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„Polar Domain Walls in Lead Titanate“

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Abstract

The polarity of domain walls in $PbTiO_3$ in its tetragonal phase are investigated via a layer group approach. It is shown that domain walls in 90° (ferroelastic) domain twins can be polar. The anti-phase domain walls predicted to be polar are not in agreement with previous calculations using density-functional theory. None of the anti-phase domain walls exhibit polarization. It is further shown that not all ferroelastic domain walls are crystallographically equivalent and therefore the magnitude of polarization may differ depending on the composition of the domain states in domain twins. The predictions made in this thesis and discrepancies to previous calculations are also discussed.

Zusammenfassung

Es wird auf Polarität von Domänenwänden in $PbTiO_3$ in seiner tetragonalen Phase untersucht mit Hilfe von einem "layer group" Ansatz. Es wird gezeigt, dass Domänenwände in 90° (ferroelastischen) Domänenzwillingen polar sind. Die polaren anti-phase Domänenwände stimmen nicht überein mit Vorhersagen vorheriger Berechnungen über "density-functional" Theorie. Keine der anti-phase Domänenwänden sind polar. Für ferroelastische Domänenwände wird gezeigt, dass nicht alle kristallographisch äquivalent sind und daher die Stärke der Polarisation abhängig von der Zusammensetzung der Domänenzustände in Domänenzwillingen variieren kann. Die Ergebnisse dieser Arbeit und Diskrepanzen zu den Vorhersagen vorheriger Berechnungen werden ebenfalls diskutiert. Dazu werden potentielle Erklärungen mit Hilfe moderner Überlegungen besprochen.

Contents

1 Introduction

Group theory finds many applications in physics. Amongst them is crystallography. When a material undergoes a phase transition, its crystal structure changes and thus its symmetry. In the case of $PbTiO_3$, the phase transition that is looked at leads to the loss of symmetries and with it, the possibility of various domain states which can be paired to domain pairs, separated by domain walls. Based on this information, combined with the mathematical tools of group theory, it is possible to make statements about ferroic properties of the material – specifically about possible polarizations of the domain walls, which is the motivation for this thesis [1].

2 Phase Transition of Lead Titanate

Lead titanate possesses a perovskite crystal structure and undergoes a phase transition at a temperature of 753K[2]. In its high symmetry (parent) phase above 753K, $PbTiO_3$ features a cubic crystal system with the space group $\mathcal{G} = Pm\bar{3}m$ (O_h^1, space group 221)[3]. The corresponding point group G is comprised of $|G| = 48$ symmetry elements. In its low symmetry (ferroic) phase below 753K, this changes to a tetragonal system with the space group $\mathcal{F} = P4mm$ (C_{4v}^1 space group 99). The corresponding point group F is comprised of $|F| = 8$ symmetry elements.

Looking at the atomic structure in the parent phase we have a primitive cubic lattice with the atoms located in the following positions: (see $1(a)$)

- Ti atom located in the centre $(0.5, 0.5, 0.5)$
- Pb atoms at the corners $(0, 0, 0)$
- O atoms face centred $(0, 0.5, 0.5)$.

The unit-cell volume $V_G = (62.273 \pm 0.019)\text{Å}^3$ with a lattice parameter of $a = (3.9637 \pm 0.0007)\text{Å}$.

In the low symmetry phase the lattice parameters change to $a = b = (3.9503 \pm 0.0009)\text{Å}$ and $c = (4.0161 \pm 0.0012)\text{Å}$ with a new volume of $V_F = (62.67 \pm 0.03)\text{Å}^3$. For all further calculation we consider the change of volume insignificant ($V_G = V_F$). Within the lattice the following observations are made: (see $1(b)$)

- Pb atoms remain at $(0, 0, 0)$.
- Ti atom changes its location along the z-axis to $(0.5, 0.5, 0.523)$.
- O atoms change their location along the z-axis to $(0.5, 0.5, 0.061)$ and $(0.5, 0, 0.563)$.

This results in a first domain state (DS) S_1 with its own symmetry group F_1, which is polarized along the z-axis.

The number n of different DSs is given by the ratio of the number of symmetry elements in the parent phase to the number of symmetry elements in the ferroic phase times the change in volume.

$$n = \frac{|G|}{|F|} \cdot \frac{V_G}{V_F} \tag{1}$$

In the case of $PbTiO_3$, $n = 6$.

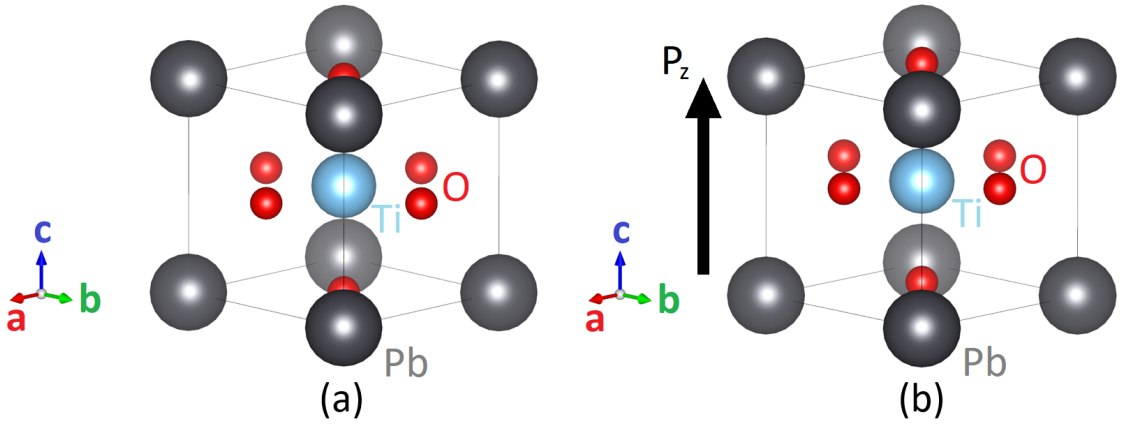

Figure 1: (a) atomic structure in the parent phase / (b) atomic structure in the ferroic phase. Ti = blue, Pb = grey, O = red
Graphics made with VESTA, source: [5]

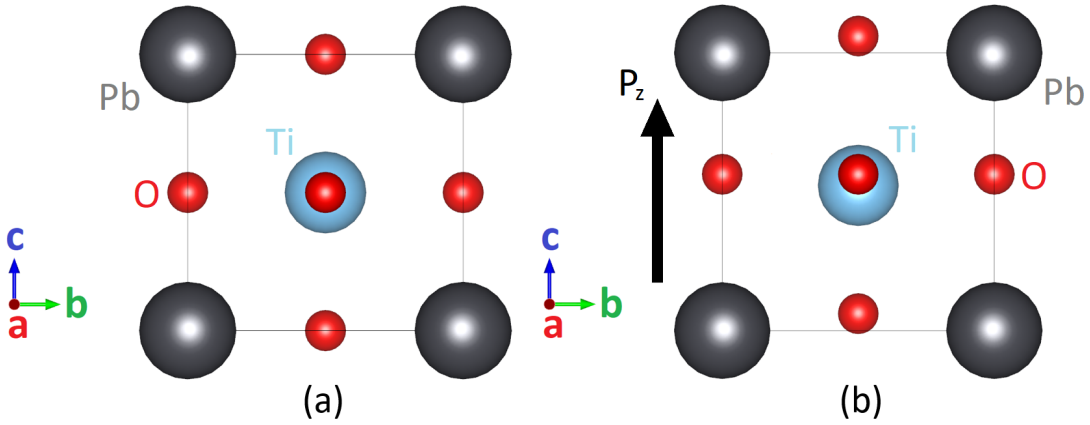

Figure 2: The polarization along the z-axis is better seen comparing (a) the parent phase to (b) the ferroic phase with the x-axis pointing towards the reader. Ti = blue, Pb = grey, O = red
Graphics made with VESTA, source: [5]

