Effective symmetry and physical properties of twinned perovskite ferroelectric single crystals

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(Received 21 July 1999; accepted 15 November 2000)

The effective symmetry and material properties of twinned ferroelectric crystals with perovskite structure were analyzed. The twins or twinbands studied here were formed during ferroelectric phase transitions, which resulted in one of the following symmetry changes: $m\bar{3}m \rightarrow 3m$, $m\bar{3}m \rightarrow 4mm$, and $m\bar{3}m \rightarrow mm2$. It was found that the volume ratios of the two domains in a twin structure were not always equal due to the existence of defect pinning to the domain walls. This unequal partition changed the effective symmetry; hence, the effective macroscopic physical properties of the twin system. Using the data of $LiNbO_3$, $BaTiO_3$, and $KNbO_3$, a detailed analysis has been carried out on macroscopic material property changes caused by the deviation from equal domain volume partition for crystals having 3*m*, 4*mm*, and *mm*2 symmetries.

I. INTRODUCTION

The macroscopic properties of a multidomain ferroelectric system are the collective contribution of many differently oriented domains. The macroscopic symmetry is in general different from the microscopic symmetry of the crystal when it is not in a single domain state. The recently developed relaxor-based ferroelectric single crystals $(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (PZN–PT) and $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (PMN–PT) with intentionally created multidomain configurations are practical examples of such systems.[1] For these crystals, the microscopic crystal symmetry belongs to the rhombohedral 3*m* with dipoles formed in ⟨111⟩ family of the parent cubic perovskite structure. When a single ferroelectric crystal is poled along [001] of the cubic coordinates, four domain states, [111], $[\bar{1}11]$, $[1\bar{1}1]$, and $[\bar{1}\bar{1}1]$, are energetically equivalent to exist. Statistically, the effective macroscopic symmetry of the multidomain system has been assumed to have tetragonal 4*mm* symmetry. However, experimental measurements of the physical properties showed that the symmetry of many multidomain PZN–PT samples could be lower than 4*mm*.[2,3] Further study of the domain patterns in these samples using optical microscopy revealed that most of the poled samples consist of only two of the four symmetry-allowed low-temperature domains.[4] For a two-domain system, the proper symmetry for the effective macroscopic properties should be *mm*2 or lower.[5]

Experimental evidence showed that the domains often form a twinband in which only two variants exist.[4] Even for a ceramic system, domains observed in each grain are mostly twin pairs rather than involving all the low-temperature variants. Such limited variant twinning patterns are more pronounced in a single-crystal system because all orientations must be coherently joined together. Generally speaking, two-variant twinning is the basis of all multidomain systems in ferroelectrics.

Understanding the symmetry of a multidomain system is very important for proper characterization of the macroscopic properties. It has been shown in Ref. 5 that a simple statistical model[6] would not provide accurate macroscopic properties because the interactions between the domains must be taken into account while responding to external fields. For this purpose, a new average scheme has been developed,[5] which takes into account the coherent interaction between the two domains across the domain wall in a twin structure.

Energetically, equal size domains are expected in a twinband because the domain wall energy is positive and the interactions between the walls are repulsive.[7,8] This may not be true in practical situations because the domain size adjustment is through domain wall (DW) movement while the wall movement is usually pinned by defects, preventing the equal domain size state to be reached. The pinning of surfaces and other elastic and electric boundary constraints to the domain movements could also cause the unequal partition of domains. This unequal volume partition has been observed experimentally in the twinband structures of lead titanate,[9] doped barium titanate,[10,11] and PZT,[12] and, practically speaking, in all other systems to a certain degree.

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In this article, we generalize the method described in Ref. 5, in which only equal domain systems were studied, to analyze the symmetries of a twinned single crystal and calculate the corresponding changes of the macroscopic physical properties due to the change of domain ratio for three ferroelectric species: $m\bar{3}m \rightarrow 3m$, $m\bar{3}m \rightarrow 4mm$, and $m\bar{3}m \rightarrow mm2$. The objective is to provide the definition of effective macroscopic physical properties and the associated macroscopic symmetry for realistic twin structures, and more importantly, to quantify the variation of these properties caused by the change of domain volume ratio.

II. MICROSCOPIC AND MACROSCOPIC SYMMETRIES

In a $m\bar{3}m \rightarrow 3m$ ferroelectric phase transition, the possible directions for dipole formation are along the cube diagonals; i.e., the $\langle 111 \rangle$ family in the cubic coordinate system. The so-called domain enegineering of the PZN–PT and PMN–PT single crystals is to apply a poling field along the [001] direction rather than along the dipolar directions of $\langle 111 \rangle$ family. Four domain states, [111], $[\bar{1}11]$, $[1\bar{1}1]$, and $[\bar{1}\,\bar{1}1]$, remain energetically equivalent after poling with all dipoles at a 54.7° angle to the field direction of [001].[4] Permissible DWs[13] among these four ferroelectric states are listed in Table I. N/A means that DW does not exist. Two perpendicular DWs always exist between any two given domains states; one is charged and the other is neutral. The DW orientations are illustrated in Fig. 1 in the cubic coordinates.

For a charged DW between $\boldsymbol{P}^I$ and $\boldsymbol{P}^{II}$ oriented in [010] and a neutral DW between $\boldsymbol{P}^I$ and $\boldsymbol{P}^{III}$ oriented in [001], the effective macroscopic symmetry of the twin structure is monoclinic *m* [Figs. 1(a) and 1(b)]. The symmetry can be raised to orthorhombic *mm*2 when the two domains have identical size [Fig. 1(c)]. The twofold axis, which is also the direction of the effective polarization, is oriented in [101] as shown in Fig. 1(c).

For a $m\bar{3}m \rightarrow 4mm$ ferroelectric phase transition (such as $BaTiO_3$), the possible spontaneous polarization directions are in $\langle 100 \rangle$ family (in the cubic coordinate system). If the poling field is applied in [111] rather than one of the polarization directions, three domain states remain energetically equivalent to exist after poling with the dipoles in each of the unit cells also at a 54.7° angle to the poling field direction. Permissible DWs[13] among these three remaining ferro-

TABLE I. Permissible DW orientations[13] in ferroelectrics resulting from a $m\bar{3}m \rightarrow 3m$ phase transition and poled in [001] direction.

