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Scanning of magnetic space groups and the analysis of non-magnetic domain walls

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Similarly to atomic positions in a crystal being fixed, or at least constrained by the space group of that crystal, the displacements of atoms in a domain wall are determined or constrained by the symmetry of the wall given by the sectional layer group of the corresponding domain pair. The sectional layer group can be interpreted as comprised of operations that leave invariant a plane transecting two overlapping structures, the domain states of the two domains adhering to the domain wall. The procedure of determining the sectional layer groups for all orientations and positions of a transecting plane is called scanning of the space group. Scanning of non-magnetic space groups has been described and tabulated. It is shown here that the scanning of magnetic groups can be determined from that of non-magnetic groups. The information provided by scanning of magnetic space groups can be utilized in the symmetry analysis of domain walls in non-magnetic crystals since, for any dichromatic space group, which expresses the symmetry of overlapped structures of two non-magnetic domains, there exists an isomorphic magnetic space group. Consequently, a sectional layer group of a magnetic space group expresses the symmetry of a non-magnetic domain wall. Examples of this are given in the symmetry analysis of ferroelectric domain walls in non-magnetic perovskites.

1. Introduction

Crystals are distinguished from other forms of matter by both their symmetry and their periodicity which are specified by the 230 crystallographic space groups. Their zero-, one- and two-dimensional subgroups, called *site point groups*, *penetrating rod groups* and *sectional layer groups*, describe, respectively, the symmetry of points, lines and planes in a crystal, and allow one to classify these objects into equivalence classes with the same structure and properties but at different orientations and/or positions within the crystal.

A similar classification of interfaces between two crystals, *e.g.* domain walls between two domains, can be carried out. However, instead of the space group $\boldsymbol{G}$ of either of the crystals, one uses the space group $\boldsymbol{J}_{ij}$ of the overlapping of the two crystal structures, the latter in terms of domains referred to as a *pair of domain states*, or simply as a *domain pair*. These space groups $\boldsymbol{J}_{ij}$ can be formally treated as dichromatic (black-and-white) space groups with the color exchange operation being interpreted as the exchange of the two crystal structures in the domain pair (Janovec & Přívratská, 2003). The groups $\boldsymbol{J}_{ij}$ are then also isomorphic with magnetic space groups. Consequently, from the knowledge of the layer subgroups of *magnetic* space groups, one can determine the symmetries of *non-magnetic* domain walls and subsequently provide a symmetry classification of the atomic structure of these domain walls.

Since the layer subgroups of magnetic space groups have yet to be tabulated, we first describe a simple method (Litvin & Kopský, 1997) of their derivation from the tabulations of the layer subgroups of non-magnetic space groups (*International Tables for Crystallography*, 2002; Litvin & Kopský, 2004). As an example, we then derive the domain-wall symmetry of ferroelectric domain walls in the tetragonal phase of perovskite crystals and use the derived symmetry in determining the topology of atomic displacements at the center of these walls.

2. Scanning of magnetic space groups

If a crystal of space-group symmetry $\boldsymbol{G}$ is transected by a plane, the subgroup of all operations of the space group $\boldsymbol{G}$ which leaves the plane invariant is called the sectional layer group of the plane. The process of determining these sectional layer groups is called *scanning of space groups* and has been considered by Wondratschek (1973), Guigas (1975), Kopský & Litvin (1989), Kopský (1990) and Davies & Dirl (1993). Complete scanning tables, *i.e.* tables of the layer-group symmetry for planes of all orientation and position in crystals of any space group have been tabulated (*International Tables*

Table 1
Partial scanning table for the space group $P4_x/m_xm_ym_{yz}$, the magnetic space group $P4_x/m'_xm_ym_{yz}$ and the dichromatic space group $P4_x/\hat{m}_xm_ym_{yz}$.

Without the primes in the right-hand-column, this is a partial scanning table of the space group $P4_x/m_xm_ym_{yz}$, with the primes (time inversion), that of the magnetic space group $P4_x/m'_xm_ym_{yz}$, and, replacing the primes with a caret ^ (color exchange, domain-state exchange), that of a dichromatic space group $P4_x/\hat{m}_xm_ym_{yz}$. In a layer-group symbol, an underlined operation signifies that the operation reverses the normal to the domain wall.

