An empirical approach to measuring interface energies in mixed-phase bismuth ferrite

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KEYWORDS
bismuth ferrite, thin films, strain engineering, thickness effects, energetics

ABSTRACT

In complex oxide heteroepitaxy, strain engineering is a powerful tool to obtain phases in thin films that may be otherwise unstable in bulk. A successful example of this approach is mixed phase bismuth ferrite (BiFeO₃) epitaxial thin films. The coexistence of a tetragonal-like (T-like) matrix and rhombohedral-like (R-like) striations provides an enhanced electromechanical response, along with other attractive functional behaviors. In this paper, we compare the energetics associated with two thickness dependent strain relaxation mechanisms in this system: domain walls arising from monoclinic distortion in the T-like phase, and the interphase boundary between the host T-like matrix and tilted R-like phases. Combining x-ray diffraction measurements with scanning probe microscopy, we extract quantitative values using an empirical energy balance approach. The domain wall and phase boundary energies are found to be 0.11 ± 0.02 and 35.19 ± 0.06 Jm⁻², respectively. These numerical estimates will help us realize...
designer phase boundaries in multiferroics, which possess colossal responses to external stimuli, attractive for a diverse range of functional applications.

**INTRODUCTION**

Bismuth ferrite (BiFeO$_3$; BFO) is a multiferroic perovskite oxide which forms in the $R3c$ space group, extensively studied for its room temperature ferroelectric, electromechanical and antiferromagnetic properties. [1] Although BFO was first synthesized in epitaxial thin film form in 2003, [2] a dramatic surge in interest – particularly regarding the effects of epitaxial strain – occurred in 2009 upon the discovery of a giant axial ratio phase of BFO (“T-like” or “T’ BFO”, with $c/a = 1.23$), induced by large (> 4%) compressive misfit strains. [3] Under intermediary strain states, the material can also be grown with a mixed phase microstructure, *i.e.* partially forming bulk-like tilted phases (R-like; R’) within a matrix comprising the T-like phase of BFO. [4] This “mixed phase BFO” is commonly observed when the film is grown on lanthanum aluminate, LaAlO$_3$, (LAO) substrates, to thicknesses above about 25 nm. In mixed phase BFO, electrical switching transitions between both structural (T’ and R’) and polar variants (+T’ and –T’), [5] doping, [6] enhanced response from electromechanical switching, [7–10] pinning mechanisms, [11] optical effects [12,13], ferroelectric tunnel junctions [14] and deterministic control of phases [15,16] have been studied extensively. These films routinely display an increase in mixed phase population upon increasing film thickness, driven by strain relaxation. Interestingly, in some cases where defects are incorporated throughout the film volume, the formation of the mixed phase can be completely inhibited. [17–19] This complex equilibrium provides a wide scope of stimuli which can locally tailor the functionality of the system.
To accurately describe these stimuli and the associated energy landscape, we require a numerical handle of the physical parameters governing the strain relaxation process. Strain relief in mixed phase BFO is manifested through the formation of new interfaces, either domain walls or interphase boundaries (Figure 1). [20] However, an explicit value of the energy density of either of these remains unknown. Having a knowledge of these energy values would help guide studies of new phase space in BFO and similar epitaxial thin film multiferroics.

Here, we analyze the energy landscape associated with mixed phase BFO as a function of film thickness within the framework of an energy balance approach and a modification of the general Kittel’s law. [21] Piezoresponse force microscopy (PFM) and atomic force microscopy (AFM) were utilized to calculate the periodicities of monoclinic domain walls within the T-like matrix (referred to as T'/T' twins) and the boundaries between coexistent structural phases (T'/R’ phase boundaries), respectively. A substantial amount of data was collected and processed to ensure significant statistical weight when obtaining these periodicities. X-ray diffraction (XRD) techniques were used to quantitatively demonstrate the thickness-dependent strain. Following thermodynamic analyses based on elastic potentials, the energies associated with each of these strain relief mechanisms are addressed.
Figure 1. Schematic of various types of strain-relaxation mechanisms in strongly epitaxially strained BFO films grown on LAO substrates. (a,b) T'/T’ twin domain walls (DWs), which are observed along the <110>-type directions, are observed for films with thickness below about 25 nm. (c,d) T'/T’ twin DWs and T’/R’ mixed phase boundaries are observed for films with thickness above about 25 nm. The arrows denote the local direction of ferroelectric polarization.

