O2	0	7/8	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2(m+3)}$	$-(m+3)/16$
$V_{x1} = V_{x3} = 0$ for all sites.						

operations, which means exchange of the subsystems so that the *M* ions act as the first subsystem and the O ions as the second one. Derived symmetry operations correspond to the superspace group $Cmcm(00\gamma)000$. The space group at the three-dimensional section $t_0 = 0$ of $Cmcm(00\gamma)000$ with $\gamma = (m+3)/(m+2)$ is consequently $Cmcm$ for odd *m* ($\gamma = \text{even/odd}$), as shown in Table 2. In short, the two settings O/M for the first/second subsystems with $Cmmm(00\gamma)0s0$ [$\gamma = (m+2)/(m+3)$] and M/O for the first/second subsystems with $Cmcm(00\gamma)000$ [$\gamma = (m+3)/(m+2)$], are equivalent and both settings are possible for odd *m*. Possible settings for even and odd *m* are summarized in Table 4. Note that it is possible to take O/M for the first/second subsystems with $Cmcm(00\gamma)000$ [$\gamma = (m+2)/(m+3)$] for even *m*.

Zigzag arrangements of *M* and O ions on the $x = 0$ plane in the $m = 7$ phase are indicated in Fig. 6. Structural parameters for odd *m* with the superspace group $Cmcm(00\gamma)000$ [$\gamma = (m+3)/(m+2)$] in Table 3 are obtained by the same manner as that used for even *m*. It should be noted that the arrangement of *M* ions in the $m = 7$ phase (Fig. 6a) is basically identical to that of O ions in the $m = 6$ phase in Fig. 3(b). Also, the arrangement of O ions in the $m = 7$ phase is basically identical to that of *M* ions in the $m = 8$ phase. In general, the arrangement of *M* ions in the $m + 1$ phase is basically identical to that of O ions in the *m* phase. Therefore, it is natural that all parameters except V_{x2} of *M* ions for odd *m* in Table 3 are equal to those of O ions for even *m*. The amplitude V_{x2} for *M* ions of $m = 7$ is $-9/16$, which is opposite in sign to that for O ions of $m = 6$, i.e. $9/16$. This is because the modulation wavevector of the former is in the opposite direction to that of the latter. That is, the modulation wavevector of the first (*M*) subsystem for $m = 7$, $q_1 = 10\mathbf{c}_1^*/9$, is reduced to $\mathbf{c}_1^*/9$, while that of the second (O)

subsystem for $m = 6$, $q_2 = 8\mathbf{c}_2^*/9$, is reduced to $-\mathbf{c}_2^*/9$. The same relations are seen between O ions for odd *m* and *M* ions for even *m*.

3.3. Alternative settings

Structures of the $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ homologous series were treated as typical composite crystals in the preceding section. That is, the whole structure consists of two subsystems and each subsystem is modulated with the period of the other subsystem. The modulation wavevector of a subsystem is simply related to the basic period of another subsystem, $\mathbf{q}_1 = \mathbf{c}_2^*$ and $\mathbf{q}_2 = \mathbf{c}_1^*$. The γ component of the modulation wavevector based on the first subsystem is consequently $c_2^*/c_1^* = c_1/c_2$. Hereafter, we call this setting the ‘conventional setting’. In this section ‘non-conventional settings’ are presented to