Knowing the parent and ferroic phase, one can get more information about the DSs from tables and calculations [4]:

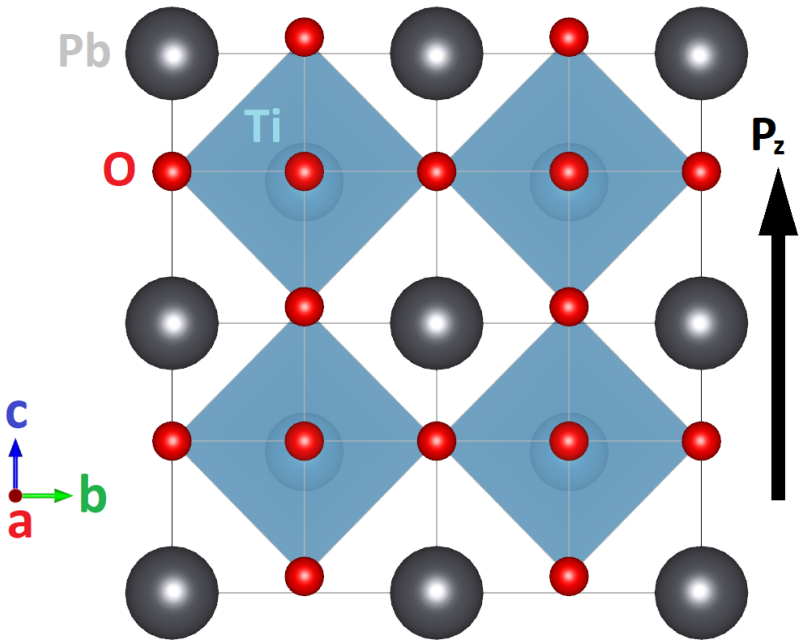

Figure 3: The tetragonal phase and polarization along the z-axis with polyhedral view. Ti = blue, Pb = grey, O = red
Graphics made with VESTA, source: [5]

- The normalizer of F_1 in G, $N_G(F_1) = 4/mmm$. Similar to 1, the number of DSs with the same symmetry group, d_f, is calculated with $d_f = \frac{|N_G(F_1)|}{|F|} = \frac{16}{8} = 2$.
- The number of ferroelectric DSs $n_e = 6$. Since $n = n_e$, the phase is fully ferroelectric and each DS can be associated with a polarization.
- In its ferroic phase, it is ferroelastic due to the change of crystal family during the transition. Specifically, it is partly ferroelastic, since the number of principal DSs compatible with one ferroelastic DS $d_a = 2$. This implies that 2DSs share the same strain.

To summarize, the phase transition $m\bar{3}m \rightarrow 4mm$ of $PbTiO_3$ is proper ferroelectric, improper ferroelastic.[6]
Two twinning groups are associated with the phase transition. $m\bar{3}m$ and $4/mmm$. These twinning groups give information about the angle between the spontaneous polarizations of two DSs. $m\bar{3}m$ and $4/mmm$ correspond to 180° and 90° respectively.

3 Single Domain States

In conclusion, the polarization P of the 6 orientational DSs are $z, -z(4), y, -y(5), x, -x$ (6).

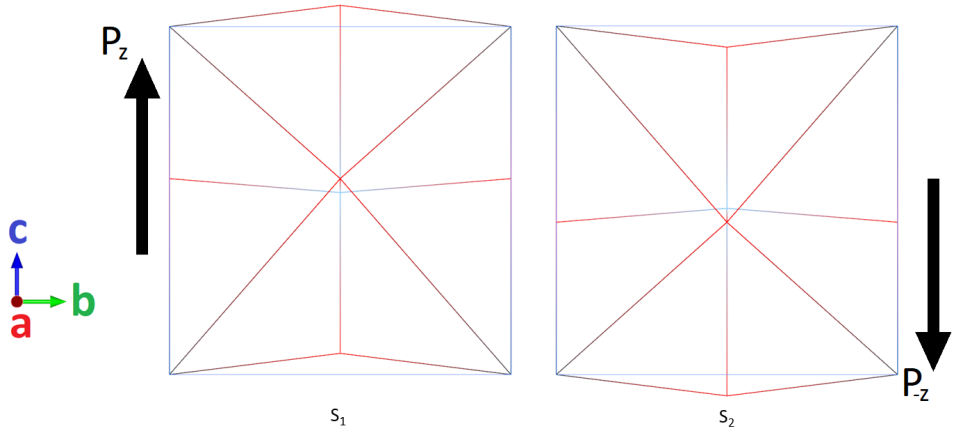

Figure 4: DSs S_1 and S_2 (Polarization along the z-axis);
Graphics made with VESTA, source: [5]

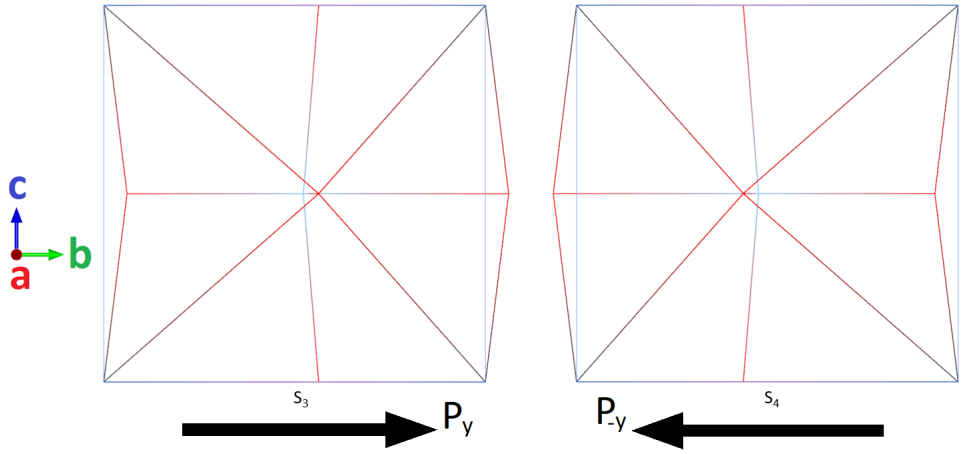

Figure 5: DSs S_3 and S_4 (Polarization along the y-axis);
Graphics made with VESTA, source: [5]

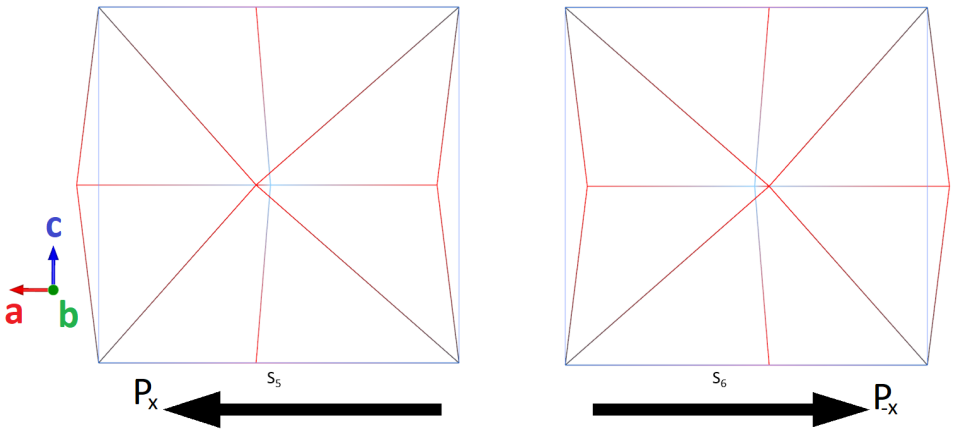

Figure 6: DSs S_5 and S_6 (Polarization along the x-axis);
Graphics made with VESTA, source: [5]

Since the volume of $PbTiO_3$ does not change during the phase transition, there exist 6 orientational and 0 translational DSs. The symmetry group F_i of each DS is defined by all symmetry operations that leave it invariant. They are listed in Table 1.