Domain state	$\mathbf{P}^I = \frac{P_S}{\sqrt{3}}[111]$	$\mathbf{P}^{II} = \frac{P_S}{\sqrt{3}}[1\bar{1}1]$	$\mathbf{P}^{III} = \frac{P_S}{\sqrt{3}}[\bar{1}\,\bar{1}\,1]$	$\mathbf{P}^{IV} = \frac{P_S}{\sqrt{3}}[\bar{1}11]$
$\mathbf{P}^I = \frac{P_S}{\sqrt{3}}[111]$	N/A	[010]	[001]	[100]
		[101]	[110]	[011]
$\mathbf{P}^{II} = \frac{P_S}{\sqrt{3}}[1\bar{1}1]$		N/A	[100]	[001]
			$[0\bar{1}1]$	$[\bar{1}10]$
$\mathbf{P}^{III} = \frac{P_S}{\sqrt{3}}[\bar{1}\,\bar{1}\,1]$			N/A	[010]
				$[\bar{1}01]$

The four domain states are energetically equivalent and P_S is the spontaneous polarization in a single domain state.

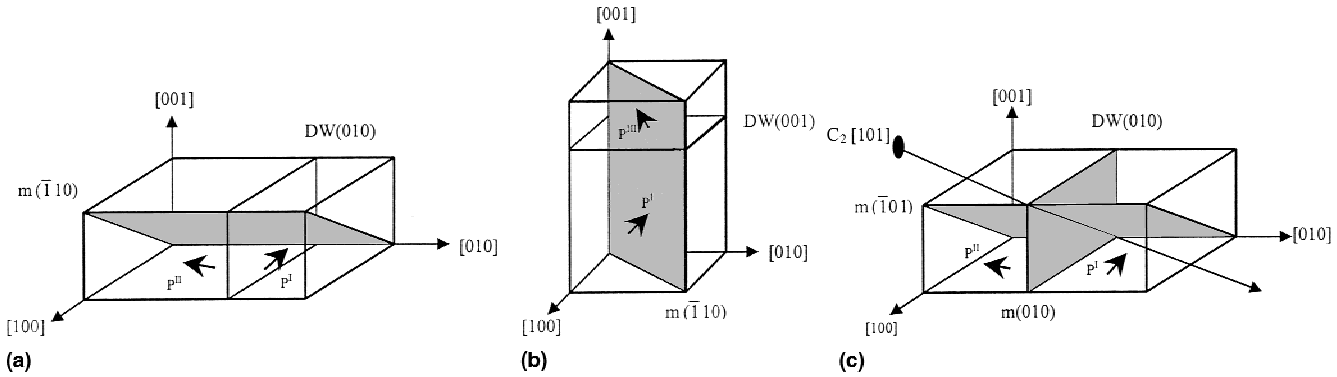

FIG. 1. Twin systems and their symmetry in a $m\bar{3}m \rightarrow 3m$ ferroelectrics. (a) Unequally partitioned twin of $\boldsymbol{P}^I$ and $\boldsymbol{P}^{II}$ with a charged DW oriented in [010]. The shaded plane is the mirror plane. (b) Unequally portioned twin of $\boldsymbol{P}^I$ and $\boldsymbol{P}^{III}$ with a neutral wall oriented in [001]. Both (a) and (b) have monoclinic *m* symmetry. (c) The same as (a) but with equal partition of the two domains. The symmetry is now orthorhombic *mm*2 because the DW becomes another mirror symmetry plane. The structures shown in (a) and (c) are used to make the calculations of Table IV and $\nu^{(1)}$ is the volume ratio of $\mathbf{P}^I = P_S/\sqrt{3}\,[111]$.

TABLE II. Permissible DW orientations[13] in ferroelectrics resulting from a $m\bar{3}m \rightarrow 4mm$ phase transition and poled in [111] direction.

Domain	$\mathbf{P}^I = P_S[100]$	$\mathbf{P}^{II} = P_S[010]$	$\mathbf{P}^{III} = P_S[001]$
$\mathbf{P}^I = P_S[100]$	N/A	[110]	[101]
		[1$\bar{1}$0]	[10$\bar{1}$]
$\mathbf{P}^{II} = P_S[010]$		N/A	[011]
			[01$\bar{1}$]

Three domain states are energetically equivalent and the value P_S is the spontaneous polarization.

electric states are listed in Table II. Similarly, two perpendicular DWs between any two given domains are permitted: One is charged and the other is neutral. The DW orientations for this case are illustrated in Fig. 2.

Again, twins containing neutral DWs and charged DWs have monoclinic *m* symmetry unless the domains are identical in size (for neutral DW the macroscopic symmetry cannot be higher than monoclinic *m*). Figs. 2(a) and 2(b) illustrate a twin of $\boldsymbol{P}^I$ and $\boldsymbol{P}^{III}$ with DW oriented in [101], and a twin of $\boldsymbol{P}^I$ and $\boldsymbol{P}^{III}$ with the DW oriented in [$\bar{1}$01], respectively. For the special case of equal domain size twins, the symmetry becomes orthorhombic *mm*2 with a twofold axis oriented in [101] direction as shown in Fig. 2(c). The twofold axis is also the direction of the effective polarization of the system.

For a $m\bar{3}m \rightarrow mm2$ ferroelectric phase transition (e.g., $KNbO_3$), the possible spontaneous polarization directions are the face diagonals ⟨110⟩ (in the cubic coordinate system). Assuming we apply a poling field in [001] of the cubic coordinates, four domain states will remain energetically equivalent with permissible domain walls among them[13] listed in Table III. The dipoles are at a 45° angle to the poling field. A new feature for this $m\bar{3}m \rightarrow mm2$ system is the presence of S walls[13,14] (or W′ walls), which do not lie on lattice planes. Instead, their orientations depend on the values of the elastic distortion in the two domains involved, and, therefore, change with temperature. There are four types of S-wall orientations determined by the following relationships[13]

$$S_1: \quad ds_1 + ds_2 + Kds_3 = 0 \qquad \text{(II.1)}$$

$$S_2: \quad ds_1 - ds_2 + Kds_3 = 0 \qquad \text{(II.2)}$$

$$S_3: \quad ds_1 - ds_2 - Kds_3 = 0 \qquad \text{(II.3)}$$

$$S_4: \quad ds_1 + ds_2 - Kds_3 = 0 \qquad \text{(II.4)}$$

$$K = \frac{Q_{44}}{Q_{11} - Q_{12}} \qquad \text{(II.5)}$$

where $Q_{\alpha\beta}$ are the electrostrictive coefficients in the cubic $m\bar{3}m$ phase.