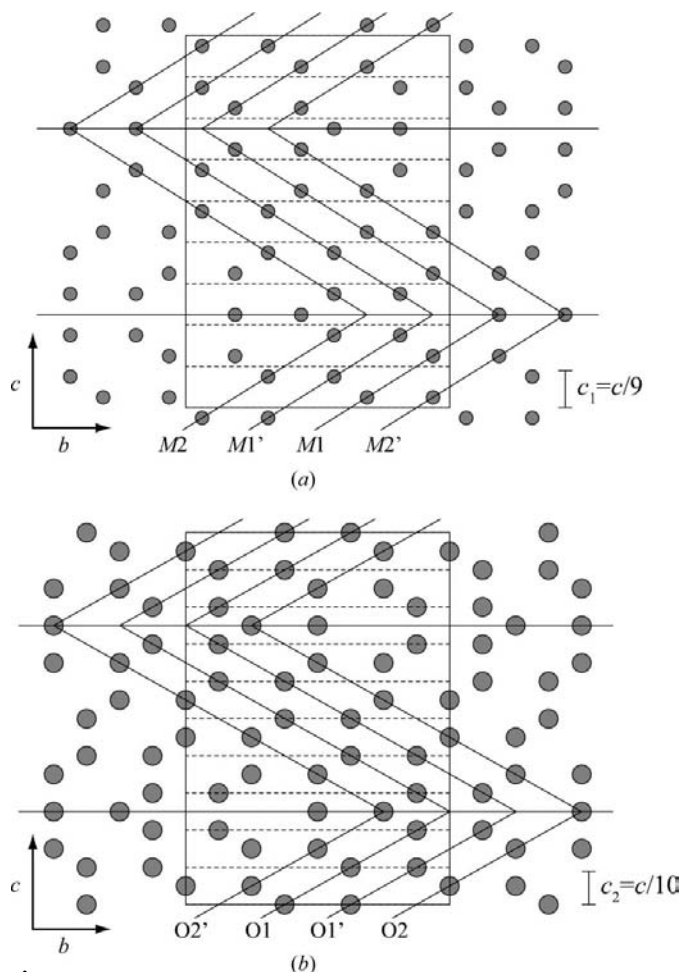


Figure 6
Arrangement of (a) metal and (b) oxygen ions on the $x = 0$ plane in the ideal model for $\text{Ga}_2\text{O}_3(\text{ZnO})_7$.

Table 4
Superspace groups giving the space group $Cmcm$ at the three-dimensional section $t_0 = 0$.

Subsystem 1/subsystem 2	Metal/oxygen [$\gamma = (m + 3)/(m + 2)$]	Oxygen/metal [$\gamma = (m + 2)/(m + 3)$]
m : even	$Cmmm(00\gamma)0s0$	$Cmcm(00\gamma)000$
m : odd	$Cmcm(00\gamma)000$	$Cmmm(00\gamma)0s0$

demonstrate the similarity of the structures to those of the modular structures, for which a superspace description was recently reported (Elcoro *et al.*, 2008). In these settings the modulation wavevector of a subsystem is not given by the basic period of another subsystem; $\mathbf{q}_1 \neq \mathbf{c}_2^*$ and $\mathbf{q}_2 \neq \mathbf{c}_1^*$.

As seen in Fig. 7(a), $2(m + 2)$ layers of M ions are contained in a unit cell along \mathbf{c} , and $2(m + 3)$ O layers are also seen (Fig. 7b). Zigzag arrangements for M and O ions are indicated in the figures, of which amplitudes are far larger than those in Fig. 3. It seems possible that the structure is described with basic vectors $\mathbf{c}_1 = \mathbf{C}_m/2(m + 2)$ and $\mathbf{c}_2 = \mathbf{C}_m/2(m + 3)$. It is, however, impossible to take such basic vectors in a conventional setting, because a fraction $2(m + 3)/2(m + 2)$ as a wavevector component $\gamma = c_2^*/c_1^* = c_1/c_2$ is reduced to $(m + 3)/(m + 2)$. This means that the superstructure is reduced to half; $\mathbf{c}' = (m + 2)\mathbf{c}_1 = \mathbf{C}_m/2$. However, due to the zigzag modulation with respect to x_2 , the period of the superstructure should be \mathbf{C}_m . Thus, the present homologous series is essentially different from the usual composite crystals. We need to consider the non-conventional setting for the description with $\mathbf{c}_1 = \mathbf{C}_m/2(m + 2)$ and $\mathbf{c}_2 = \mathbf{C}_m/2(m + 3)$. This situation is similar to that discussed in the modular structures of the lillianite

homologous series (Elcoro *et al.*, 2008). Three types of non-conventional setting are presented below in analogy with the misfit composite model of the lillianite series. Here we use the following matrix w instead of W (van Smaalen, 1991), as $\mathbf{a}_1^* = \mathbf{a}_2^*$ and $\mathbf{b}_1^* = \mathbf{b}_2^*$ for all the cases

$$\begin{pmatrix} \mathbf{c}_2^* \\ \mathbf{q}_2 \end{pmatrix} = w \begin{pmatrix} \mathbf{c}_1^* \\ \mathbf{q}_1 \end{pmatrix}. \quad (1)$$

In a conventional setting, the two subsystems are related to each other by just exchanging a basic vector and a modulation wavevector

$$w = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}. \quad (2)$$

In the projection on the x_3 - x_4 plane for this setting, the M ions in the first subsystem extend along x_4 (Figs. 4b and d), and the O ions in the second subsystem extend along x_3 (Fig. 4f).

As the first one of the non-conventional settings, we take a unit basis set $\mathbf{a}, \mathbf{b}, \mathbf{c}_1 = \mathbf{C}_m/2(m + 2)$, and a modulation wavevector $\mathbf{q}_1 = \mathbf{C}_m^* = \mathbf{c}_1^*/2(m + 2)$ [that is, $\gamma = 1/2(m + 2)$] for the first subsystem of M ions, while $\mathbf{a}, \mathbf{b}, \mathbf{c}_2 = \mathbf{C}_m/2(m + 3)$, and $\mathbf{q}_2 = \mathbf{C}_m^*$ are taken for the second subsystem of O ions. The second subsystem is related to the first subsystem by