	$\breve{\mathbf{a}}$	$\breve{\mathbf{b}}$	**d**	s**d**	Layer group
(100)	**b**	**c**	**a**	0**d**; $\frac{1}{2}$**d**	$p_{y,z}4_x/m'_xm_ym_{yz}$
				[s**d**, −s**d**]	$p_{y,z}4_xm_ym_{yz}$
(010)	**c**	**a**	**b**	0**d**; $\frac{1}{2}$**d**	$p_{z,x}m_zm'_x\underline{m}_y$
				[s**d**, −s**d**]	$p_{z,x}m_zm'_x2'_y$
(011)	−**b**+**c**	**a**	**b**+**c**	[0**d**, $\frac{1}{2}$**d**]	$p_{\bar{y}z,x}m_{\bar{y}z}m'_x\underline{m}_{yz}$
				[$\frac{1}{4}$**d**, $\frac{3}{4}$**d**]	$p_{\bar{y}z,x}m_{\bar{y}z}m'_x\underline{a}_{yz}$ ($\breve{\mathbf{a}}$/4)
				[±s**d**, (±s+$\frac{1}{2}$)**d**]	$p_{\bar{y}z,x}m_{\bar{y}z}m'_x2'_{yz}$
In the following, $nq+mp = 1$					
(0mn)	**a**	n**b**−m**c**	p**b**+q**c**	0**d**; $\frac{1}{2}$**d**	$p_{x,\breve{b}}\underline{2}_x/m'_x$
(0$\bar{n}m$)	**a**	m**b**+n**c**	−q**b**+p**c**	[s**d**, −s**d**]	$p_{x,\breve{b}}m'_x$
(nm0)	**c**	m**a**−n**b**	q**a**+p**b**	0**d**; $\frac{1}{2}$**d**	$p_{z,\breve{b}}\underline{2}'_z/m_z$
($\bar{n}m$0)	**c**	m**a**+n**b**	−q**a**+p**b**	[s**d**, −s**d**]	$p_{z,\breve{b}}m_z$

for Crystallography, 2002; Litvin & Kopský, 2004). A partial scanning table for the space group $\boldsymbol{G} = P4_x/m_xm_ym_{yz}$, partial in that we list only some of the planar orientations, is given in Table 1.

Starting from the left-hand-side of Table 1, the first column gives the orientation, in Miller indices, of the planes under consideration. This is followed, to the right, by the translations $\breve{\mathbf{a}}$ and $\breve{\mathbf{b}}$, which are the generating translations of the translational subgroup of the sectional layer group of planes of this orientation. The vector **d** defines the *scanning direction* and is also used to define the position of the plane within the crystal. The origin of the space group is denoted by '0'. The position of the plane is specified by s**d**, given in the next column, by specifying the value 's' of the vector s**d** of the point 0 + s**d** on the plane. The sectional layer-group symmetry of the plane is given in the final column. The origin of this layer group is at 0 + s**d** or at 0 + s**d** + **t**, where **t**, a vector in the plane, if non-zero, is given in parentheses after the layer-group symbol. For example, from Table 1, for the space group $\boldsymbol{G} = P4_x/m_xm_ym_{yz}$, the sectional layer group of a plane of orientation (100) at position 0 + $\frac{1}{2}$**a** is $p_{y,z}4_x/m_xm_ym_{yz}$. Multiple vectors s**d** within brackets represent positions of planes related by operations of the space-group symmetry.