F_i	symmetry elements $g \in G$	DS	P
$F_1 = 4_z m_x m_{xy}$	$1, 2_z, 4_z, 4_z^-, m_x, m_y, m_{xy}, m_{\bar{x}y}$	S_1 S_2	$(0/0/P)$ $(0/0/-P)$
$F_2 = 4_y m_z m_{zx}$	$1, 2_y, 4_y, 4_y^-, m_x, m_z, m_{zx}, m_{\bar{z}x}$	S_3 S_4	$(0/P/0)$ $(0/-P/0)$
$F_3 = 4_x m_y m_{yz}$	$1, 2_x, 4_x, 4_x^-, m_z, m_y, m_{yz}, m_{\bar{y}z}$	S_5 S_6	$(P/0/0)$ $(-P/0/0)$

Table 1: Symmetry groups of DSs of $PbTiO_3$

Translations need not be considered since there is no change in volume and the coordinate system of the cubic and tetragonal crystal system align. Therefore the point group elements are all that is needed.

Another way of determining the polarizations is by the method of left cosets [4].
To begin, the symmetry elements of the point group F are chosen for the first coset F_1. All further cosets are calculated by picking a point group operation g_i of the parent phase G (i.e. $g \in (G \backslash F_1)$) and multiplying it with F_1. This results in a second coset $g_1 F_1 = F_2$. Out of the remaining $g \in G$ (i.e. $g \in (G \backslash (F_1 \bigcup F_2))$) another one is chosen

($g_2F_1 = F_3$) and the procedure is repeated until no $g \in G$ is left.
Each coset describes the symmetries of one DS with respect to the DS described by F_1.
In this case, the first coset describes the symmetries of DS S_1.
This leads to the same conclusions regarding the polarizations and symmetry groups of each DS as with the previous method. (see Table 2)

DS	F_i	P	symmetry elements $g \in G$
S_1	$F_1 = 4_z m_x m_{xy}$	$(0,0,P)$	$1, 2_z, 4_z, 4_z^-, m_y, m_x, m_{xy}, m_{\overline{x}y}$
S_2	$F_1 = 4_z m_x m_{xy}$	$(0,0,-P)$	$2_y, 2_x, 2_{xy}, 2_{\overline{x}y}, \overline{1}, m_z, \overline{4}_z, \overline{4}_z^-$
S_3	$F_2 = 4_y m_z m_{zx}$	$(0,P,0)$	$3_{xyz}, 3^-_{x\overline{y}z}, 2_{xz}, 4_y, \overline{3}^-_{\overline{x}yz}, \overline{3}^-_{xy\overline{z}}, \overline{4}_y^-, m_{\overline{x}z}$
S_4	$F_2 = 4_y m_z m_{zx}$	$(0,-P,0)$	$3^-_{\overline{x}yz}, 3^-_{xy\overline{z}}, 4_y^-, 2_{\overline{x}z}, \overline{3}_{xyz}, \overline{3}^-_{x\overline{y}z}, m_{xz}, \overline{4}_y$
S_5	$F_3 = 4_x m_y m_{yz}$	$(P,0,0)$	$3^-_{xyz}, 3_{\overline{x}yz}, 4_x^-, 2_{yz}, \overline{3}_{xy\overline{z}}, \overline{3}_{x\overline{y}z}, \overline{4}_x, m_{\overline{y}z}$
S_6	$F_3 = 4_x m_y m_{yz}$	$(-P,0,0)$	$3_{xy\overline{z}}, 3_{x\overline{y}z}, 4_x, 2_{\overline{y}z}, \overline{3}^-_{xyz}, \overline{3}_{\overline{x}yz}, \overline{4}_x^-, m_{yz}$

Table 2: left coset decomposition of F in G

4 Domain Pairs

Domain Pairs (DP) are an intermediate step between Domain States (DS) and Domain Walls (DW). A DP consists of a pair of Domain States. The two DSs are interpenetrating but do not influence each other [4].
DPs can be denoted as ordered or unordered. An ordered DP (S_i, S_j) is defined by the sequence of the DSs $(S_i, S_j) \neq (S_j, S_i)$. If the sequence of the DSs does not matter, it is called an unordered DP, denoted as $\{S_i, S_j\}$.
With 6 different Domain States it is possible to form 30 distinct Domain Pairs. If there exists a symmetry operation $g \in G$ that transforms one DP into another $g(S_i, S_j) = (gS_i, gS_j) = (S_l, S_m)$, then these DPs are crystallographically equivalent.
There are two possible options. DPs that are related to another in an angle of either 90° or 180°. (see Figure 7)

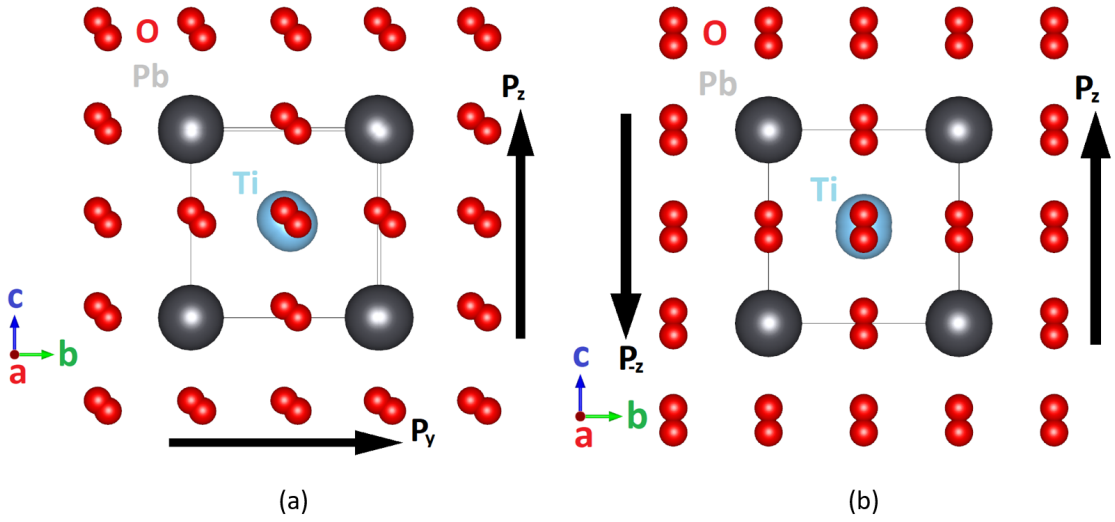

Figure 7: (a) Example of 90° DP with (S_1, S_3) / (b) Example of 180° DP with (S_1, S_2), the x-axis is pointing toward the reader;
Graphics made with VESTA, source: [5]

- 90° DPs are ferroelastic because the DSs' spontaneous strains are not equal in reference to the same coordinate system.
- 180° DPs are nonferroelastic since both DSs exhibit the same spontaneous strain.

In Table 3 and Table 4 it is by example of (S_1, S_3) and (S_1, S_2) respectively shown that all DPs are crystallographically equivalent to all other possible DPs.