DW orientations in the *mm*2 system are illustrated in Fig. 3. For a charged DW, such as a wall between $\boldsymbol{P}^I$ and $\boldsymbol{P}^{III}$ oriented in [$\bar{1}$10], the effective symmetry of this twin

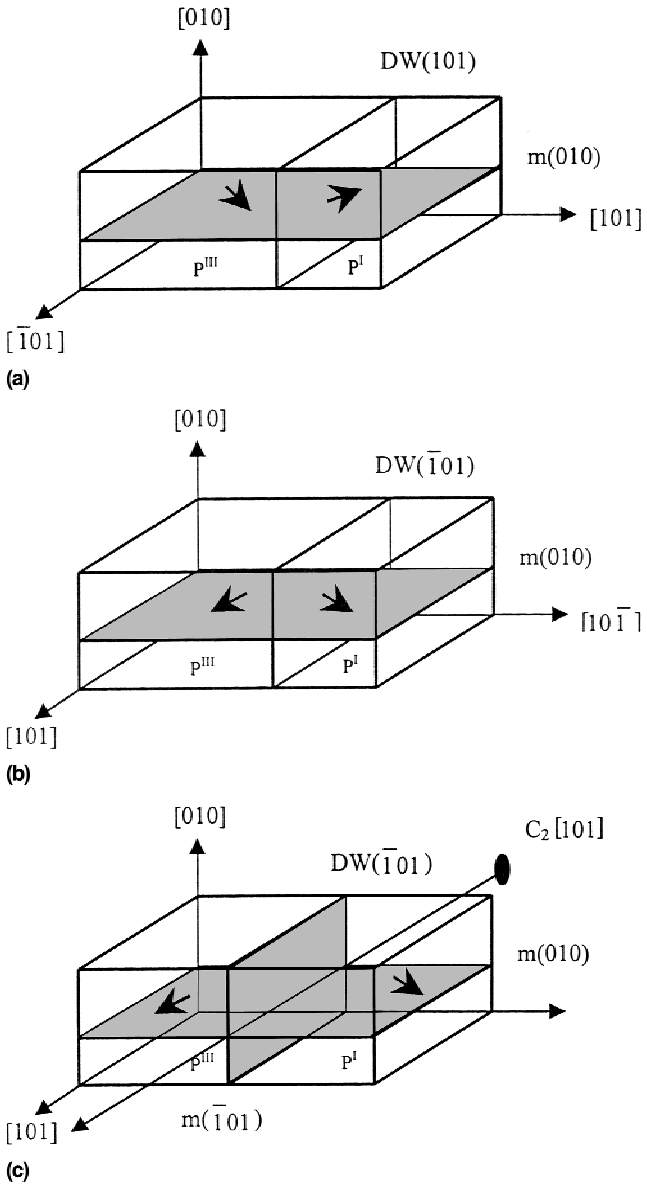

FIG. 2. Twin systems and their symmetry in a $m\bar{3}m \rightarrow 4mm$ ferroelectrics. (a) Unequally partitioned twin of $\boldsymbol{P}^I$ and $\boldsymbol{P}^{III}$ with a neutral DW oriented in [101] and the shaded plane (010) is the mirror plane of the structure. (b) Unequally partitioned twin of $\boldsymbol{P}^I$ and $\boldsymbol{P}^{III}$ with a charged DW oriented in [10$\bar{1}$]. Both (a) and (b) have monoclinic *m* symmetry. (c) The same structure as (b) but with equal partition of the two domains. The symmetry is orthorhombic *mm*2 in this case because the DW becomes another mirror symmetry plane.

structure is triclinic with symmetry group *1* [Fig. 3(a)]. If the two domains have equal volume ratio, the symmetry is monoclinic *m* [Fig. 3(b)]. For a twin between $\boldsymbol{P}^{III}$ and $\boldsymbol{P}^{IV}$ with a charged DW oriented in [010], the effective symmetry is monoclinic *m* [Fig. 3(c)] for unequal volume ratio, and orthorhombic *mm*2 when the sizes of the two domains become equal. The twofold axis is oriented in [001], which is also the direction of the total effective polarization [Fig. 3(d)].

The twin state between $\boldsymbol{P}^{III}$ and $\boldsymbol{P}^{IV}$ has a neutral DW oriented in [001], which again has a monoclinic symmetry *m* [Fig. 3(e)]. The S walls are charge neutral in all cases as listed in Table III, and the macroscopic symmetry of a twin crystal with an S wall is always triclinic *1*.

III. EFFECTIVE MATERIAL PROPERTIES OF TWINNED SINGLE CRYSTALS CONTAINING ONLY ONE SET OF TWINS

All of the effective material properties of a twin system can be determined from nine simple loads and enforcement of the usual electric and elastic continuity at the DW for certain twin configurations.[5] It was showed that the consideration of nine simple loads permits the determination of all the effective properties of the twin structure.[5] Here, instead of using the complex procedure described in Ref. 5, we combine the components of the elastic stress and the electric field to form a vector (note: the $T_4^{(i)}$ and $T_6^{(i)}$ components must be used twice):

$$\tau^{(i)} = [T_1^{(i)},T_2^{(i)},T_3^{(i)},T_4^{(i)},T_4^{(i)},T_5^{(i)},T_6^{(i)},T_6^{(i)},E_1^{(i)},E_2^{(i)},E_3^{(i)}], \quad (i = 1, 2) \quad . \tag{III.1}$$

The averaging conditions can now be expressed as

$$\tau^{eff} = \nu^{(1)}\tau^{(1)} + \nu^{(2)}\tau^{(2)} \quad , \tag{III.2}$$

and

$$\mathbf{M}^{eff}\tau^{eff} = \nu^{(1)}\mathbf{M}^{(1)}\tau^{(1)} + \nu^{(2)}\mathbf{M}^{(2)}\tau^{(2)} \quad . \tag{III.3}$$

TABLE III. Permissible DW orientations[13] in ferroelectrics resulting from a $m\bar{3}m \rightarrow mm2$ phase transition and poled in [001] direction.

Domain	$\mathbf{P}^{I} = \frac{P_S}{\sqrt{2}}[101]$	$\mathbf{P}^{II} = \frac{P_S}{\sqrt{2}}[\bar{1}01]$	$\mathbf{P}^{III} = \frac{P_S}{\sqrt{2}}[011]$	$\mathbf{P}^{IV} = \frac{P_S}{\sqrt{2}}[0\bar{1}1]$
$\mathbf{P}^{I} = \frac{P_S}{\sqrt{2}}[101]$	N/A	[100]	$[1\bar{1}0]$	[110]
		[001]	S_1	S_2
$\mathbf{P}^{II} = \frac{P_S}{\sqrt{2}}[\bar{1}01]$		N/A	[110]	$[1\bar{1}0]$
			S_3	S_4
$\mathbf{P}^{III} = \frac{P_S}{\sqrt{2}}[011]$			N/A	[010]
				[001]

Four domain states are energetically equivalent and the value P_S is the spontaneous polarization.