METHODS

Thin film fabrication

BiFeO$_3$ thin films were deposited on LaAlO$_3$ (001) substrates by pulsed laser deposition (PLD). A ceramic target of Bi$_{1.1}$FeO$_3$ was ablated at a repetition rate of 10 Hz using a KrF excimer laser (wavelength of 248 nm) in an oxygen partial pressure of ~0.1 Torr. The laser fluence and film growth rate were measured to be ~1.8 J cm$^{-2}$ and ~0.04 Å pulse$^{-1}$, respectively. The substrate was held at a temperature of 590 °C at a distance of ~5 cm from the target. After a
predetermined number of pulses dependent on film thickness, each sample was cooled at a rate of 20 °C min⁻¹ in an oxygen pressure of 5 Torr.

**X-ray diffraction and structural characterization**

Structural characterization by x-ray diffraction, including high-angle θ-2θ scans and low-angle reflectometry (not shown), was carried out using Kα₁ radiation (λ = 1.5406 Å) on a Philips Materials Research Diffractometer (MRD), equipped with a two-bounce (220) Ge monochromator. To determine the phase composition (R’ and T’ phases) and the in- and out-of-plane lattice parameters, reciprocal space maps (RSMs) were collected on the same machine using a 1D detector (PIXcel). The lattice parameters were calculated by Gaussian peak-fitting the film peaks in the RSMs at each thickness.

**Atomic force microscopy and piezoresponse force microscopy**

Topography imaging and ferroic domain mapping was carried out on an Oxford Instruments Asylum Cypher in contact atomic force microscopy (AFM) and piezoresponse force microscopy (PFM) modes. Due to the in-plane nature of the T’/T’ domain walls, the PFM data was collected with the lateral displacement channel. Vertical displacement (not shown) provided no contrast in the domain images in the regions of T’/T’ walls. The AFM and PFM images were analyzed with WSxM software [30] through both line profiling and image flooding to calculate the periodicities of T’/T’ and T’/R’ interfaces (see Supplementary Figure 3 for examples).
RESULTS AND DISCUSSION

BFO films were fabricated by pulsed laser deposition (PLD) on (001) oriented LaAlO$_3$ substrates (see Methods). [17,22–24] This substrate induces a misfit strain of approximately -4.5% at growth temperature. As previously reported, the film grows in a pure T’ phase at the growth temperature (590 °C), but during post-growth cooling to room temperature, the material relaxes to a mixture of tilted tetragonal and rhombohedral phases, of which the volume phase fractions are thickness dependent. [25–27] The films were fabricated at thicknesses within the range of 15-120 nm. The film thickness was measured by x-ray reflectometry (XRR) for thinner films (thickness $d < 50$ nm) (not shown), and the growth rate extrapolated to estimate the thicknesses for samples with $d > 50$ nm. This sample set demonstrated the typically observed pure T-like phase in thinner films, while a mixed phase microstructure was present at greater thicknesses.

To establish a framework which can account for the two aforementioned strain relieving mechanisms, we must first calculate the strain energies and then periodicities for the T’/T’ twins and the mixed phase interfaces. Thus, we begin with detailed XRD investigations to address the strain energies.

The data presented in Figure 2a, b) are XRD reciprocal space maps (RSMs) of the 120 nm thick film, around the 001 (symmetric) and 103 (asymmetric) reflections. The phases are labelled according to the following convention: T’ is the tetragonal-like phase that forms the matrix of the film (the smooth flat regions in Figure 1a), T’$_\text{tilt}$ (R’$_\text{tilt}$) is the tilted T-like (secondary strained R-like) phase which is observed within the mixed-phase regions as striations on the film surface, and R’$_\text{relaxed}$ is the almost fully relaxed R-like phase (not observed in the AFM images). For the remainder of this paper, for simplicity we use T’/T’ to denote the domain walls separating the T-
like ferroelastic domains, and $T'\!/R'$ to denote the interphase boundary between the $T'_{\text{tilt}}$ and $R'_{\text{tilt}}$ phases.