$g \in G$	DP	$g \in G$	DP
$1, m_x$	(S_1, S_3)	$4_x, \overline{4}_x^-$	(S_4, S_1)
$2_z, m_y$	(S_1, S_4)	$2_{\overline{y}z}, m_{yz}$	(S_4, S_2)
$4_z^-, m_{\overline{x}y}$	(S_1, S_5)	$3_{xy\overline{z}}, \overline{3}_{\overline{x}yz}$	(S_4, S_5)
$4_z, m_{xy}$	(S_1, S_6)	$3_{x\overline{y}z}, \overline{3}_{xyz}^-$	(S_4, S_6)
$2_y, m_z$	(S_2, S_3)	$3_{xyz}, \overline{3}_{xy\overline{z}}^-$	(S_5, S_1)
$2_x, \overline{1}$	(S_2, S_4)	$3_{x\overline{y}z}^-, \overline{3}_{\overline{x}yz}^-$	(S_5, S_2)
$2_{xy}, \overline{4}_z$	(S_2, S_5)	$4_y, m_{\overline{x}z}$	(S_5, S_3)
$2_{\overline{x}y}, \overline{4}_z^-$	(S_2, S_6)	$2_{xz}, \overline{4}_y^-$	(S_5, S_4)
$m_{\overline{y}z}, 2_{yz}$	(S_3, S_1)	$3_{\overline{x}yz}^-, \overline{3}_{x\overline{y}z}^-$	(S_6, S_1)
$4_x^-, \overline{4}_x$	(S_3, S_2)	$3_{xy\overline{z}}^-, \overline{3}_{xyz}$	(S_6, S_2)
$3_{xyz}^-, \overline{3}_{x\overline{y}z}$	(S_3, S_5)	$4_y^-, m_{xz}$	(S_6, S_3)
$3_{\overline{x}yz}, \overline{3}_{xy\overline{z}}$	(S_3, S_6)	$2_{\overline{xz}}, \overline{4}_y$	(S_6, S_4)

Table 3: DPs equivalent to (S_1, S_3)

Since there exists an operation $g \in G$ for each ferroelastic DP so that all possible ferroelastic DPs are crystallographically equivalent only (S_1, S_3) will be considered as an example in the future.

$g \in G$	DP
$1, 2_z, 4_z^-, 4_z, m_y, m_x, m_{xy}, m_{\overline{x}y}$	(S_1, S_2)
$2_y, 2_x, 2_{xy}, 2_{\overline{x}y}, \overline{1}, \overline{4}_z^-, \overline{4}_z, m_z$	(S_2, S_1)
$3_{xyz}^-, 3_{\overline{x}yz}, 4_x^-, 2_{yz}, \overline{3}_{xy\overline{z}}, \overline{3}_{x\overline{y}z}, \overline{4}_x, m_{\overline{y}z}$	(S_3, S_4)
$3_{xy\overline{z}}, 3_{x\overline{y}z}, 2_{\overline{y}z}, 4_x, \overline{3}_{xyz}^-, \overline{3}_{\overline{x}yz}, \overline{4}_x^-, m_{yz}$	(S_4, S_3)
$3_{xyz}, 3_{x\overline{y}z}^-, 4_y, 2_{xz}, \overline{3}_{\overline{x}yz}^-, \overline{3}_{xy\overline{z}}^-, \overline{4}_y^-, m_{\overline{x}z}$	(S_5, S_6)
$3_{\overline{x}yz}^-, 3xy\overline{z}^-, 4_y^-, 2_{\overline{x}z}, \overline{3}_{xyz}, \overline{3}_{x\overline{y}z}^-, \overline{4}_y, m_{xz}$	(S_6, S_5)

Table 4: DPs equivalent to (S_1, S_2)

Since there exists an operation $g \in G$ for each nonferroelastic DP so that all possible nonferroelastic DPs are crystallographically equivalent, only (S_1, S_2) will be considered as an example in the future.

These results can be reached geometrically by applying all symmetry operations $g \in G$ to the tetragonal structure of S_1. Another way is to do it algebraically by multiplying all $g \in G$ with all symmetry operations of S_1 in their matrix form. For this thesis both methods have been used and both yield the same results.

The symmetry group F_{ij} of an ordered DP (S_i, S_j) is composed of all symmetry elements that leave the DP unchanged. It is therefore the intersection of the symmetry groups F_i and F_j of DSs S_i, S_j

$$F_{ij} = F_i \bigcap F_j \tag{2}$$

The symmetry group J_{ij} of an unordered DP $\{S_i, S_j\}$ is composed of all symmetry elements $f \in F_{ij}$ that leave the DP unchanged and additionally all symmetry elements $g^\star$ that simultaneously exchange S_i and S_j.

$$J_{ij} = F_{ij} \bigcup g^\star F_{ij} \tag{3}$$

For 90° DPs:

- $F_{13} = F_{DS(1)} \bigcap F_{DS(3)} = F_1 \bigcap F_2 = \{1, m_x\}$
- $J_{13} = F_{13} \bigcup g^\star F_{13} = \{1, m_x, 2_{yz}, m_{\overline{y}z}\}$

For 180° DPs:

- $F_{12} = F_{DS(1)} \bigcap F_{DS(2)} = F_1 \bigcap F_1 = F_1$
- $J_{12} = F_{12} \bigcup g^\star F_{12} = F_1 \bigcup g^\star F_1 = F_1 \bigcup \overline{1} F_1 =$
  $= \{1, 2_z, 4_z, 4_z^-, m_y, m_x, m_{xy}, m_{\overline{x}y}, m_z, \overline{1}, \overline{4}_z^-, \overline{4}_z, 2_y, 2_x, 2_{\overline{x}y}, 2_{xy}\}$

5 Domain Twins

A domain twin (DT) is comprised of two DSs which are separated by a plane. In other words, a DT is a pair of DSs which do not intersect but meet at a plane of zero thickness. This plane is called a domain wall (DW). A DW is defined by a vector $\vec{n}$ orthogonal to its inclination. A DT is denoted with $(S_i|\vec{n}|S_j)$. The orientation of a DW is determined by minimization of free energy: [6]

- minimization of electrostatic energy
- minimization of elastic energy

For 90° DPs, this results is a DW that is inclined 45° between both DSs. For 180° DPs, the possible DWs are either horizontally or vertically oriented. All possible DTs are shown in Figure 8 and Figure 9.

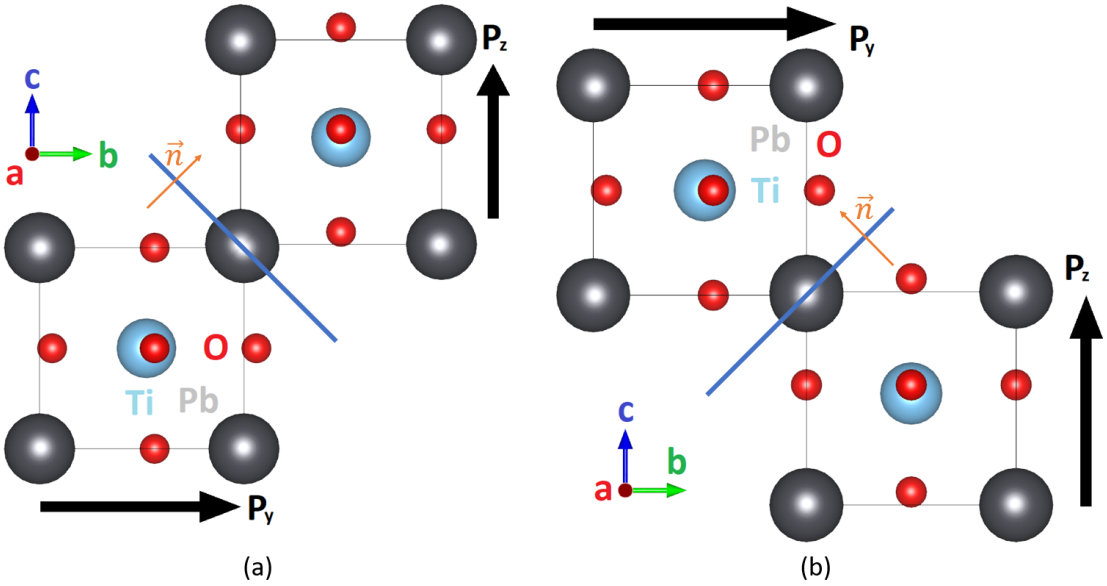

Figure 8: (a) DT $S_1|\vec{n}|S_3$ with wall normal $\vec{n} = [0, 1, 1]$ / (b) DT $S_1|\vec{n}|S_3$ with wall normal $\vec{n} = [0, -1, 1]$, the x-axis is pointing toward the reader;
Graphics made with VESTA