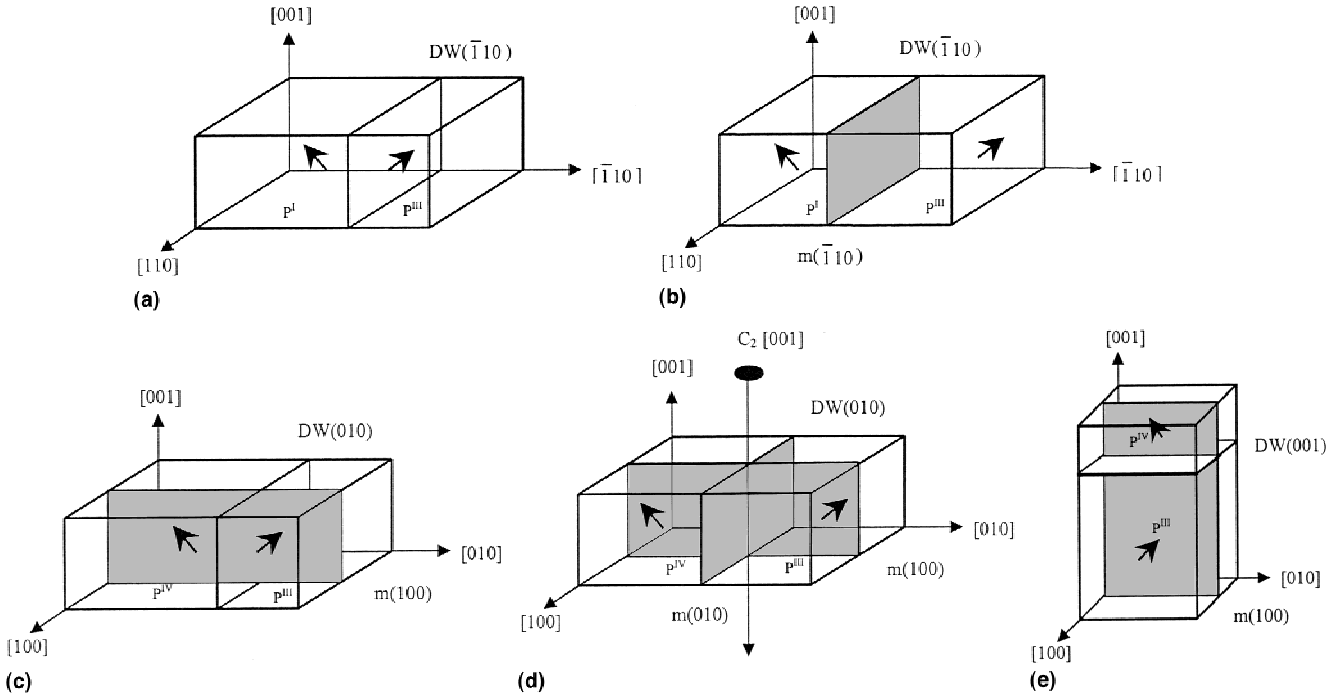

FIG. 3. Twin systems and their symmetry in a $m\bar{3}m \rightarrow mm2$ ferroelectrics. (a) Unequally portioned twin of $\boldsymbol{P}^{I}$ and $\boldsymbol{P}^{III}$ of Table III with a charged DW oriented in $[\bar{1}10]$. The symmetry is triclinic *1*. (b) The same as (a) but equal partition of the two domains. The symmetry is increased to monoclinic *m* with the DW as the mirror plane. (c) Unequally partitioned twin of $\boldsymbol{P}^{III}$ and $\boldsymbol{P}^{IV}$ with a charged DW oriented in [010]. The symmetry is monoclinic *m* with (100) plane as the mirror plane. (d) The same as (c) but equally partitioned domains. The symmetry is orthorhombic *mm*2.

Boundary conditions at the interfaces now can be described by the compact matrix equation

$$\mathbf{b}^{(1)}\tau^{(1)} = \mathbf{b}^{(2)}\tau^{(2)} \quad . \tag{III.4}$$

Combining Eqs. (*III*.1)–(*III*.4), the following matrix equation can be found for the effective material properties of a twin structure:

$$\mathbf{M}^{eff} = \{\nu^{(1)}\mathbf{M}^{(1)}[\mathbf{b}^{(1)}]^{-1} + \nu^{(2)}\mathbf{M}^{(2)}[\mathbf{b}^{(2)}]^{-1}\}\{\nu^{(1)}[\mathbf{b}^{(1)}]^{-1} + \nu^{(2)}[\mathbf{b}^{(2)}]^{-1}\}^{-1} \quad , \tag{III.5}$$

where $\nu^{(1)}$ and $\nu^{(2)}$ are the volume ratios of the two domains with $\nu^{(1)} + \nu^{(2)} = 1$, and the matrices $\mathbf{M}^{(i)}$ and $\mathbf{b}^{(i)}$ are defined by ($i = 1,2$):

$$\mathbf{M}^{(i)} = \begin{bmatrix} s_{11}^{(i)} & s_{12}^{(i)} & s_{13}^{(i)} & s_{14}^{(i)} & s_{14}^{(i)} & s_{15}^{(i)} & s_{16}^{(i)} & s_{16}^{(i)} & d_{11}^{(i)} & d_{21}^{(i)} & d_{31}^{(i)} \\ s_{12}^{(i)} & s_{22}^{(i)} & s_{23}^{(i)} & s_{24}^{(i)} & s_{24}^{(i)} & s_{25}^{(i)} & s_{26}^{(i)} & s_{26}^{(i)} & d_{12}^{(i)} & d_{22}^{(i)} & d_{32}^{(i)} \\ s_{13}^{(i)} & s_{23}^{(i)} & s_{33}^{(i)} & s_{34}^{(i)} & s_{34}^{(i)} & s_{35}^{(i)} & s_{36}^{(i)} & s_{36}^{(i)} & d_{13}^{(i)} & d_{23}^{(i)} & d_{33}^{(i)} \\ s_{14}^{(i)} & s_{24}^{(i)} & s_{34}^{(i)} & s_{44}^{(i)} & s_{44}^{(i)} & s_{45}^{(i)} & s_{46}^{(i)} & s_{46}^{(i)} & d_{14}^{(i)} & d_{24}^{(i)} & d_{34}^{(i)} \\ s_{14}^{(i)} & s_{24}^{(i)} & s_{34}^{(i)} & s_{44}^{(i)} & s_{44}^{(i)} & s_{45}^{(i)} & s_{46}^{(i)} & s_{46}^{(i)} & d_{14}^{(i)} & d_{24}^{(i)} & d_{34}^{(i)} \\ s_{15}^{(i)} & s_{25}^{(i)} & s_{35}^{(i)} & s_{45}^{(i)} & s_{45}^{(i)} & s_{55}^{(i)} & s_{56}^{(i)} & s_{56}^{(i)} & d_{15}^{(i)} & d_{25}^{(i)} & d_{35}^{(i)} \\ s_{16}^{(i)} & s_{26}^{(i)} & s_{36}^{(i)} & s_{46}^{(i)} & s_{46}^{(i)} & s_{56}^{(i)} & s_{66}^{(i)} & s_{66}^{(i)} & d_{16}^{(i)} & d_{26}^{(i)} & d_{36}^{(i)} \\ s_{16}^{(i)} & s_{26}^{(i)} & s_{36}^{(i)} & s_{46}^{(i)} & s_{46}^{(i)} & s_{56}^{(i)} & s_{66}^{(i)} & s_{66}^{(i)} & d_{16}^{(i)} & d_{26}^{(i)} & d_{36}^{(i)} \\ d_{11}^{(i)} & d_{12}^{(i)} & d_{13}^{(i)} & d_{14}^{(i)} & d_{14}^{(i)} & d_{15}^{(i)} & d_{16}^{(i)} & d_{16}^{(i)} & \epsilon_{11}^{(i)} & \epsilon_{12}^{(i)} & \epsilon_{13}^{(i)} \\ d_{21}^{(i)} & d_{22}^{(i)} & d_{23}^{(i)} & d_{24}^{(i)} & d_{24}^{(i)} & d_{25}^{(i)} & d_{26}^{(i)} & d_{26}^{(i)} & \epsilon_{12}^{(i)} & \epsilon_{22}^{(i)} & \epsilon_{23}^{(i)} \\ d_{31}^{(i)} & d_{32}^{(i)} & d_{33}^{(i)} & d_{34}^{(i)} & d_{34}^{(i)} & d_{35}^{(i)} & d_{36}^{(i)} & d_{36}^{(i)} & \epsilon_{13}^{(i)} & \epsilon_{23}^{(i)} & \epsilon_{33}^{(i)} \end{bmatrix} \tag{III.6}$$