$$w = \begin{pmatrix} 1 & 2 \\ 0 & 1 \end{pmatrix}. \quad (3)$$

The M ion projected on the x_3 - x_4 plane extends along x_4 , while the O ion extends along the direction $(x_3, x_4) = (-2, 1)$, as shown in Fig. 8(a). This is different from the situation in the conventional setting, in which the O1 ion extends along x_3 (Fig. 4f). The superspace group $Cmmm(00\gamma)0s0$ [$\gamma = 1/2(m + 2)$] is given, as the space group at the three-dimensional section $t_0 = 0$ is $Cmcm$ for both even and odd m (*i.e.* $\gamma = \text{odd/even}$). It is not difficult to obtain structural parameters for this setting in Table 5, as a similar method to that used for the conventional setting is applied. At the first step, two models were given by taking the three-dimensional section $t_0 = 0$ (modulo γ); one is for even m (model 1), and another is for odd m (model 2). Each subsystem contains only one ion, and fractional coordinates x_1 - x_4 of the M ion for odd m are equal to those of the O ion for even m . It should be noted that structure parameters of model 1 are equal to those of model 2, although the origin of the former is shifted by $\mathbf{r}_t = (x_1, x_2, x_3) = (0, \frac{1}{2}, \frac{1}{2})$. Considering the correction of $\mathbf{q} \cdot \mathbf{r}_t = \gamma/2$, the three-dimensional section after the origin shift should be $t_0 = \gamma/2$, which also gives the space

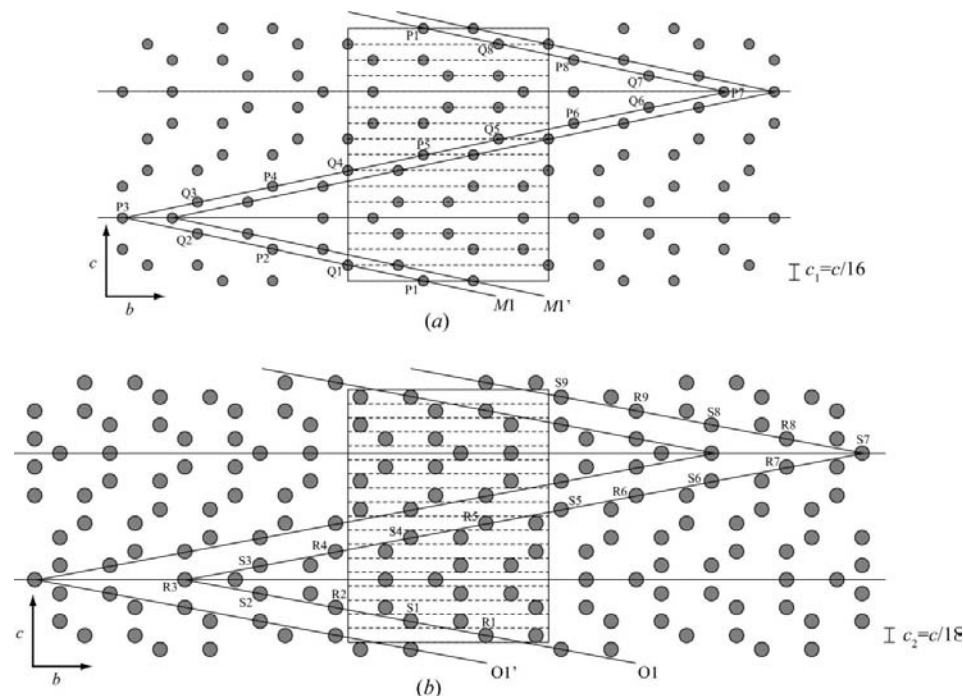


Figure 7
Arrangement of (a) metal and (b) oxygen ions on the $x = 0$ plane in the ideal model for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ of alternative settings.

group $Cmcm$ in three-dimensional space as it is included in the case of $t_o = 0$ (modulo $1/2M$) in Table 2. Thus, we can finally take model 1 as a common structure model for both even and odd m , although the three-dimensional section $t_o = \gamma/2$ (modulo γ) must be taken for odd m . Of course, instead, model 2 can also be used for even m by taking the three-

dimensional section $t_o = \gamma/2$ (modulo γ). The highest order of refinable parameters is $m + 2$ for $M1$ and $m + 3$ for $O1$, which are approximately twice those in the conventional setting with $\gamma = (m + 3)/(m + 2)$. As two M and two O ions are contained in the conventional setting, the number of total refinable parameters is equal in the two settings.