The following relation is true:

- $(S_i|\vec{n}|S_j) = (S_j|-\vec{n}|S_i)$

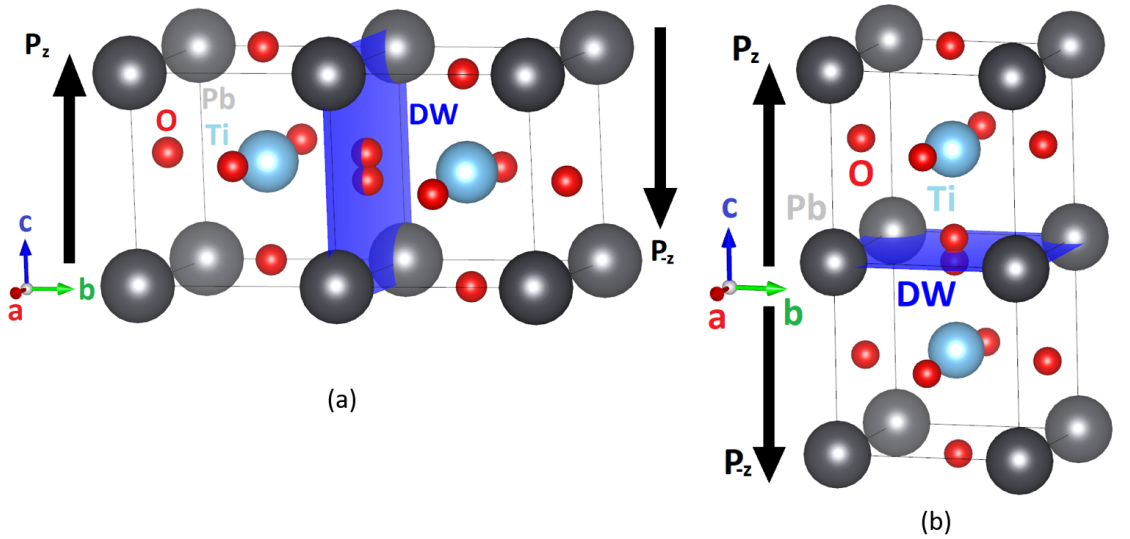

Figure 9: (a) DT $S_1|\vec{n}|S_2$ with wall normal $\vec{n} = [0, 1, 0]$ / (b) DT $S_1|\vec{n}|S_2$ with wall normal $\vec{n} = [0, 0, 1]$;
Graphics made with VESTA

A sectional layer group $\overline{J}_{ij}$ [4] is comprised of all symmetry operations,

- f_{ij} which leave invariant the normal $\vec{n}$ and both domain states S_i and S_j. The set of all these operations is found in the face group $\hat{F}_{ij}$.
- $\underline{t}^{\star}_{ij}$ which inverts $\vec{n}$ and also exchanges S_i and S_j
- $r^{\star}_{ij}$ which leaves $\vec{n}$ invariant but exchanges S_i and S_j
- $\underline{s}_{ij}$ which inverts $\vec{n}$ but does not change S_i and S_j

$$\overline{J}_{ij} = \hat{F}_{ij} \cup \underline{t}^{\star}_{ij}\hat{F}_{ij} \cup r^{\star}_{ij}\hat{F}_{ij} \cup \underline{s}_{ij}\hat{F}_{ij} \tag{4}$$

[11]

A layer group T_{ij} [4] is comprised of all symmetry operations that do not change the DT. This includes operations:

- f_{ij} which leave invariant the normal $\vec{n}$ and both domain states S_i and S_j.
- $\underline{t}^{\star}_{ij}$ which inverts $\vec{n}$ and also exchanges S_i and S_j

$$T_{ij} = \hat{F}_{ij} \cup \underline{t}^{\star}_{ij}\hat{F}_{ij} \tag{5}$$

[11]

To determine the layer groups, each of the four DTs needs to be analysed for equivalence with other DTs and operations needed for the layer groups. The results are found in Table 5, Table 6, Table 7 and Table 8.

$g \in G$	DT	$g \in G$	DT
$1, m_x$	$(S_1\|(0,-1,1)\|S_3)$	$4_x, \overline{4}_x^-$	$(S_4\|(0,-1,-1)\|S_1)$
$2_z, m_y$	$(S_1\|(0,1,1)\|S_4)$	$2_{\overline{y}z}, m_{yz}$	$(S_4\|(0,-1,1)\|S_2)$
$4_z^-, m_{\overline{x}y}$	$(S_1\|(-1,0,1)\|S_5)$	$3_{xy\overline{z}}, \overline{3}_{\overline{x}yz}$	$(S_4\|(-1,-1,0)\|S_5)$
$4_z, m_{xy}$	$(S_1\|(1,0,1)\|S_6)$	$3_{x\overline{y}z}, \overline{3}_{xyz}^-$	$(S_4\|(1,-1,0)\|S_6)$
$2_y, m_z$	$(S_2\|(0,-1,-1)\|S_3)$	$3_{xyz}, \overline{3}_{xy\overline{z}}^-$	$(S_5\|(1,0,-1)\|S_1)$
$2_x, \overline{1}$	$(S_2\|(0,1,-1)\|S_4)$	$3_{x\overline{y}z}^-, \overline{3}_{\overline{x}yz}^-$	$(S_5\|(1,0,1)\|S_2)$
$2_{xy}, \overline{4}_z$	$(S_2\|(-1,0,-1)\|S_5)$	$4_y, m_{\overline{x}z}$	$(S_5\|(1,-1,0)\|S_3)$
$2_{\overline{x}y}, \overline{4}_z^-$	$(S_2\|(1,0,-1)\|S_6)$	$2_{xz}, \overline{4}_y^-$	$(S_5\|(1,1,0)\|S_4)$
$m_{\overline{y}z}, 2_{yz}$	$(S_3\|(0,1,-1)\|S_1)$	$3_{\overline{x}yz}^-, \overline{3}_{x\overline{y}z}^-$	$(S_6\|(-1,0,-1)\|S_1)$
$4_x^-, \overline{4}_x$	$(S_3\|(0,1,1)\|S_2)$	$3_{xy\overline{z}}^-, \overline{3}_{xyz}$	$(S_6\|(-1,0,1)\|S_2)$
$3_{xyz}^-, \overline{3}_{x\overline{y}z}$	$(S_3\|(-1,1,0)\|S_5)$	$4_y^-, m_{xz}$	$(S_6\|(-1,-1,0)\|S_3)$
$3_{\overline{x}yz}, \overline{3}_{xy\overline{z}}$	$(S_3\|(1,1,0)\|S_6)$	$2_{\overline{x}z}, \overline{4}_y$	$(S_6\|(-1,1,0)\|S_4)$

Table 5: DTs equivalent to $(S_1|\vec{n}|S_3)$ with $\vec{n} = [0,-1,1]$

The operations that leave the DSs and the wall (defined by its normal $\vec{n}$) unchanged are: $\{1, m_x\}$. Furthermore, operations $\underline{t}_{13}^{\star} = \{2_{yz}, m_{\overline{y}z}\}$ are found.
As a result:

- $\hat{F}_{13(0,-1,1)} = \{1, m_x\}$
- $\overline{J}_{13(0,-1,1)} = \{1, m_x, 2_{yz}, m_{\overline{y}z}\} = T_{13(0,-1,1)}$

The table also shows that, as expected, the DT $(S_1|(0,-1,1)|S_3)$ is not crystallographically equivalent with all other possible ferroic DTs $(S_1|\vec{n}|S_3)$. To illustrate this with an example: For the DT $(S_1|\vec{n}|S_3)$, we only find DT $(S_3|-\vec{n}|S_1)$, which is equivalent. $(S_1|-\vec{n}|S_3)$ and $(S_3|\vec{n}|S_1)$ do not appear. The ones that are missing are found in Table 6.