$$\mathbf{b}^{(i)} = \begin{bmatrix} s_{11}^{(i)} & s_{12}^{(i)} & s_{13}^{(i)} & s_{14}^{(i)} & s_{14}^{(i)} & s_{15}^{(i)} & s_{16}^{(i)} & s_{16}^{(i)} & d_{11}^{(i)} & d_{21}^{(i)} & d_{31}^{(i)} \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ s_{13}^{(i)} & s_{23}^{(i)} & s_{33}^{(i)} & s_{34}^{(i)} & s_{34}^{(i)} & s_{35}^{(i)} & s_{36}^{(i)} & s_{36}^{(i)} & d_{13}^{(i)} & d_{23}^{(i)} & d_{33}^{(i)} \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ s_{14}^{(i)} & s_{24}^{(i)} & s_{34}^{(i)} & s_{44}^{(i)} & s_{44}^{(i)} & s_{45}^{(i)} & s_{46}^{(i)} & s_{46}^{(i)} & d_{14}^{(i)} & d_{24}^{(i)} & d_{34}^{(i)} \\ s_{15}^{(i)} & s_{25}^{(i)} & s_{35}^{(i)} & s_{45}^{(i)} & s_{45}^{(i)} & s_{55}^{(i)} & s_{56}^{(i)} & s_{56}^{(i)} & d_{15}^{(i)} & d_{25}^{(i)} & d_{35}^{(i)} \\ s_{16}^{(i)} & s_{26}^{(i)} & s_{36}^{(i)} & s_{46}^{(i)} & s_{46}^{(i)} & s_{56}^{(i)} & s_{66}^{(i)} & s_{66}^{(i)} & d_{16}^{(i)} & d_{26}^{(i)} & d_{36}^{(i)} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ d_{21}^{(i)} & d_{22}^{(i)} & d_{23}^{(i)} & d_{24}^{(i)} & d_{24}^{(i)} & d_{25}^{(i)} & d_{26}^{(i)} & d_{26}^{(i)} & \epsilon_{12}^{(i)} & \epsilon_{22}^{(i)} & \epsilon_{23}^{(i)} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{III.7}$$

The material properties in $\boldsymbol{M}^{(i)}$ and $\mathbf{b}^{(i)}$ refer to the same cubic coordinate system as indicated in Fig. 1. The $\mathbf{b}^{(i)}$ matrix results directly from the electric and elastic continuity conditions.[5] The superscript *eff*, (1), and (2) describe the physical properties of effective, domain 1, and domain 2, respectively. The *y* axis is perpendicular to the DW as shown in Fig. 1. The formula in Eq. (*III*.5) is another form of the ones given in Ref. 5, which is different from the statistical average formula of Ref. 6. (The dimension here is 11×11, whereas in Ref. 6 the dimension is 9×9.)

Effective material properties of ferroelectrics resulting from a $m\bar{3}m \rightarrow 3m$ phase transition were calculated for a twin of $\boldsymbol{P}^{I}$ and $\boldsymbol{P}^{II}$ with a DW in [010] as shown in Fig. 1(a). Both cases $\nu^{(1)} \neq \nu^{(2)}$ and $\nu^{(1)} = \nu^{(2)}$ were studied.

Because there were no complete single-crystal data for ferroelectrics with a $m\bar{3}m \rightarrow 3m$ phase transition in the current literature, we borrowed the material data of $LiNbO_3$,[15] but used the domain structures of $m\bar{3}m \rightarrow 3m$ phase transition to demonstrate the method. ($LiNbO_3$ has a $\bar{3}m \rightarrow 3m$ transition and only has 180° coherent twins).

A. $\nu^{(1)} \neq \nu^{(2)}$

To perform the effective material property evaluation, the tensor components of elastic constants, piezoelectric coefficients, and dielectric constants were first transformed to a common coordinate system (i.e., the cubic coordinates), and then these transformed properties were put into Eqs. (*III*.6) and (*III*.7). Finally, the effective properties were calculated using Eq. (*III*.5) for different volume ratios. Numerical solutions show that the following relations are fulfilled within the relative errors of less than 10^{-12}.

$$s_{15}^{eff} = s_{35}^{eff}, s_{12}^{eff} = s_{23}^{eff}, s_{11}^{eff} = s_{33}^{eff}, s_{24}^{eff} = s_{26}^{eff}, s_{34}^{eff} = s_{16}^{eff}, \\ s_{36}^{eff} = s_{14}^{eff}, s_{56}^{eff} = s_{45}^{eff}, s_{66}^{eff} = s_{44}^{eff} \tag{III.8}$$

$$d_{23}^{eff} = d_{21}^{eff}, d_{26}^{eff} = d_{24}^{eff}, d_{31}^{eff} = d_{13}^{eff}, d_{32}^{eff} = d_{12}^{eff}, d_{33}^{eff} = d_{11}^{eff}, \\ d_{34}^{eff} = d_{16}^{eff}, d_{35}^{eff} = d_{15}^{eff}, d_{36}^{eff} = d_{14}^{eff} \tag{III.9}$$

$$\epsilon_{11}^{eff} = \epsilon_{33}^{eff}, \epsilon_{23}^{eff} = \epsilon_{12}^{eff} \quad . \tag{III.10}$$

Numerical data verified that the symmetry of this twin structure is monoclinic *m* with a mirror symmetry plane perpendicular to $[\bar{1}01]$.