If a crystal of magnetic space-group symmetry $\boldsymbol{M}$ (Opechowski, 1986) is transected by a plane, the subgroup of all operations of the magnetic space group $\boldsymbol{M}$ which leaves the plane invariant is called the magnetic sectional layer group of the plane (Litvin, 1999, 2005). The process of determining these sectional layer groups is called, in analogy with the non-magnetic case, *scanning of magnetic space groups*. A method to determine the scanning tables of magnetic space groups from the existing scanning tables of space groups has been developed (Litvin & Kopský, 1997). Let $\boldsymbol{M}$ be a magnetic space group of the form $\boldsymbol{M} = \boldsymbol{F} + g'\boldsymbol{F}$, where the prime denotes time inversion and $\boldsymbol{F}$ the non-magnetic space group of index 2 in $\boldsymbol{M}$. The scanning table of the magnetic space group $\boldsymbol{M}$ is obtained from the scanning table of the space group $\boldsymbol{G} = \boldsymbol{F} + g\boldsymbol{F}$ by putting a prime on every operation of the second coset $g\boldsymbol{F}$ which is contained in each layer group. For example, for the magnetic space group $P4_x/m'_xm_ym_{yz} = P4_xm_ym_{yz} + \bar{1}'P4_xm_ym_{yz}$, one uses the scanning tables for the space group $P4_x/m_xm_ym_{yz} = P4_xm_ym_{yz} + \bar{1}P4_xm_ym_{yz}$. In the listings of the layer groups of the latter tables, one leaves unchanged all operations of the first coset $P4_xm_ym_{yz}$ and one inserts a prime on all operations belonging to the second coset $\bar{1}P4_xm_ym_{yz}$. That is, all translations and operations $\{1, 4_x, 2_x, 4_x^{-1}, m_y, m_z, m_{yz}, m_{y\bar{z}}\}$ remain unchanged, the operations $\{\bar{1}, \bar{4}_x, m_x, \bar{4}_x^{-1}, 2_y, 2_z, 2_{yz}, 2_{y\bar{z}}\}$ and these operations combined with any translation are primed. For example, see Table 1, the sectional layer group $p_{y,z}4_x/m_xm_ym_{yz}$ becomes $p_{y,z}4_x/m'_xm_ym_{yz}$.

Scanning tables of magnetic space groups can immediately be used as scanning tables of dichromatic space groups due to the isomorphism between these two types of groups. A magnetic space group $\boldsymbol{M} = \boldsymbol{F} + g'\boldsymbol{F}$ can be converted to a dichromatic group $\boldsymbol{F} + \hat{\boldsymbol{g}}\boldsymbol{F}$ simply by replacing the prime (time inversion) associated with operations of $\boldsymbol{M}$ with a caret (color exchange). Consequently, scanning tables for dichromatic groups $\boldsymbol{F} + \hat{\boldsymbol{g}}\boldsymbol{F}$ can be derived from scanning tables for magnetic groups $\boldsymbol{F} + g'\boldsymbol{F}$ by replacing the prime on operations of the sectional layer groups with a caret. For example, the scanning table for the dichromatic space group $P4_x/\hat{m}_xm_ym_{yz} = P4_xm_ym_{yz} + \hat{\bar{1}}P4_xm_ym_{yz}$ is derived from the scanning table of the magnetic space group $P4_x/m'_xm_ym_{yz} = P4_xm_ym_{yz} + \bar{1}'P4_xm_ym_{yz}$. One replaces each prime with a caret, for

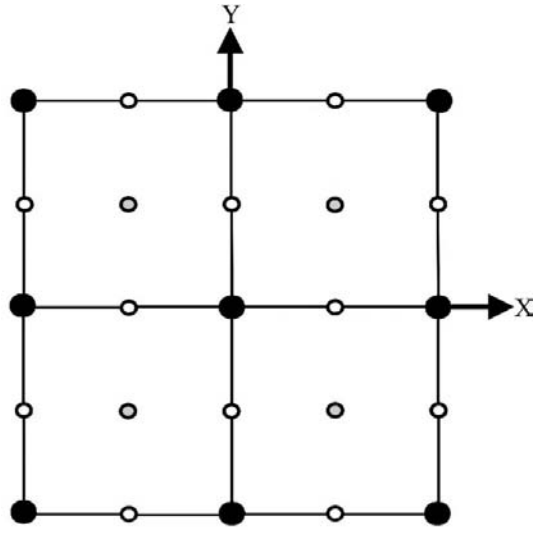

Figure 1
The cubic phase of barium titanate. Ba atoms are denoted by larger filled circles. O atoms at $z = \frac{1}{2}$ and $z = 1$ are denoted by open or shaded smaller circles, respectively. Ti atoms at the center of each cubic cell are represented by smaller filled circles which in this figure are hidden from view by the O atoms at $z = 1$.

example in Table 1, the sectional layer group $p_{y,z}4_x/m'_x m_y m_{yz}$ becomes $p_{y,z}4_x/\hat{m}_x m_y m_{yz}$.