$g \in G$	DT	$g \in G$	DT
$1, m_x$	$(S_1\|(0,1,1)\|S_3)$	$4_x, \overline{4}_x^-$	$(S_4\|(0,-1,1)\|S_1)$
$2_z, m_y$	$(S_1\|(0,-1,1)\|S_4)$	$2_{\overline{y}z}, m_{yz}$	$(S_4\|(0,-1,-1)\|S_2)$
$4_z^-, m_{\overline{x}y}$	$(S_1\|(1,0,1)\|S_5)$	$3_{xy\overline{z}}, \overline{3}_{\overline{x}yz}$	$(S_4\|(1,-1,0)\|S_5)$
$4_z, m_{xy}$	$(S_1\|(-1,0,1)\|S_6)$	$3_{x\overline{y}z}, \overline{3}_{xyz}^-$	$(S_4\|(-1,-1,0)\|S_6)$
$2_y, m_z$	$(S_2\|(0,1,-1)\|S_3)$	$3_{xyz}, \overline{3}_{xy\overline{z}}^-$	$(S_5\|(1,0,1)\|S_1)$
$2_x, \overline{1}$	$(S_2\|(0,-1,-1)\|S_4)$	$3_{x\overline{y}z}^-, \overline{3}_{\overline{x}yz}^-$	$(S_5\|(1,0,-1)\|S_2)$
$2_{xy}, \overline{4}_z$	$(S_2\|(1,0,-1)\|S_5)$	$4_y, m_{\overline{x}z}$	$(S_5\|(1,1,0)\|S_3)$
$2_{\overline{x}y}, \overline{4}_z^-$	$(S_2\|(-1,0,-1)\|S_6)$	$2_{xz}, \overline{4}_y^-$	$(S_5\|(1,-1,0)\|S_4)$
$m_{\overline{y}z}, 2_{yz}$	$(S_3\|(0,1,1)\|S_1)$	$3_{\overline{x}yz}^-, \overline{3}_{x\overline{y}z}^-$	$(S_6\|(-1,0,1)\|S_1)$
$4_x^-, \overline{4}_x$	$(S_3\|(0,1,-1)\|S_2)$	$3_{xy\overline{z}}^-, \overline{3}_{xyz}$	$(S_6\|(-1,0,-1)\|S_2)$
$3_{xyz}^-, \overline{3}_{x\overline{y}z}$	$(S_3\|(1,1,0)\|S_5)$	$4_y^-, m_{xz}$	$(S_6\|(-1,1,0)\|S_3)$
$3_{\overline{x}yz}, \overline{3}_{xy\overline{z}}$	$(S_3\|(-1,1,0)\|S_6)$	$2_{\overline{xz}}, \overline{4}_y$	$(S_6\|(-1,-1,0)\|S_4)$

Table 6: DTs equivalent to $(S_1|\vec{n}|S_3)$ with $\vec{n} = [0,1,1]$

The operations that leave the DSs and the wall (defined by its normal $\vec{n}$) unchanged are: $\{1, m_x\}$. Furthermore, operations $r_{13}^\star = \{2_{yz}, m_{\overline{y}z}\}$ are found.
As a result:

- $\hat{F}_{13(0,1,1)} = \{1, m_x\}$
- $\overline{J}_{13(0,-1,1)} = \{1, m_x, 2_{yz}, m_{\overline{y}z}\}$
- $T_{13(0,1,1)} = \{1, m_x\}$

With the DTs from this table, combined with the DTs from the previous one, all possible 90° (ferroic) DTs are accounted for.

$g \in G$	DP
$1, 2_z, 4_z^-, 4_z, m_y, m_x, m_{xy}, m_{\overline{x}y}$	$(S_1\|(0,0,1)\|S_2)$
$2_y, 2_x, 2_{xy}, 2_{\overline{x}y}, \overline{1}, \overline{4}_z^-, \overline{4}_z, m_z$	$(S_1\|(0,0,-1)\|S_2)$
$3_{xyz}^-, 3_{\overline{x}yz}, 4_x^-, 2_{yz}, \overline{3}_{xy\overline{z}}, \overline{3}_{x\overline{y}z}, \overline{4}_x, m_{\overline{y}z}$	$(S_3\|(0,1,0)\|S_4)$
$3_{xy\overline{z}}, 3_{x\overline{y}z}, 2_{\overline{y}z}, 4_x, \overline{3}_{xyz}^-, \overline{3}_{\overline{x}yz}, \overline{4}_x^-, m_{yz}$	$(S_3\|(0,-1,0)\|S_4)$
$3_{xyz}, 3_{x\overline{y}z}^-, 4_y, 2_{xz}, \overline{3}_{\overline{x}yz}^-, \overline{3}_{xy\overline{z}}^-, \overline{4}_y^-, m_{\overline{x}z}$	$(S_5\|(1,0,0)\|S_6)$
$3_{\overline{x}yz}^-, 3xy\overline{z}^-, 4_y^-, 2_{\overline{x}z}, \overline{3}_{xyz}, \overline{3}_{x\overline{y}z}^-, \overline{4}_y, m_{xz}$	$(S_5\|(-1,0,0)\|S_6)$

Table 7: DTs equivalent to $(S_1|\vec{n}|S_2)$ with $\vec{n} = [0,0,1]$

Eight operations f_{12} leave the DP unchanged. Another eight are operations $\underline{s}_{12}$.
As a result:

- $\hat{F}_{12(0,0,1)} = \{1, 2_z, 4_z, 4_z^-, m_x, m_y, m_{xy}, m_{\overline{x}y}\}$
- $\overline{J}_{12(0,0,1)} = \{1, 2_z, 4_z^-, 4_z, m_y, m_x, m_{xy}, m_{\overline{x}y}, 2_y, 2_x, 2_{xy}, 2_{\overline{x}y}, \overline{1}, \overline{4}_z^-, \overline{4}_z, m_z\}$
- $T_{12(0,0,1)} = \{1, 2_z, 4_z^-, 4_z, m_y, m_x, m_{xy}, m_{\overline{x}y}, 2_y, 2_x, 2_{xy}, 2_{\overline{x}y}, \overline{1}, \overline{4}_z^-, \overline{4}_z, m_z\}$

This DT is equivalent to all other possible anti-phase DTs with the wall normals (anti-) parallel to the polarizations of the individual DSs.