B. $\nu^{(1)} = \nu^{(2)}$

For this case, in addition to the relationships (*III*.8)–(*III*.10), the following components become zero[5]

$$s_{15}^{eff} = s_{35}^{eff} = s_{24}^{eff} = s_{26}^{eff} = s_{34}^{eff} = s_{16}^{eff} = s_{36}^{eff} = s_{14}^{eff} \\ = s_{56}^{eff} = s_{45}^{eff} = 0 \quad , \tag{III.11}$$

$$d_{23}^{eff} = d_{21}^{eff} = d_{34}^{eff} = d_{16}^{eff} = d_{36}^{eff} = d_{14}^{eff} = d_{22}^{eff} = d_{25}^{eff} = 0 \quad , \tag{III.12}$$

$$\epsilon_{23}^{eff} = \epsilon_{12}^{eff} = 0 \quad . \tag{III.13}$$

For twins with a charged DW, if the volume ratios of the two domains are the same, the effective symmetry could be raised to orthohombic *mm*2, whereas for twins with a neutral DW, the effective symmetry cannot be higher than monoclinic *m*.

TABLE IV. Calculated effective material constants of a twinned crystal of rhombohedral 3*m* symmetry by using the single domain data of $LiNbO_3$ [Units: $s_{\alpha\beta}$ (10^{-12} m^2N^{-1}), $d_{i\alpha}$ (10^{-12} CN^{-1}), ϵ_{ij} (ϵ_0)].

$\nu^{(1)}$	1.00	0.00	0.50	0.55	0.60	0.65	0.70
Elastic properties							
S_{11}	5.60	5.60	5.42	5.43	5.43	5.44	5.45
S_{12}	−1.36	−1.36	−1.10	−1.10	−1.11	−1.11	−1.12
S_{13}	−1.36	−1.36	−1.38	−1.38	−1.38	−1.38	−1.38
S_{14}	−1.35	1.35	…	−0.13	−0.25	−0.38	−0.51
S_{15}	0.26	0.26	−0.49	−0.48	−0.47	−0.45	−0.42
S_{16}	0.26	−0.26	…	0.03	0.06	0.09	0.12
S_{22}	5.60	5.60	4.65	4.66	4.67	4.70	4.73
S_{23}	−1.36	−1.36	−1.10	−1.10	−1.11	−1.11	−1.12
S_{24}	0.26	−0.26	…	0.00	0.00	0.01	0.02
S_{25}	−1.35	−1.35	1.36	1.35	1.30	1.23	1.13
S_{26}	0.26	−0.26	…	0.00	0.00	0.01	0.02
S_{33}	5.60	5.60	5.42	5.43	5.43	5.44	5.45
S_{34}	0.26	−0.26	…	0.03	0.06	0.09	0.12
S_{35}	0.26	0.26	−0.49	−0.48	−0.47	−0.45	−0.42
S_{36}	−1.35	1.35	…	−0.13	−0.25	−0.38	−0.51
S_{44}	15.65	15.65	15.27	15.27	15.28	15.30	15.32
S_{45}	−0.98	0.98	…	−0.03	−0.07	−0.11	−0.16
S_{46}	−0.98	−0.98	−0.99	−0.99	−0.99	−0.99	−0.99
S_{55}	15.65	15.65	7.92	7.96	8.08	8.27	8.57
S_{56}	−0.98	0.98	…	−0.03	−0.07	−0.11	−0.16
S_{66}	15.65	15.65	15.27	15.27	15.28	15.30	15.32
Piezoelectric properties							
d_{11}	16.28	16.28	11.84	11.88	12.01	12.22	12.52
d_{12}	−5.83	−5.83	−5.03	−5.04	−5.04	−5.06	−5.08
d_{13}	−5.83	−5.83	−3.14	−3.17	−3.25	−3.39	−3.59
d_{14}	−47.11	47.11	…	−4.59	−9.19	−13.80	−18.43
d_{15}	26.44	26.44	23.84	23.85	23.88	23.94	24.03
d_{16}	26.44	−26.44	…	2.60	5.20	7.81	10.43
d_{21}	−5.83	5.83	…	−0.34	−0.68	−1.05	−1.43
d_{22}	16.28	−16.28	…	0.77	1.56	2.41	3.34
d_{23}	−5.83	5.83	…	−0.34	−0.68	−1.05	−1.43
d_{24}	26.44	26.44	22.23	22.26	22.32	22.44	22.61
d_{25}	−47.11	47.11	…	−2.25	−4.57	−7.05	−9.78
d_{26}	26.44	26.44	22.23	22.26	22.32	22.44	22.61
d_{31}	−5.83	−5.83	−3.14	−3.17	−3.25	−3.39	−3.59
d_{32}	−5.83	−5.83	−5.03	−5.04	−5.04	−5.06	−5.08
d_{33}	16.28	16.28	11.84	11.88	12.01	12.21	12.52
d_{34}	26.44	−26.44	…	2.60	5.20	7.81	10.43
d_{35}	26.44	26.44	23.84	23.85	23.88	23.94	24.03
d_{36}	−47.11	47.11	…	−4.59	−9.19	−13.80	−18.43
Dielectric properties							
ϵ_{11}	38.97	38.97	18.97	19.20	19.77	20.78	22.14
ϵ_{12}	−4.97	4.97	…	−0.34	−0.79	−1.13	−1.58
ϵ_{13}	−4.97	−4.97	11.63	11.52	11.07	10.28	9.04
ϵ_{22}	38.97	38.97	21.57	21.69	22.02	22.48	23.04
ϵ_{23}	−4.97	4.97	…	−0.34	−0.79	−1.13	−1.58
ϵ_{33}	38.97	38.97	18.97	19.20	19.77	20.78	22.14

The two domains are $\mathbf{P}^I = P_S/\sqrt{3}\,[111]$ and $\mathbf{P}^{II} = P_S/\sqrt{3}\,[1\bar{1}1]$ from Table I and the twin stucture is illustrated in Fig. 1(a). Data blanks represent that the corresponding component is zero and the column of $\nu^{(1)} = 0.5$ are the values from Ref. 5. Domain wall orientation is [010].