Alternatively, if a unit basis set $\mathbf{a}, \mathbf{b}, \mathbf{c}_1 = \mathbf{C}_m/2(m + 3)$, and a modulation wavevector $\mathbf{q}_1 = \mathbf{C}_m^* = \mathbf{c}_1^*/2(m + 3)$ [that is, $\gamma = 1/2(m + 3)$] are taken for the first subsystem of O ions, the second subsystem of M ions is defined by $\mathbf{a}, \mathbf{b}, \mathbf{c}_2 = \mathbf{C}_m/2(m + 2)$ and $\mathbf{q}_2 = \mathbf{C}_m^*$ with

$$w = \begin{pmatrix} 1 & -2 \\ 0 & 1 \end{pmatrix}. \quad (4)$$

In this setting, the $O1$ ion extends along x_4 and the $M1$ ion extends along the $(x_3, x_4) = (2, 1)$ direction, as shown in Fig. 8(b). The superspace group $Cm\bar{m}(00\gamma)0s0$ [$\gamma = 1/2(m + 3)$] is also taken in this case. Structural parameters for this setting are the same as those in Table 5, although $O1$ is allocated for the first subsystem and $M1$ for the second subsystem.

Furthermore, an intermediate setting is also possible. That is, the unit basis set $\mathbf{a}, \mathbf{b}, \mathbf{c}_0 = \mathbf{C}_m/(2m + 5)$ with a modulation wavevector $\mathbf{q}_0 = \mathbf{C}_m^* = \mathbf{c}_0^*/(2m + 5)$ is taken for a void zeroth subsystem, *i.e.* a subsystem containing no atoms. A unit basis set of $\mathbf{a}, \mathbf{b}, \mathbf{c}_1 = \mathbf{C}_m/2(m + 2)$ with a modulation wavevector $\mathbf{q}_1 = \mathbf{C}_m^*$ is taken for the first subsystem of M ions, and $\mathbf{a}, \mathbf{b}, \mathbf{c}_2 = \mathbf{C}_m/(2m + 3)$, and $\mathbf{q}_2 = \mathbf{C}_m^*$ are for the second subsystem of O ions. The first and second subsystems are related to the zeroth subsystem by

$$w^1 = \begin{pmatrix} 1 & -1 \\ 0 & 1 \end{pmatrix} \text{ and } w^2 = \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix}, \text{ where} \\ \begin{pmatrix} \mathbf{c}_1^* \\ \mathbf{q}_1 \end{pmatrix} = w^1 \begin{pmatrix} \mathbf{c}_0^* \\ \mathbf{q}_0 \end{pmatrix} \text{ and } \begin{pmatrix} \mathbf{c}_2^* \\ \mathbf{q}_2 \end{pmatrix} = w^2 \begin{pmatrix} \mathbf{c}_0^* \\ \mathbf{q}_0 \end{pmatrix}. \quad (5)$$

The M ion extends along the $(x_3, x_4) = (1, 1)$ direction, while the O ion extends along $(x_3, x_4) = (-1, 1)$, as shown in Fig. 8c. The superspace group $Cmcm(00\gamma)0s0$ [$\gamma = 1/(2m + 5)$] is used in this case, because the space group at the three-dimensional section $t_o = 0$ is $Cmcm$ for even and odd m (*i.e.* $\gamma = \text{odd/odd}$), as shown in Table 2. Structural parameters for this setting are the same as those in Table 5.

4. Structure refinements

The conventional setting needs two structure models (Table 3) with different superspace groups; one is for odd m and another is for even m . On the other hand, either model 1 or model 2 in the non-conventional setting (Table 5) provides a common structure model for even and odd m . Therefore, it is concluded that the non-conventional setting is more suitable for the unified description of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$. There are six options for the possible combination of the model (1 and 2) and the non-conventional setting type (I–III). In this section only one case, that is model 1 with type I setting, is presented, as all of the six options are equivalent.