3. Application in symmetry analysis of domain walls

Fig. 1 shows the structure of the cubic phase of barium titanate, of symmetry $Pm\bar{3}m$ along with the coordinate system we shall use. The z axis is out of the paper. Ba atoms are denoted by larger filled circles. O atoms at $z = \frac{1}{2}$ and $z = 1$ are denoted by open or shaded smaller circles, respectively. Ti atoms at the center of each cubic cell are represented by smaller filled circles, which in Fig. 1 are hidden from view by the O atoms at $z = 1$. Two single-domain states, denoted by S_1 and S_2, of the tetragonal phase with $\mathbf{a} \neq \mathbf{b} = \mathbf{c}$, of barium titanate are shown in Figs. 2(a) and 2(b), respectively (Janovec *et al.*, 2004). The magnitude and direction of exaggerated atomic displacements relative to their original positions in the cubic phase are represented by arrows.

In Fig. 3, we show the domain pair consisting of the superposition of these two single-domain states S_1 and S_2. The space-group symmetry of each of the two single-domain states S_1 and S_2 is $P4_x m_y m_{yz}$. The symmetry group $\boldsymbol{J}_{ij}$ of a domain pair can be considered as a *dichromatic* space group with the two *colored* single-domain states. The dichromatic space-group symmetry of the domain pair in Fig. 3 is $P4_x m_y m_{yz} + \hat{\bar{1}} P4_x m_y m_{yz} = P4_x/\hat{m}_x m_y m_{yz}$, where the caret ^ denotes that the corresponding symmetry operation exchanges the two single-domain states (Janovec & Přívratská, 2003). Half of the operations of this group, the operations of the first coset $P4_x m_y m_{yz}$, transform atoms of one single-domain state (one color) into atoms of the same single-domain state (the same color), while the operations of the second coset $\hat{\bar{1}} P4_x m_y m_{yz}$, those with a caret, transform atoms of one single-domain state (one color) into atoms of the other single-domain state (the opposite color).

A domain twin is obtained by passing a plane through the domain pair and deleting from one side of the plane the atoms of one of the single-domain states, and the atoms of the second single-domain state from the other side of the plane. Atoms in and near the plane represent the structure of the central part of the domain wall. The displacement of atoms at the center of the domain wall is fixed or at least constrained by the layer-group symmetry of the domain wall. The layer-group symmetry of the domain wall, in turn, depends on both the domain wall's orientation and position within the domain pair. Consequently, since the domain twin's symmetry is a dichromatic space group, to determine the domain-wall symmetry we