One must remember that the macroscopic and microscopic symmetries are different in multidomain systems. The former refers to symmetry relations between different components of macroscopic physical properties whereas the latter refers to the crystal lattice structure. The lower symmetry of the twinned crystal increases the difficulty to fully characterize the physical properties because the number of nonzero components grows rapidly with the decrease of symmetry.[16]

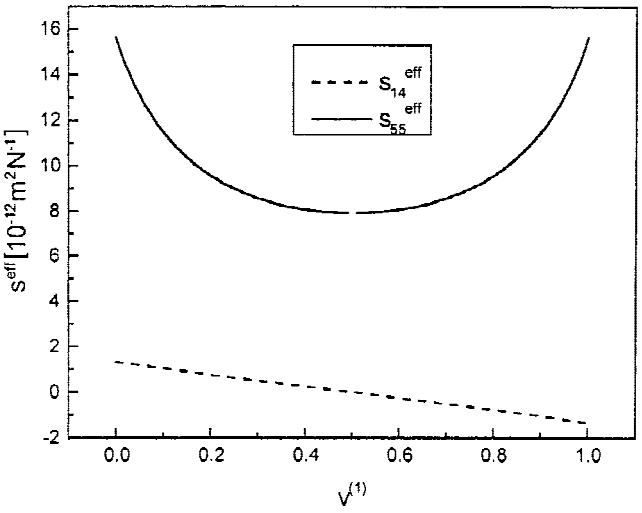

FIG. 4. Calculated effective elastic constants, s_{14}^{eff} and s_{55}^{eff}, of different volume ratios for a twinned crystal resulting from a $m\bar{3}m \rightarrow 3m$ phase transition. The components of material properties are either symmetric (e.g. s_{55}^{eff}) or antisymmetric (e.g. s_{14}^{eff}) with respect to $\nu^{(1)} = 0.50$.

As analyzed above, the effective symmetry of a twin becomes lower if the domain volume ratio deviates from 50:50. Experience tells us that this deviation is usually within a few percent for most of twinned crystals. The question is: Which quantities are influenced the most by this volume-ratio-induced symmetry breaking? We used a few numerical examples to gain quantitative understanding on this issue and to give the reader some understanding of the degree of property changes.

Listed in Table IV are some numerical results calculated by using the single-crystal data of $LiNbO_3$ for the twin structure of rhombohedral 3*m* system. One can see that if a component is nonzero for the case of $\nu^{(1)} = 0.5$, the relative change caused by small deviation from equal volume ratio is not significant for most of the quantities, particularly the elastic properties (see Fig. 4). The symmetry breaking is, however, important for those components that change from zero to nonzero when the volume ratio deviates from equal partition. The relative changes are very large. Twins with a charge-neutral DW cannot reach orthorhombic *mm*2 symmetry for any volume ratio; therefore, they must be treated as monoclinic *m* symmetry at all times.

We have also calculated two other materials resulting from $m\bar{3}m \rightarrow 4mm$ ($BaTiO_3$)[6] and from $m\bar{3}m \rightarrow mm2$ ($KNbO_3$)[17] ferroelectric phase transitions.

For $BaTiO_3$, the effective material properties shown in Table V were calculated for a twin of $\boldsymbol{P}^I$ and $\boldsymbol{P}^{II}$ in Table II with a DW oriented in [110]. Using the same

TABLE V. Calculated effective material constants of twinned $BaTiO_3$ crystal with a neutral DW[110] (units are the same as in Table IV).

$\nu^{(1)}$	1.00	0.00	0.50	0.55	0.60	0.65	0.70
Elastic properties							
S_{11}	7.92	7.92	7.49	7.49	7.51	7.52	7.55
S_{12}	−1.28	−1.28	−1.71	−1.71	−1.69	−1.68	−1.65
S_{13}	−3.80	−3.80	−3.47	−3.47	−3.48	−3.50	−3.52
S_{14}	…	…	…	…	…	…	…
S_{15}	…	…	…	…	…	…	…
S_{16}	3.83	−3.83	…	0.34	0.69	1.04	1.39
S_{22}	7.92	7.92	7.49	7.49	7.51	7.52	7.55
S_{23}	−3.80	−3.80	−3.47	−3.47	−3.48	−3.50	−3.52
S_{24}	…	…	…	…	…	…	…
S_{25}	…	…	…	…	…	…	…
S_{26}	3.83	−3.83	…	0.34	0.69	1.04	1.39
S_{33}	8.05	8.05	7.81	7.81	7.81	7.83	7.84
S_{34}	…	…	…	…	…	…	…
S_{35}	…	…	…	…	…	…	…
S_{36}	−2.89	2.89	…	−0.26	−0.52	−0.78	−1.05
S_{44}	13.62	13.62	11.94	11.96	12.00	12.08	12.18
S_{45}	4.78	−4.78	…	0.42	0.84	1.27	1.71
S_{46}	…	…	…	…	…	…	…
S_{55}	13.62	13.62	11.94	11.96	12.00	12.08	12.18
S_{56}	…	…	…	…	…	…	…
S_{66}	34.23	34.23	30.63	30.66	30.76	30.92	31.16
Piezoelectric properties							
d_{11}	−156.66	156.66	…	−16.14	−32.24	−48.30	−64.28
d_{12}	120.53	−120.53	…	11.58	23.19	34.85	46.59
d_{13}	24.40	−24.40	…	2.79	5.57	8.30	10.98
d_{14}	…	…	…	…	…	…	…
d_{15}	…	…	…	…	…	…	…
d_{16}	−84.92	−84.92	−127.29	−126.92	−125.77	−123.85	−121.12
d_{21}	120.53	120.53	130.02	129.93	129.68	129.44	128.63
d_{22}	−156.66	−156.66	−147.17	−147.26	−147.51	−147.94	−148.55
d_{23}	24.40	24.40	17.23	17.29	17.48	17.81	18.27
d_{24}	…	…	…	…	…	…	…
d_{25}	…	…	…	…	…	…	…
d_{26}	−84.92	84.92	…	−7.61	−15.26	−23.02	−30.92
d_{31}	…	…	…	…	…	…	…
d_{32}	…	…	…	…	…	…	…
d_{33}	…	…	…	…	…	…	…
d_{34}	−277.19	−277.19	−179.91	−180.76	−183.33	−187.67	−193.83
d_{35}	−277.19	277.19	…	−24.33	−48.85	−73.73	−99.17
d_{36}	…	…	…	…	…	…	…
Dielectric properties							
ϵ_{11}	1530	1530	272	285	322	385	472
ϵ_{12}	−1362	1362	…	−135	−270	−405	−541
ϵ_{13}	…	…	…	…	…	…	…
ϵ_{22}	1530	1530	1506	1506	1507	1508	1509
ϵ_{23}	…	…	…	…	…	…	…
ϵ_{33}	2891	2891	2254	2260	2277	2305	2345

The two domains are $\mathbf{P}^{I} = P_S$ [100] and $\mathbf{P}^{II} = P_S$ [010] of Table II. Data blanks represent that the corresponding component is zero and the column of $\nu^{(1)} = 0.5$ are the values from Ref. 5.