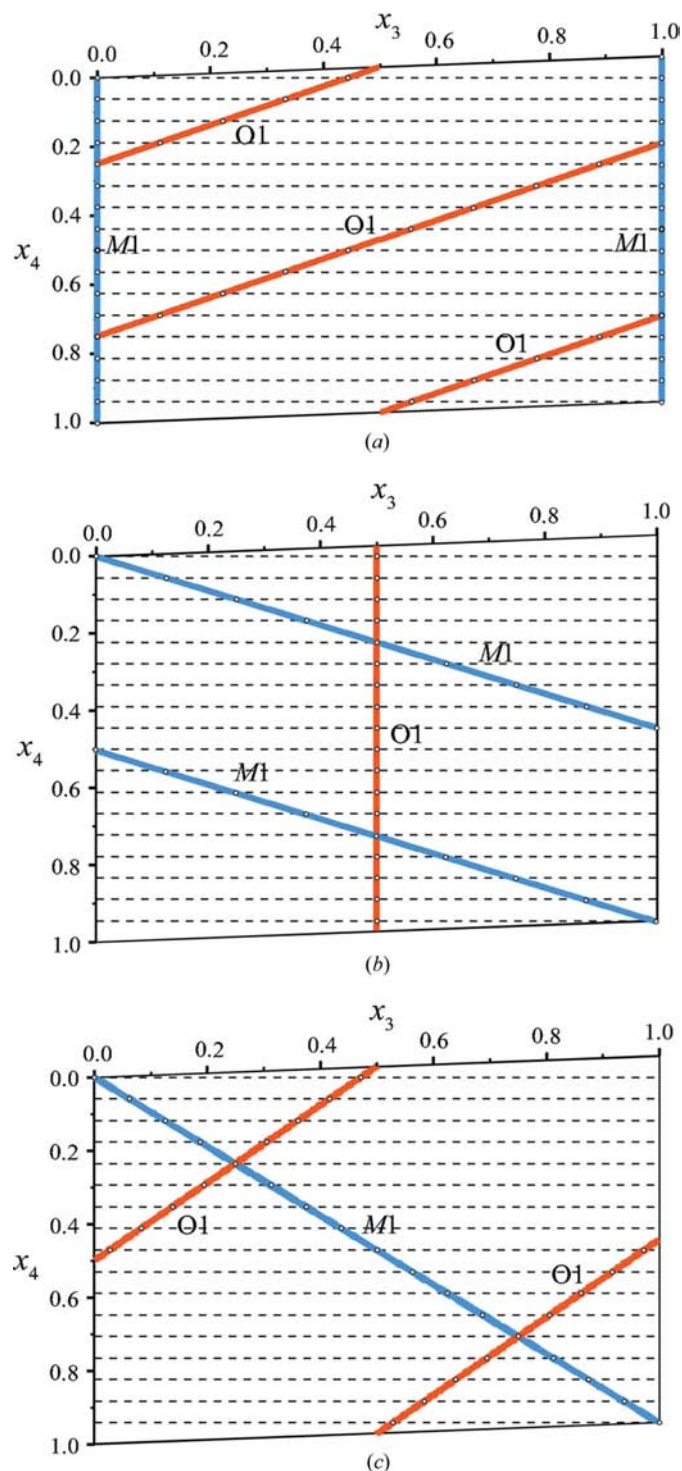


Figure 8
Projection of the $M1$ and $O1$ ions for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ on the x_3 – x_4 plane in the non-conventional setting of (a) type I, (b) type II and (c) type III.

Table 5

Crystallographic data and structural parameters for the ideal structure of Ga₂O₃(ZnO)_m in the non-conventional setting.

Type I	Orthorhombic, <i>Cmmm</i> (00γ)0s0 <i>a</i> ≈ 3.25, <i>b</i> ≈ 19.7, <i>c</i> ₁ ≈ 1.53 Å, <i>c</i> ₂ = (<i>m</i> + 2) <i>c</i> ₁ / <i>m</i> + 3, q ₁ = c ₁ ⁰ /2(<i>m</i> + 2), γ = 1/2(<i>m</i> + 2)					
Type II	Orthorhombic, <i>Cmmm</i> (00γ)0s0 <i>a</i> ≈ 3.25, <i>b</i> ≈ 19.7, <i>c</i> ₁ ≈ 1.38 Å, <i>c</i> ₂ = (<i>m</i> + 3) <i>c</i> ₁ / <i>m</i> + 2, q ₁ = c ₁ ⁰ /2(<i>m</i> + 3), γ = 1/2(<i>m</i> + 3)					
Type III	Orthorhombic, <i>Cmcm</i> (00γ)0s0 <i>a</i> ≈ 3.25, <i>b</i> ≈ 19.7, <i>c</i> ₀ ≈ 1.46 Å, <i>c</i> ₁ = (2 <i>m</i> + 5) <i>c</i> ₀ /2(<i>m</i> + 2), <i>c</i> ₂ = (2 <i>m</i> + 5) <i>c</i> ₀ /2(<i>m</i> + 3), q ₀ = c ₀ ⁰ /2(<i>m</i> + 5), γ = 1/(2 <i>m</i> + 5)					
Model 1: for even <i>m</i> at <i>t</i> ₀ = 0 (modulo γ), and for odd <i>m</i> at <i>t</i> ₀ = γ/2 (modulo γ)						
	<i>x</i> ₁ ⁰	<i>x</i> ₂ ⁰	<i>x</i> ₃ ⁰	<i>x</i> ₄ ⁰	Δ	<i>V</i> _{<i>x</i>₂}
Subsystem 1						
<i>M</i> 2	0	3/8	0	0	1/2	−3(<i>m</i> + 2)/16
Subsystem 2						
<i>O</i> 1	0	7/8	1/2	0	1/2	−3(<i>m</i> + 3)/16
<i>V</i> _{<i>x</i>₁} = <i>V</i> _{<i>x</i>₃} = 0 for all sites.						
Model 2: for odd <i>m</i> at <i>t</i> ₀ = 0 (modulo γ), and for even <i>m</i> at <i>t</i> ₀ = γ/2 (modulo γ)						
	<i>x</i> ₁ ⁰	<i>x</i> ₂ ⁰	<i>x</i> ₃ ⁰	<i>x</i> ₄ ⁰	Δ	<i>V</i> _{<i>x</i>₂}
Subsystem 1						
<i>M</i> 1	0	7/8	1/2	0	1/2	−3(<i>m</i> + 2)/16
Subsystem 2						
<i>O</i> 1	0	3/8	0	0	1/2	−3(<i>m</i> + 3)/16
<i>V</i> _{<i>x</i>₁} = <i>V</i> _{<i>x</i>₃} = 0 for all sites.						
In type II setting, <i>O</i> 1 is allocated for the first subsystem, and <i>M</i> 1 is for the second one.						