In the XRD RSMs (Figure 2a,b) a multitude of diffraction peaks are observed, which correspond to the various phases related to the striations on the sample surface. We first consider the $T'$ phase. As mentioned above, it is well established that T-like BFO typically forms as a monoclinic structure. [26,28] A signature of such crystallographic symmetry is the three-fold splitting of the T-like peak in the asymmetric (103) frame, as labelled in Figure 2b). Combining symmetric and asymmetric RSMs measured on the full thickness series of films allows us to calculate the in-plane lattice parameters of the T-like host matrix. All three lattice parameters for the T-like phase are shown in Figure 2c, e), where the $a$, $b$ and $c$ lattice parameters are shown as red, blue, and green symbols, respectively.

The behavior of the average unit cell in the T-like phase as a function of thickness can be separated into three regimes:

1) ~0 to 40 nm, shaded in purple. The thinnest films, prior to nucleation of mixed phase, could arguably be deviating from the pseudo-cubic lattice parameter of LAO (3.791 Å). All of the films possess a large in-plane distortion (Supplementary Figure 1a). In this thickness range, where the $a$ parameter increases while $b$ decreases, the distortion exponentially increases with thickness. The out-of-plane lattice parameter, $c$, remains virtually unchanged.

2) ~40 to 80 nm, shaded in yellow. At thickness values at which one would expect the mixed phase striations to form, the $c$ lattice parameter increases, and the tetragonality of the unit cell appears to rapidly increase (Supplementary Figure 1b). The $a$ parameter decreases slightly while $b$ remains roughly constant.
3) 80 to 120 nm, shaded in pink. When a significant volume of mixed phase striations is formed in the thickest films, the $a$ and $c$ lattice parameters remain constant while the $b$ parameter continues to decrease slightly. This is seemingly caused by the striations compressing the T-like unit cell. One could suggest that the freedom along the $b$ axis in the T-like phase is linked to the preferential nucleation direction of the secondary phase.

In general, the monoclinicity (i.e. deviation of $\beta$ from 90°) of the T-like phase decreases in thicker films, while the average in-plane lattice parameter is dominated by $a$ as opposed to $b$ (Supplementary Figure 1c,d). As XRD is a volume sensitive technique, the relative intensity of the secondary peaks decreases dramatically for the thinner films. Consequently, it was only possible to obtain lattice parameters for the striations in films of thickness above 70 nm. The lattice parameters of the striations tend only to change noticeably for the thickest sample. The in-plane parameter increases, while the out-of-plane parameter falls, with both migrating towards the BFO bulk pseudo-cubic lattice parameter of 3.965 Å (Supplementary Figure 2). [29]

Having characterized the lattice parameters of each film, the next step was to estimate the volume fractions of the R’ and T’ phases as a function of the thickness, particularly at the local scale. This thickness dependence of the mixed phase microstructure is more distinct when imaged through atomic force microscopy (AFM). AFM imaging was carried out across the sample series in order to establish the ratio of mixed phase for a given film thickness. Alongside this, an image processing technique was applied to quantify the density of the phase interfaces – boundaries between the stripe-like structures and their host matrix. Supplementary Figure 3 presents 5x5 μm topography scans of sample surfaces for three film thicknesses, alongside images highlighting the approximate phase interfaces created with the microscopy analysis software described in reference [30].
Figure 2. a) Symmetric x-ray diffraction reciprocal space map (RSM) near the (001) peaks of LAO and BFO. b) Asymmetric RSM near the (103) reflection, analyzed to calculate in-plane lattice parameters. The three-fold splitting of the T' peak is a signature of an $M_C$ monoclinic phase. The dashed lines in both RSMs indicate the theoretically calculated position of the corresponding LAO peak. c), d), e) The $a$ (red symbols), $b$ (blue symbols) and $c$ (green symbols) lattice parameters of the T-like phase as a function of thickness, respectively. The dashed lines are a guide to the eye; however, one should note the position of the LAO pseudo-cubic lattice parameter (3.791 Å) with respect to the in-plane parameters, $a$ and $b$. Three approximate
thickness regimes are apparent, as discussed in the main text, and are shaded purple (~0 to 40 nm), yellow (~40 to 80 nm) and pink (~80 to 120 nm).

Figure 3. a) Average interface density (blue) and R’-T’ phase ratio (orange) as a function of film thickness. The shading is in reference to the thickness regimes discussed in the main text and in Figure 1. The lines are guides to the eye.