$g \in G$	DT	$g \in G$	DT
$1, m_x$	$(S_1\|(0,1,0)\|S_2)$	$2_z, m_y$	$(S_1\|(0,-1,0)\|S_2)$
$4_z^-, m_{\overline{x}y}$	$(S_1\|(1,0,0)\|S_2)$	$4_z, m_{xy}$	$(S_1\|(-1,0,0)\|S_2)$
$2_y, m_z$	$(S_2\|(0,1,0)\|S_1)$	$2_x, \overline{1}$	$(S_2\|(0,-1,0)\|S_1)$
$2_{xy}, \overline{4}_z$	$(S_2\|(1,0,0)\|S_1)$	$2_{\overline{x}y}, \overline{4}_z^-$	$(S_2\|(-1,0,0)\|S_1)$
$3_{xyz}^-, \overline{3}_{x\overline{y}z}$	$(S_3\|(1,0,0)\|S_4)$	$3_{xyz}^-, \overline{3}_{x\overline{y}z}$	$(S_3\|(-1,0,0)\|S_4)$
$m_{\overline{y}z}, 2_{yz}$	$(S_3\|(0,0,1)\|S_4)$	$4_x^-, \overline{4}_x$	$(S_3\|(0,0,-1)\|S_4)$
$3_{xy\overline{z}}, \overline{3}_{\overline{x}yz}$	$(S_4\|(1,0,0)\|S_3)$	$3_{x\overline{y}z}, \overline{3}_{xyz}^-$	$(S_4\|(-1,0,0)\|S_3)$
$4_x, \overline{4}_x^-$	$(S_4\|(0,0,1)\|S_3)$	$2_{\overline{y}z}, m_{yz}$	$(S_4\|(0,0,-1)\|S_3)$
$3_{xyz}, \overline{3}_{xy\overline{z}}^-$	$(S_5\|(0,0,1)\|S_6)$	$3_{x\overline{y}z}^-, \overline{3}_{\overline{x}yz}^-$	$(S_5\|(0,0,-1)\|S_6)$
$4_y, m_{\overline{x}z}$	$(S_5\|(0,1,0)\|S_6)$	$2_{xz}, \overline{4}_y^-$	$(S_5\|(0,-1,0)\|S_6)$
$3_{\overline{x}yz}^-, \overline{3}_{x\overline{y}z}^-$	$(S_6\|(0,0,1)\|S_5)$	$3_{xy\overline{z}}^-, \overline{3}_{xyz}$	$(S_6\|(0,0,-1)\|S_5)$
$4_y^-, m_{xz}$	$(S_6\|(0,1,0)\|S_5)$	$2_{\overline{x}z}, \overline{4}_y$	$(S_6\|(0,-1,0)\|S_5)$

Table 8: DTs equivalent to $(S_1|\vec{n}|S_2)$ with $\vec{n} = [0,1,0]$

All possible anti-phase DWs with wall normals orthogonal to the polarization of the DSs are equivalent to each other. They include all kinds of exchanging operations $f_{12}, \underline{t}_{12}^\star, r_{12}^\star$ and $\underline{s}_{12}$. As a result:

- $\hat{F}_{12(0,1,0)} = \{1, m_x\}$
- $\overline{J}_{12(0,1,0)} = \{1, 2_z, 2_y, 2_x, \overline{1}, m_z, m_y, m_x\}$
- $T_{12(0,1,0)} = \{1, m_x, \overline{1}, 2_x\}$

This table shows that all anti-phase DTs with wall normals orthogonal to the polarizations of the individual DSs are crystallographically equivalent. Important examples to mention are $(S_5|(0,0,1)|S_6)$ and $(S_5|(0,0,-1)|S_6)$, for they are the prime example in [1] which inspired this thesis.

6 Domain Walls

A layer group T_{ij} describes the symmetry group of a DW of zero thickness. If the layer groups are known, characteristics about the DWs can be determined. [11]

- If $T_{ij} > \hat{F}_{ij}$ the wall is symmetrical (S).
- If $T_{ij} = \hat{F}_{ij}$ the wall is asymmetrical (A). Depending on whether state-reversing $r^{\star}_{ij}$ or side-reversing $\underline{s}_{ij}$ operations are present, it is more precisely differentiated between $AR^{\star}$ and $A\underline{R}$ respectively.
- If $\overline{J}_{ij} > T_{ij}$ the wall is reversible (R).
- If $\overline{J}_{ij} = T_{ij}$ the wall is irreversible (I).

This results in $DT_{13(0,-1,1)} = SI$, $DT_{13(0,1,1)} = AR$, $DT_{12(0,0,1)} = AR$, $DT_{12(0,1,0)} = SR$.

DWs of zero thickness are a purely mathematical construct. In reality DWs have a finite thickness. For symmetric walls it indeed holds true that T_{ij} describes the symmetry of a wall of finite thickness because there exists a central plane. For asymmetric walls no central plane exists, but the local symmetry everywhere in the wall equals the face group $\hat{F}_{ij}$. [11] (see 10)

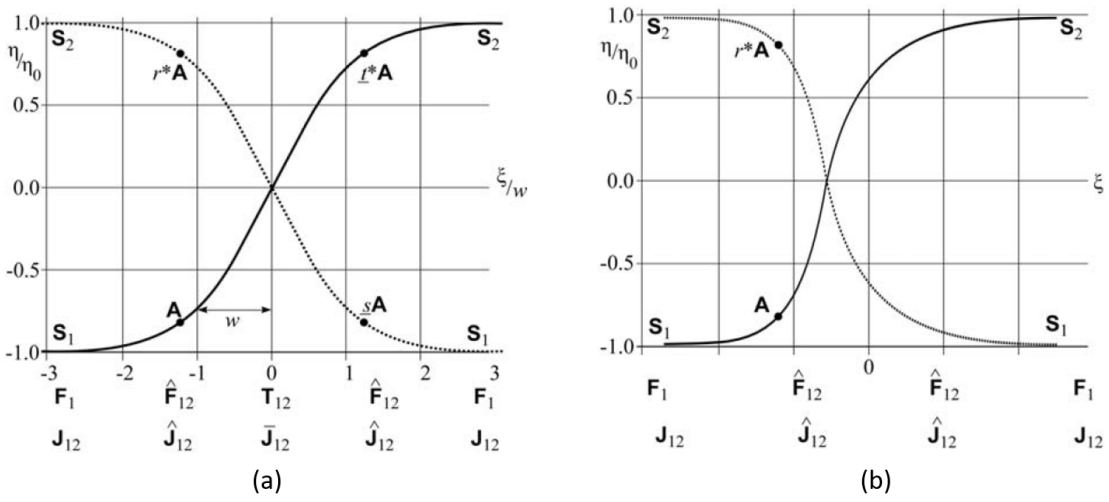

Figure 10: (a) Profile of a symmetric-reversible wall / (b) Profile of an asymmetric-reversible wall;
Graphics taken from [4]

With this information it is possible to make predictions about polarizations $\vec{P}$ of the DWs. The goal is to identify a limiting symmetry element of the layer group, which then determines the possible polarizations.

The limiting symmetry element is a symmetry element that when applied to the DW does not allow or limit polarizations.

- If a symmetry element does not allow for any polarization in the DW, the limitation is absolute and it is chosen as the limiting symmetry element. Inversion $\overline{1}$ is a prime example.
- If no such symmetry element can be found, one has to look for ones that allow for polarizations. These will then be chosen as the limiting symmetry element.

The polarizations of each DW of 90° and 180° DPs are listed in Table 9 and Table 10 respectively. The symmetry approach used in this thesis yields only qualitative and not quantitative results.

DT	Possible $\vec{P}$	limiting symmetry element
$(S_1\|(0,-1,1)\|S_3)$	$\vec{P} = (0, P, P)$	2_{yz}
$(S_1\|(0,1,1)\|S_3)$	$\vec{P} = (0, -P, P)$	m_x

Table 9: Polarizations of DWs in 90° DTs

Both DWs show polarizations. Since both DTs are not crystallographically equivalent, it cannot be assumed that the polarizations of both DWs are of the same magnitude.

DT	Possible $\vec{P}$	limiting symmetry element
$(S_1\|(0,0,1)\|S_2)$	$\vec{P} = (0,0,0)$	$\overline{1}$
$(S_1\|(0,1,0)\|S_2)$	$\vec{P} = (0,0,0)$	$\overline{1}$

Table 10: Polarizations of DWs in 180° DTs

No DWs in 180° DTs show polarizations. As previously demonstrated, $(S_5|(0,0,1)|S_6)$ and $(S_5|(0,0,-1)|S_6)$ are crystallographically equivalent to $(S_1|(0,1,0)|S_2)$. This contradicts the claim made in [1] that a polarization is to be expected in this DW as seen in 11.