Table 6

Modified structure parameters for Ga₂O₃(ZnO)_m in model 1 with the non-conventional setting.

	<i>x</i> ₁ ⁰	<i>x</i> ₂ ⁰	<i>x</i> ₃ ⁰	<i>x</i> ₄ ⁰	Δ	<i>V</i> _{<i>x</i>₂}
Subsystem 1						
<i>M</i> 1	0	3/8	0	0	(<i>m</i> + 1)/2(<i>m</i> + 2)	−3(<i>m</i> + 2)Δ/8
<i>M</i> 1 <i>a</i>	0	3(<i>m</i> + 4)/16	0	3/4	1/2(<i>m</i> + 2)	
<i>M</i> 1 <i>b</i>	1/2	3(<i>m</i> + 4)/16	0	3/4	1/2(<i>m</i> + 2)	
<i>M</i> 1 <i>c</i>	0	−3 <i>m</i> /16	0	1/4	1/2(<i>m</i> + 2)	
Subsystem 2						
<i>O</i> 1	0	7/8	1/2	0	1/2	−3(<i>m</i> + 3)/16

The three-dimensional section should be *t*₀ = 0 for even *m* and *t*₀ = γ/2 for odd *m*, where γ = 1/2(*m* + 2) for type I, 1/2(*m* + 3) for type II, and 1/(2*m* + 5) for type III setting as given in Table 5. The crenel function is used for the occupation function of *M*1*a*, *M*1*b* and *M*1*c*. The sum of occupation factors at *M*1*a* and *M*1*b* is fixed at the unity.

Deviation in a real structure from an ideal one is considered by additional Fourier series. To demonstrate the efficiency of the method, structure refinements were carried out for the two phases with *m* = 6 and *m* = 9 in the homologous series Ga₂O₃(ZnO)_m. The former is an example of the phases for even *m*, and the latter for odd *m*. As the refinement of the Ga/Zn ratio at a site using X-ray diffraction data is almost impossible, the Ga/Zn ratio was fixed at 2/*m* for all metal sites in refinements.

4.1. Phase of *m* = 6

As mentioned in §3, the ideal model in Fig. 1 needs a few modifications before being used in the refinement of real

structures. One of the *M* sites is in the square-pyramidal coordination, which is a rather peculiar and unstable environment for Ga and Zn ions. Structure refinement for the *m* = 6 phase in three-dimensional space (Michiue *et al.*, 2008) revealed that this *M* site, *M*8 = (0, 1/8 + δ*y*, 1/4) in the previous paper, is not fully occupied and a displaced position *M*7 = (1/2, 1/8 + δ*y*′, 1/4) was introduced for accommodation of *M* ions moving away from the *M*8 site. Further, *M*8 slightly deviated from its original position on the mirror plane *Z* = 1/4, where *Z* is the fractional coordinate based on **C**_{*m*} of the superstructure. In the ideal model in Fig. 3(*a*) the *P*7 site at (0, 7/8, 3/4) corresponds to the above *M*8 site.

Considering the situation in a real structure, an additional position corresponding to the above *M*7 is to be introduced for accommodation of part of the *M* ions moving away from the *P*7 site; *P*7′ = (1/2, 7/8, 3/4). In the (3 + 1)-dimensional model in §3 the *P*7 site was treated as part of the *M*1 site. However, it is difficult to deal with *P*7 and *P*7′ sites as part of the *M*1 site in the refinement of a real structure. So far as a site is treated as part of the *M*1 site, its position is restricted on the *x* = 0 plane because displacive modulations are forbidden in the *x*₁ direction. Occupation factors for the *P*7 and *P*7′ sites are less than unity, while the other sites allocated for *M*1 (*i.e.* *P*1–*P*6 and *P*8) are fully occupied. Furthermore, deviation of *P*7 from the mirror plane *Z* = 3/4 should be considered. Thus, it is obviously better that the occupation domain for *P*7 (and *P*7′) is separated from *M*1, and treated as an independent site.