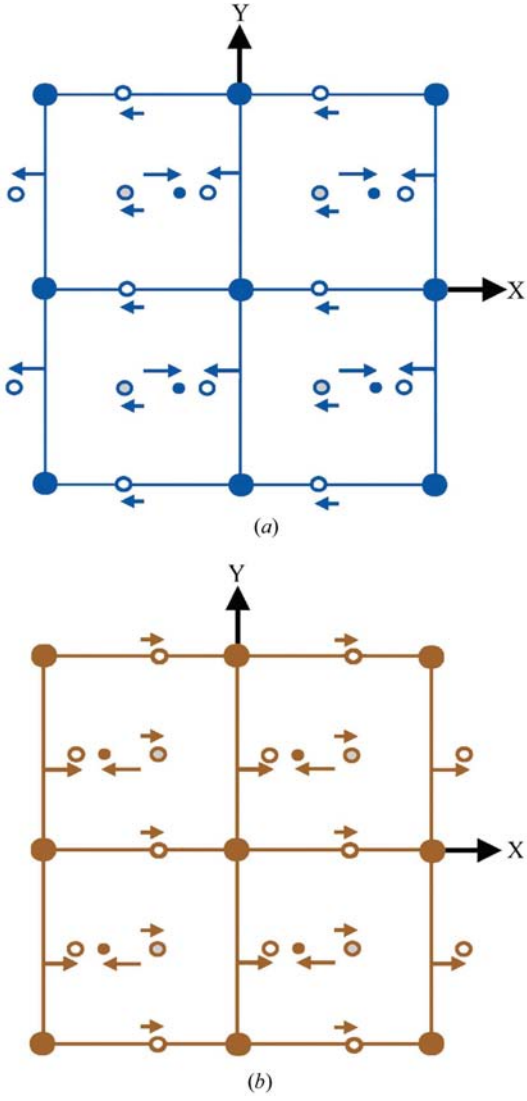

Figure 2
Two single-domain states S_1 and S_2 of the tetragonal phase of barium titanate. Ba atoms are denoted by larger filled circles, O atoms by open or shaded smaller circles and Ti atoms by smaller filled circles The magnitude and direction of exaggerated atomic displacements relative to their positions in the cubic phase are denoted by arrows.

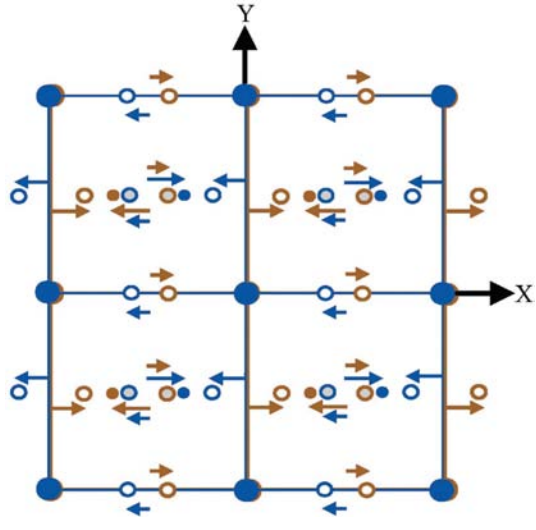

Figure 3
The domain pair consisting of the superposition of the two single-domain states S_1 and S_2 shown in Figs. 2(a) and 2(b). The space-group symmetry of both the individual single-domain states is $P4_x m_y m_{yz}$. The dichromatic space-group symmetry of the domain pair is $P4_x/\hat{m}_x m_y m_{yz}$, where the caret ^ denotes that the corresponding symmetry operation exchanges the two single-domain states.

use the concept of scanning of dichromatic space groups, *i.e.* using the scanning tables for dichromatic space groups derived from the scanning tables of magnetic space groups.

We give here two examples of using scanning tables for dichromatic space groups in the symmetry analysis of domain walls. For the two single-domain states in Figs. 2(*a*) and 2(*b*), we transect the corresponding domain pair, Fig. 3, with a plane of orientation (010) at the position 0**b** (*i.e.* 0**d** with **d** = **b**). From Table 1, the sectional layer group of this domain wall is $p_{z,x}m_z\hat{\boldsymbol{m}}_x\underline{m}_y$, found by replacing the prime in $p_{z,x}m_zm'_x\underline{m}_y$ with a caret. The underlined operations reverse the normal of the wall (Janovec & Přívratská, 2003). The symmetry diagram of this layer group is shown in Fig. 4 with an overlay of the undisplaced atoms in the center of this domain wall. The site point group of both the Ba and O atoms, with respect to this layer group, is $\hat{\boldsymbol{m}}_xm_z\underline{m}_y$. Consequently, the positions are fixed