TABLE VI. Calculated effective material constants of twinned $KNbO_3$ crystal (units are the same as in Table IV).

$\nu^{(1)}$	1.00	0.00	0.50	0.55	0.60	0.65	0.70
Elastic properties							
S_{11}	5.41	5.41	5.40	5.40	5.40	5.40	5.40
S_{12}	−1.33	−1.33	−1.35	−1.35	−1.35	−1.35	−1.35
S_{13}	−1.33	−1.33	−1.34	−1.34	−1.34	−1.34	−1.34
S_{14}	0.31	−0.31	…	0.03	0.06	0.09	0.12
S_{15}	…	…	…	…	…	…	…
S_{16}	…	…	…	…	…	…	…
S_{22}	5.28	5.28	5.20	5.20	5.20	5.21	5.21
S_{23}	−1.45	−1.45	−1.49	−1.49	−1.49	−1.49	−1.49
S_{24}	0.97	−0.97	…	0.10	0.19	0.29	0.39
S_{25}	…	…	…	…	…	…	…
S_{26}	…	…	…	…	…	…	…
S_{33}	5.28	5.28	5.21	5.21	5.21	5.21	5.22
S_{34}	0.97	−0.97	…	0.10	0.19	0.29	0.38
S_{35}	…	…	…	…	…	…	…
S_{36}	…	…	…	…	…	…	…
S_{44}	16.46	16.46	16.22	16.22	16.23	16.24	16.26
S_{45}	…	…	…	…	…	…	…
S_{46}	…	…	…	…	…	…	…
S_{55}	25.24	25.24	16.60	16.65	16.83	17.13	17.56
S_{56}	14.76	−14.76	…	0.97	1.97	3.01	4.11
S_{66}	25.24	25.24	16.60	16.65	16.83	17.13	17.56
Piezoelectric properties							
d_{11}	…	…	…	…	…	…	…
d_{12}	…	…	…	…	…	…	…
d_{13}	…	…	…	…	…	…	…
d_{14}	…	…	…	…	…	…	…
d_{15}	72.83	72.83	30.22	30.50	31.36	32.82	34.96
d_{16}	72.83	−72.83	…	4.81	9.71	14.83	20.27
d_{21}	7.00	−7.00	…	0.71	1.41	2.12	2.82
d_{22}	31.57	−31.57	…	3.17	6.35	9.52	12.69
d_{23}	−23.58	23.58	…	−2.33	−4.66	−6.99	−9.33
d_{24}	35.14	35.14	39.37	39.33	39.20	39.00	38.70
d_{25}	…	…	…	…	…	…	…
d_{26}	…	…	…	…	…	…	…
d_{31}	7.00	7.00	12.14	12.09	11.93	11.67	11.31
d_{32}	−23.58	−23.58	1.41	1.16	0.40	−0.86	−2.62
d_{33}	31.57	31.57	5.95	6.20	6.96	8.23	10.00
d_{34}	35.14	−35.14	…	3.03	6.06	9.21	12.42
d_{35}	…	…	…	…	…	…	…
d_{36}	…	…	…	…	…	…	…
Dielectric properties							
ϵ_{11}	1540	1540	1516	1516	1517	1518	1519
ϵ_{12}	…	…	…	…	…	…	…
ϵ_{13}	…	…	…	…	…	…	…
ϵ_{22}	5145	5145	5133	5133	5133	5134	5135
ϵ_{23}	−4705	4705	…	−469	−939	−1408	−1878
ϵ_{33}	5145	5145	811	854	984	1200	1503

The two domains in the twin are $\mathbf{P}^{III} = P_S/\sqrt{2}$ [011] and $\mathbf{P}^{IV} = P_S/\sqrt{2}$ [0$\bar{1}$1] (Table III) with a charged DW oriented in [010] as shown in Fig. 3(c).

argument above, the macroscopic symmetry of the twin is orthorhombic *mm*2 for equal volume ratio and monoclinic *m* for unequal partition. As expected, the tensor components are either symmetric or antisymmetric with respect to equal partition $\nu^{(1)} = 0.5$. A large change in ϵ_{11} has been observed, which is very sensitive to the domain volume ratio change.

For $KNbO_3$, which has a $m\bar{3}m \rightarrow mm2$ phase transition, effective material properties were calculated for a twin system of $\boldsymbol{P}^{III}$ and $\boldsymbol{P}^{IV}$ (see Table III) with a [010] oriented DW. The results are given in Table VI for several values of $\nu^{(1)}$. Again, the macroscopic symmetry belongs to the orthorhombic *mm*2 class for equal partition, and is reduced to monoclinic *m* if the volume ratios are not equal. Many physical quantities change significantly with the variation of the domain volume ratio; some even change signs. This demonstrated the importance of considering the symmetry breaking caused by the domain volume ratio deviation from 50:50. Note: we have chosen a convenient coordinate system for calculations, which is not the simplest coordinate system in terms of matrix quantity representation as shown in the

tables. One can convert the matrix quantities into the simplest form by a coordinate transformation for each case.

IV. SUMMARY AND CONCLUSIONS

The effective symmetry and material properties of twin crystals have been analyzed for three symmetry classes, resulting from $m\bar{3}m \rightarrow 3m$, $m\bar{3}m \rightarrow 4mm$, and $m\bar{3}m \rightarrow mm2$ ferroelectric phase transitions. It has been shown that the macroscopic symmetry could be lower than the microscopic symmetry, particularly when the volume ratios of the two domains are different. In real materials, this nonequal partition of domain volume could be caused by any defects that provide pinning to the movement of domain walls, which leads to a symmetry reduction in terms of macroscopic physical quantities. Numerical calculations on three real materials showed that the changes in those physical properties that are nonzero at equal partition were not so drastic in the cases of $m\bar{3}m \rightarrow 3m$ and $m\bar{3}m \rightarrow 4mm$, but became noticeable for the case of $m\bar{3}m \rightarrow mm2$. As shown in Tables IV to VI, the symmetry reduction is signified by the increase of the number of nonzero components in the macroscopic property matrices when the volume ratio of the two domains deviates slightly from 50:50. The changes for those quantities that are zero in the equal volume situation are quite significant, as demonstrated through real material calculations. A more concise formula has been given here, which was derived using the method of Ref. 5 but is much simpler to use for real material property calculations in twinned crystals. The formula is also applicable to bicrystals so long as the orientations of the crystals are known.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grant No. DNS 9704714 and by the Office of Naval Research under Grant Nos. N00014-98-1-0527 and N00014-96-1-1173. One of the authors (J.E.) is also grateful for partial support from the Ministry of Education of the Czech Republic (Code VS 96006, 1996).

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