Model 1 with type I setting of a superspace group *Cmmm*(00γ)0s0 in Table 5 is used taking the three-dimensional section *t*₀ = 0. The occupation domain for *P*7 is separated from *M*1, and treated as an independent site *M*1*a* using the crenel function with Δ = 1/16 [Δ = 1/2(*m* + 2) for general *m*]. Another occupation domain with Δ = 1/16 is allocated for the *P*7′ site, which is labelled as *M*1*b*. *M*1 is defined by (*x*₁⁰, *x*₂⁰, *x*₃⁰, *x*₄⁰) = (0, 3/8, 0, 0) and Δ = 1/2 − 1/16 = 7/16 [Δ = 1/2 − 1/2(*m* + 2) = (*m* + 1)/2(*m* + 2) in general]. The amplitude of the zigzag function is given by *V*_{*x*₂} = −3(*m* + 2)Δ/8 = −21/16, as the slope of the zigzag function *V*_{*x*₂}/Δ = −3(*m* + 2)/8 is unchanged. Owing to the definition of the zigzag function, the *P*3 site is consequently separated from *M*1, and treated as an independent *M*1*c* site with Δ = 1/16. Thus, four metal sites are

taken for the first subsystem as listed in Table 6, although $M1a$ is moved to a position deviating from $x_3^0 = 0$ in the final result as given in supplementary materials (Table S1). Considering the splitting of this metal site, a constraint condition was imposed on occupation factors so that $2Occ[M1a] + Occ[M1b]$

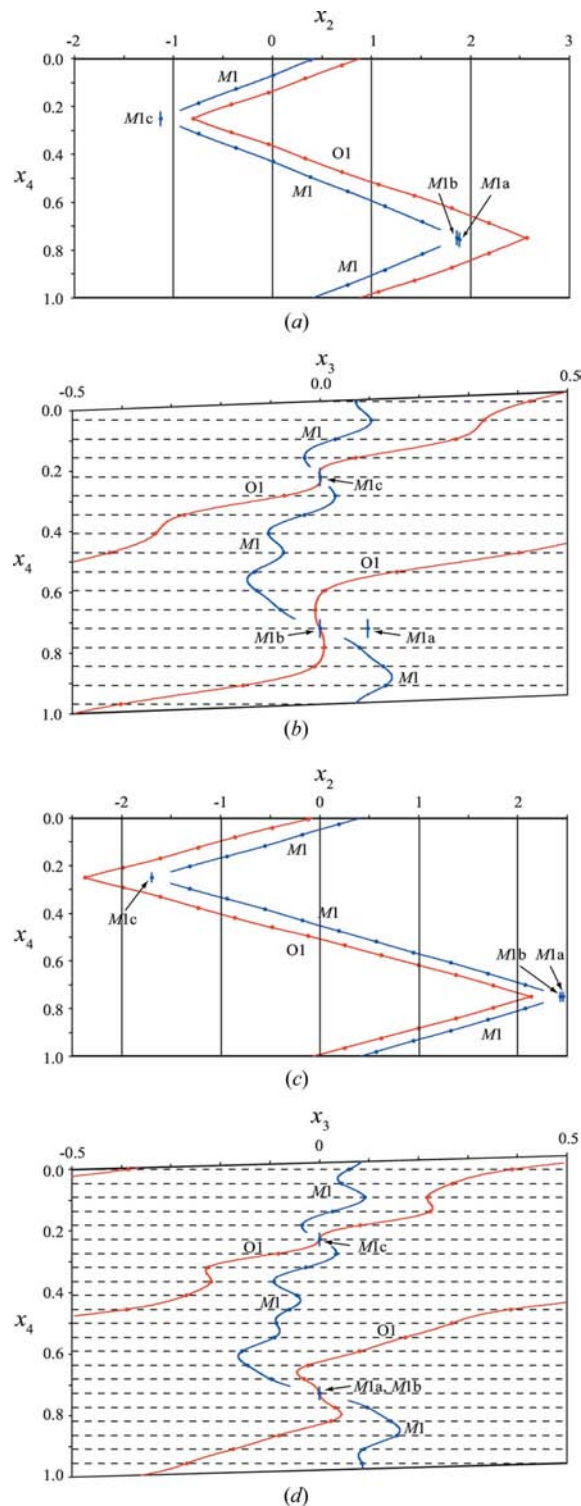


Figure 9
Projection of the metal and oxygen ions for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ on (a) x_2 - x_4 and (b) x_3 - x_4 , and for $\text{Ga}_2\text{O}_3(\text{ZnO})_9$ on (c) x_2 - x_4 and (d) x_3 - x_4 in model I with the non-conventional setting of type I.

is unity. Parameters for O1 of the second subsystem in Table 5 are used for the initial model without modification. Occupation domains of metal and oxygen atoms are projected on the x_2 - x_4 (Fig. 9a) and x_3 - x_4 (Fig. 9b) planes. Parameters in Table S1 are unchanged even when other types of the non-conventional setting are used, although M sites are taken for the second subsystem and the O1 is for the first subsystem in type II setting.