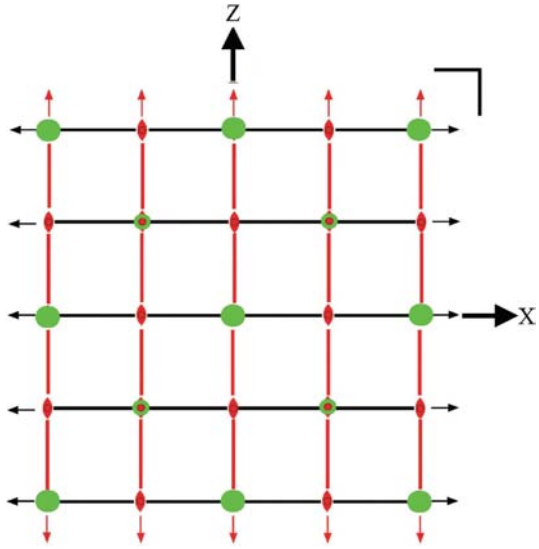

Figure 4
The symmetry diagram of $p_{z,x}m_z\hat{\boldsymbol{m}}_x\underline{m}_y$, the symmetry of the domain wall of orientation (010) at **d** = 0**b** in Fig. 3 as seen looking along the *y* axis. Operations with a caret ^ representing operations which exchange the two domain states are given in red. Overlaid on this diagram are the positions of the undisplaced Ba and O atoms at the center of the domain wall. The site point group of these atoms is $\hat{\boldsymbol{m}}_xm_z\underline{m}_y$.

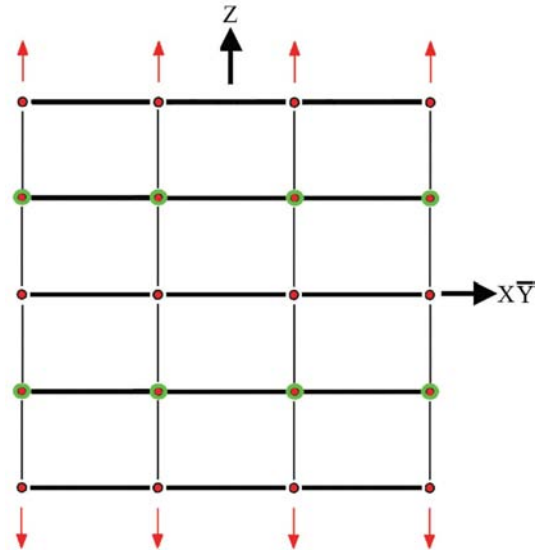

Figure 6
The symmetry $p_{z,x\bar{y}}\hat{\underline{2}}_z/m_z$ of the domain wall of orientation (110) at the position **d** = $\frac{1}{2}$**a** in Fig. 3. Overlaid on this diagram are the positions of the undisplaced O atoms at the center of the domain wall. The site point group of these O atoms is $\hat{\underline{2}}_z/m_z$.

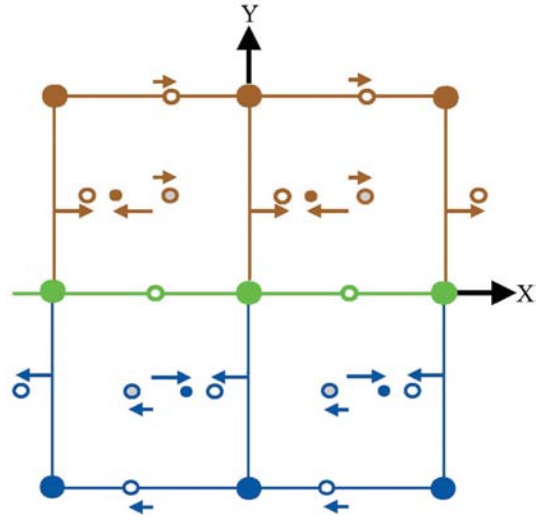

Figure 5
The domain twin consisting of the domain states S_1 and S_2 separated by a domain wall of orientation (010) at **d** = 0**b**. Atoms at the center of the domain wall are fixed by the domain-wall symmetry. The domain wall and fixed atoms are indicated in green.