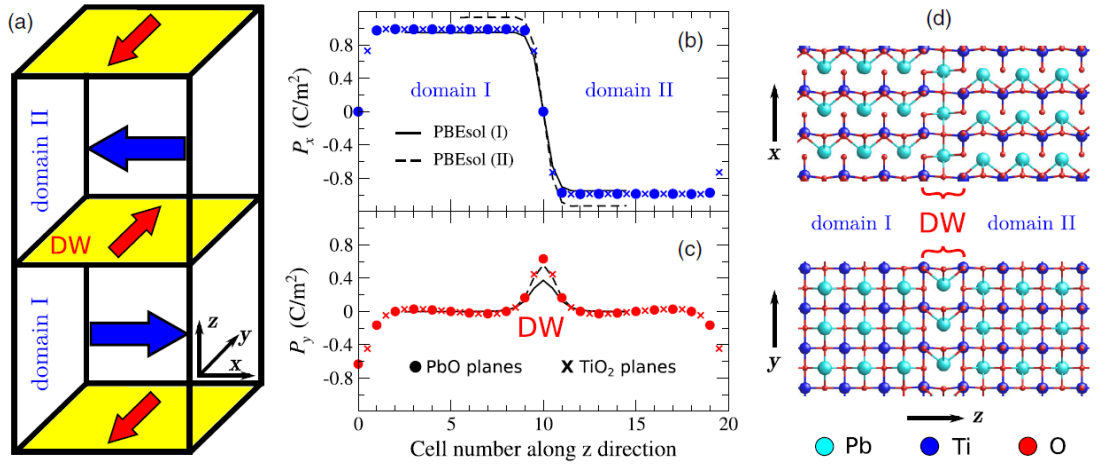

Figure 11: Graphic taken from [1]. Relevant part of the original caption: Panel (a): Sketch of the supercell used in our simulations. The indicated Cartesian axes coincide with the principal directions of the perovskite lattice. Panels (b) and (c): Polarization profile corresponding to the stable structure of our multidomain configuration. (Calculation of local polarizations) Panel (d): Views of the atomic structure of our multidomain configuration.

7 Conclusion

The approach via symmetries and group theory delivers results contradicting the paper [1]. It does not predict any possible polarizations in anti-phase DWs.

One possible explanation to allow a polarization to occur in the way it is calculated in [1], is to allow for local phase transitions within the DW. This explanation follows a rather new theory which has gained wider attention only in recent years. The polarization transition through an anti-phase DW was long expected to be of Ising-type. As recently as 2009-2017 ([15]-[14]), it was suspected that the transition could in fact be of Bloch, Néel or even mixed Bloch-Néel-Ising type (see 12). This means the magnitude of the polarization does not simply gradually diminish, getting closer to the DW. It also rotates either about the axis perpendicular or parallel to the wall, depending on whether it behaves Bloch- or Néel-like respectively.
This could possibly allow for local polarizations of the DW along the axes orthogonal to the axis of polarization of the 2 DSs of the DT. In the specific case of this thesis it is then indeed possible to have polarization as seen in [1]. Thorough calculations of this theory have been made in depth in [15].
Such local polarizations of the DW could find applications in computer memories and greatly enhance their capabilities. It could therefore be of great interest to investigate this possible phenomena in anti-phase DWs in $PbTiO_3$ further.

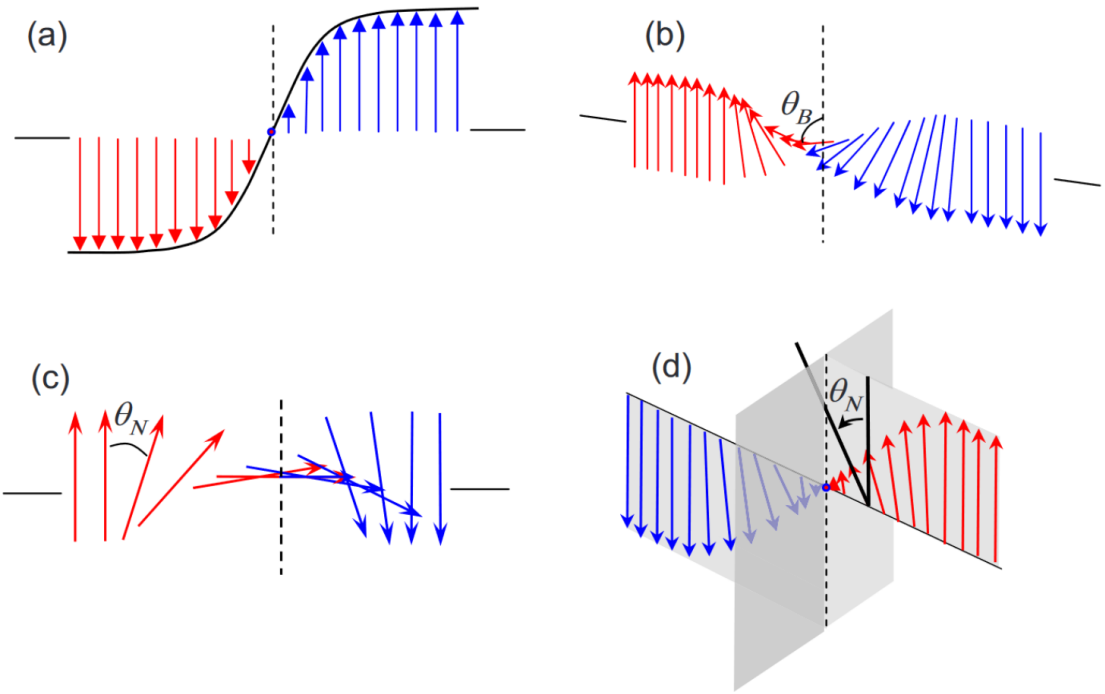

Figure 12: Graphic taken from [15]. Relevant part of the original caption: Different types of domain walls: (a) Ising type, (b) Bloch type, (c) Néel type, and (d) Mixed Ising-Néel type walls. A mixed Ising-Bloch type would look similar to (d) except that the rotation (Θ_B) would be out of the plane of the polarization vector.

The layer group approach does not yield quantitative information about the polarization. Nevertheless, the positive aspect of this method is that its qualitative results are based on purely symmetrical considerations. No estimates are needed, and thus the results are without margins of error.

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8 Appendix

Abstract

The polarity of domain walls in $PbTiO_3$ in its tetragonal phase are investigated via a layer group approach. It is shown that domain walls in 90° (ferroelastic) domain twins can be polar. The anti-phase domain walls predicted to be polar are not in agreement with previous calculations using density-functional theory. None of the anti-phase domain walls exhibit polarization. It is further shown that not all ferroelastic domain walls are crystallographically equivalent and therefore the magnitude of polarization may differ depending on the composition of the domain states in domain twins. The predictions made in this thesis and discrepancies to previous calculations are also discussed.

Zusammenfassung

Es wird auf Polarität von Domänenwänden in $PbTiO_3$ in seiner tetragonalen Phase untersucht mit Hilfe von einem "layer group" Ansatz. Es wird gezeigt, dass Domänenwände in 90° (ferroelastischen) Domänenzwillingen polar sind. Die polaren anti-phase Domänenwände stimmen nicht überein mit Vorhersagen vorheriger Berechnungen über "density-functional" Theorie. Keine der anti-phase Domänenwänden sind polar. Für ferroelastische Domänenwände wird gezeigt, dass nicht alle kristallographisch äquivalent sind und daher die Stärke der Polarisation abhängig von der Zusammensetzung der Domänenzustände in Domänenzwillingen variieren kann. Die Ergebnisse dieser Arbeit und Diskrepanzen zu den Vorhersagen vorheriger Berechnungen werden ebenfalls diskutiert. Dazu werden potentielle Erklärungen mit Hilfe moderner Überlegungen besprochen.