Results of the refinement are summarized in Table 7, which are equivalent to those from the three-dimensional refinement as all of the refinable parameters were refined. Final reliability factors are a little improved compared with those in the previous study (Michiue *et al.*, 2008) for the following reason. Ga atoms were located at certain positions of five-coordination in the previous model, and isotropic atomic displacement parameters were taken for one of the O atoms (O5 in the previous paper) because anisotropic atomic displacement parameters were not positive definite. This O atom had to be located on a position deviating from $x = 0$, which is the splitting site. On the other hand, the Ga/Zn ratio was set to equal at all metal sites in this work. It was found that anisotropic atomic displacement parameters were possible for all the O atoms in this model, and the above O atom can be on the mirror plane $x = 0$ by taking a large U_{11} .

4.2. Phase of $m = 9$

M sites of the square-pyramidal coordination are also seen in the ideal model for odd m . Therefore, it is expected that similar phenomena to those observed in the $m = 6$ phase also occur in the $m = 9$ phase. However, we first tried the refinement using the ideal model without modifications and checked the fitting. In the conventional setting, reliability factors were $R_{\text{obs}}(F) = 0.088$, $wR_{\text{all}}(F^2) = 0.200$. A modulation function of the anisotropic atomic displacement parameter U_{11} for the $M1$ had a steep peak, indicating the splitting for a specific site, although variations in the atomic displacement parameters of the $M2$ site were moderate. Therefore, we need to modify the ideal model in §3.

Model 1 with type I setting of a superspace group $Cmmm(00\gamma)0s0$ in Table 5 is used taking the three-dimensional section $t_0 = \gamma/2 = 1/44$. Modifications for the occupation domains of the M site are similar to those made for the $m = 6$ phase (Table 6). Final parameters are listed in the supplementary materials (Table S2). The occupation domains of metal and oxygen atoms are projected on the x_2 - x_4 (Fig. 9c) and x_3 - x_4 (Fig. 9d) planes. Results of refinements are summarized in Table 7.

All of the 149 refinable parameters are refined in all the cases in Table 7. Refinements with fewer parameters were also carried out, and the results were converted to superstructures in three-dimensional space. Obtained structure parameters were compared with those from the three-dimensional refinement. It was found that the difference for some parameters exceeded the standard uncertainty. That is, changes by the reduction of the number of parameters are considered as significant, although differences in reliability factors are little.

Table 7

Results of refinements for $\text{Ga}_2\text{O}_3(\text{ZnO})_6$ and $\text{Ga}_2\text{O}_3(\text{ZnO})_9$.

	$\text{Ga}_2\text{O}_3(\text{ZnO})_6$		$\text{Ga}_2\text{O}_3(\text{ZnO})_9$	
	Three-dimensional	(3 + 1)-dimensional	Three-dimensional	(3 + 1)-dimensional
Independent/observed [$I_o > 2\sigma(I_o)$] reflections	3699/1349	3699/1349	1862/993	1862/993
Number of parameters	115	115	149	149
$R_{\text{obs}}(F)/wR_{\text{all}}(F^2)$				
All	0.0439/0.0988	0.0439/0.0988	0.0340/0.0677	0.0340/0.0677
Main reflections		0.0407/0.0886		0.0348/0.0750
Satellites of order				
1		0.0448/0.1022		0.0366/0.0768
2		0.0415/0.0959		0.0304/0.0628
3		0.0468/0.1155		0.0366/0.0728
4		0.0502/0.1115		0.0329/0.0678
S	1.03	1.03	1.35	1.35

Thus, refinements using all of the refinable parameters were taken as final results, which are equivalent to that from the three-dimensional refinement. Nevertheless, the superiority of the superspace description to the three-dimensional model should be clear for phases of the larger m in the homologous series. The reduction of the number of parameters with the use of the (3 + 1)-dimensional model is valuable when the three-dimensional refinement of a phase does not converge, for example.

5. Concluding remarks

Structures of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$ were treated as a compositely modulated structure, and a unified model for the structures was presented with the use of the superspace formalism. The ideal model was given as commensurate composite crystals, in which displacive modulations of ions were well described by the zigzag function with large amplitudes with respect to x_2 . This character originates from the fact that the structures are built up by unit-cell twinning (Hyde *et al.*, 1979). In that sense, the present homologous series is essentially different from the usual composite crystals, and considered as a kind of modular structure. These considerations are important for the crystal chemistry of the homologous series and well demonstrated by the superspace description. Consequently, alternative settings were also proposed in analogy with the misfit composite model for the lillianite homologous series (Elcoro *et al.*, 2008), which gave the best model for the unified description of the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$.

The validity of the model was confirmed by the refinements for phases of $m = 6$ and $m = 9$ in the homologous series $\text{Ga}_2\text{O}_3(\text{ZnO})_m$. The ideal model was modified to take into account a few complex phenomena in real structures before being used in refinements. That is, the occupation domain for the metal site was divided into parts, which were treated as independent sites. As all of the refinable parameters have been refined in this study, the results are equivalent to those from the three-dimensional refinements. Using the (3 + 1)-dimensional model presented, the number of parameters can

be reduced (that is, less than the maximum permitted), if necessary, for refinements of the phases of the larger m of the homologous series.

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