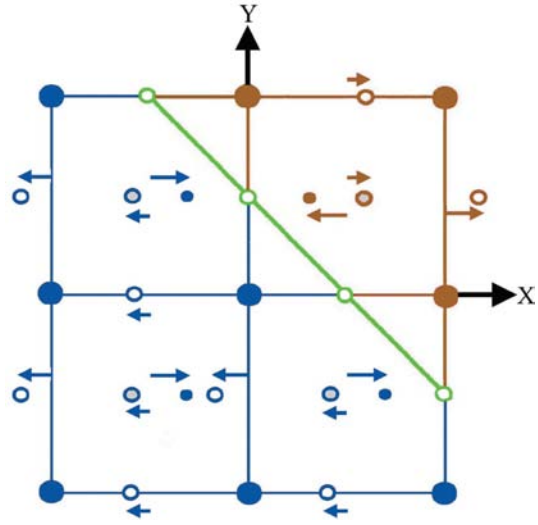

Figure 7
The domain twin consisting of the domain states S_1 and S_2 separated by a domain wall of orientation (110) at the position **d** = $\frac{1}{2}$**a**. Atoms at the center of the domain wall are fixed by the domain-wall symmetry. The domain wall and fixed atoms are indicated in green.

and the atoms in the center of the domain wall are not displaced. The resulting domain twin is shown in Fig. 5, with the domain wall and fixed atoms indicated in green.

As a second example, we consider a plane of orientation (110) at the position $\frac{1}{2}\mathbf{a}$. In Table 1, this case is found on the line with orientation ($nm0$) with $m = n = 1$. $\mathbf{d} = q\mathbf{a} + p\mathbf{b}$ and, since $nq + mp = 1$, we have taken $q = 1$ and $p = 0$. The sectional layer group of the domain wall of this orientation and position is, from Table 1, $p_{z,x\bar{y}}\hat{\underline{2}}_z/m_z$. Fig. 6 is the symmetry diagram of this sectional layer group with an overlay of the atoms in the center of the domain wall in their undistorted positions. The site point group of each of the O atoms is $\hat{\underline{2}}_z/m_z$ and consequently no displacements of these atoms are allowed. The resulting domain twin is shown in Fig. 7.

In both examples, we have shown that whether or not atoms at the center of non-magnetic domain walls are or are not displaced can be determined using scanning tables. It is not surprising that in these examples the atoms at the center of the domain walls are not displaced. In fact, the atoms at the center in all possible domain walls are not displaced. This is a consequence of (i) the overlap symmetry of the two domain states contains the inversion operation and (ii) that the site point group of every atom in the undistorted phase also contains the inversion operation. A domain wall containing atoms will then have a point-group symmetry containing the inversion operation. The site point group of each atom at the center of the domain wall will then also contain the inversion operation and consequently these atoms will not be displaced.

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References

Davies, B. L. & Dirl, R. (1993). *Proceedings of the 3rd International Wigner Symposium*. Oxford University Press.

Guigas, B. (1975), *PROSEC – a Computer Program to Calculate the Symmetry of Space-Group Sections and Projections*, Institut für Kristallographie, Universität Karlsruhe, Germany. Unpublished.

International Tables for Crystallography (2002). Vol. E, *Subperiodic Groups*, edited by V. Kopský & D. B. Litvin. Dordrecht: Kluwer Academic Publishers.

Janovec, V., Grocký, M., Kopský, V. & Kluiber, Z. (2004). *Ferroelectrics*, **303**, 65–68.

Janovec, V. & Přívratská, J. (2003). *International Tables for Crystallography*, Vol. D, edited by A. Authier, Section 3.4. Dordrecht: Kluwer Academic Publishers.

Kopský, V. (1990). *Ferroelectrics*, **111**, 81–85.

Kopský, V. & Litvin, D. B. (1989). *Group Theoretical Methods in Physics*, edited by Y. Saint-Aubin & L. Vinet, pp. 263–266. Singapore: World Scientific.

Litvin, D. B. (1999). *Acta Cryst.* A**55**, 963–964.

Litvin, D. B. (2005). *Acta Cryst.* A**61**, 382–385.

Litvin, D. B. & Kopský, V. (1997). *Ferroelectrics*, **204**, 217–233.

Litvin, D. B. & Kopský, V. (2004). *Acta Cryst.* A**60**, 637.

Opechowski, W. (1986). *Metacrystallographic Groups*. Amsterdam: North Holland.

Wondratschek, H. (1973). *The Symmetry of Planar Sections and Projections of Crystal Structures*, Institut für Kristallographie, Universität Karlsruhe, Germany. Unpublished manuscript.