Figure 3a) presents the average R’ phase percentage and interface density calculated and normalized to the film volume. Note that this is remarkably consistent with the thickness dependent thermodynamic treatment of Ouyang and Roytburd. [31,32] The weighted average lattice parameter of the complete microstructure as a function of thickness is plotted in Supplementary Figure 4. This was calculated by combining the data collected from XRD and
AFM and shows the expected behavior of strain relaxation in the system – a sharp decrease of the $c$ parameter and increase in average in-plane lattice parameter above a critical thickness.

Next, we describe how the periodicities for both the T'/T' domain walls and the mixed phase interfaces were calculated. In T-like BFO, ferroelastic monoclinic domain structure has been previously reported. [33–36] These periodic walls arising from the monoclinic distortion of the T-like unit cell partially minimize elastic self-strain energy. [37] Piezoresponse force microscopy (PFM) was used to image this domain structure, with the amplitude shown in Figures 4a) and b) for 40 and 80 nm thick films, respectively. In all cases the out-of-plane PFM phase was homogeneous, consistent with the out of plane polarization direction pointing downwards (not shown). Here one can see the presence of tilted phase striations and ferroelastic domain walls (DWs) in the host T-like phase. All thicknesses studied here exhibited these ferroelastic DWs, implying that they are not as energetically costly as mixed phase interfaces.

These T'/T' domain walls are aligned along the $<110>_{pc}$ crystallographic directions (as expected for a $M_C$ symmetry) and terminate at the boundaries between the T-like regions and the mixed phase striations. The mixed phase striations themselves are tilted by up to 15 degrees from the high symmetry [100] or [010] directions (Figure 4b). [38,39]
**Figure 4.** PFM amplitude images (5 x 5 μm) of; a) 40 nm and b) 80 nm films, where tilted phase structure and ferroelastic domain walls (DWs) are present.

Now that both the strain and periodicity for both types of interfaces have been obtained as a function of thickness, we proceed with the empirical analysis. For this, we start with the key expression employed in this work, Kittel’s scaling law for ferroic domain walls, [40] given in the general form as

\[ w^2 = \frac{\gamma}{U} d \]  

(1)

where \( w \) is domain width, \( \gamma \) is the domain wall energy, \( U \) is the domain energy per unit volume and \( d \) is the film thickness. The form of \( U \) is dependent on the ferroic order parameter associated with the domain. When empirically adopting this expression, two quantitative results must arise from experiments: 1) an energy term related to the order parameter and, 2) a periodicity of the discontinuity manifesting in the ferroic to reduce free energy. In this case, we exclusively consider elastic energy terms.

By modifying the general Kittel’s law expression to add a second strain relieving mechanism, we can incorporate the role of phase interfaces in the analysis alongside the ferroelastic domain walls. As is typical for a Kittel expression, we start from free energy, \( F \):

\[ F = A_T \left( U_{T/T} \frac{w_{T/T}}{w_{T/T}} + \frac{\gamma_{T/T} d_{T/T}}{w_{T/T}} \right) + (1 - A_T) \left( U_{T/R} \frac{w_{T/R}}{w_{T/R}} + \frac{\gamma_{T/R} d_{T/R}}{w_{T/R}} \right) \]  

(2)

where \( A_T \) and \((1 - A_T)\) are the percentage fractions of T-like and mixed phase regions, respectively, \( U_{T/T} \) is the elastic potential energy arising from the T-like monoclinic domain walls.
and $U_{T/R}$ is the elastic potential energy arising from the formation of mixed phase regions. The symbols $w$, $\gamma$ and $d$ have their usual meanings (given in the text above), and the subscripts $T/T$ and $T/R$ denote which strain relieving interface the variables refer to T-like domain walls or mixed phase boundaries, respectively. Taking partial derivatives to describe energetic equilibrium, we arrive at the following relations:

$$\frac{\partial F}{\partial w_{T/T}} = A_T \left( U_{T/T} - \frac{\gamma_{T/T} d}{w_{T/T}^2} \right) = 0;$$  \hspace{1cm} (3)

$$\frac{\partial F}{\partial w_{T/R}} = (1 - A_T) \left( U_{T/R} - \frac{\gamma_{T/R} d}{w_{T/R}^2} \right) = 0.$$  \hspace{1cm} (4)

All of our samples exhibit T'/T' twins, therefore $A_T \neq 0$. When there is little to no mixed phase in the sample, $(1 - A_T) = 0$, and the equation reduces to the ‘classic’ Kittel’s law, Equation (1). From this free energy expression, one can thus calculate the energy of formation for both the T'/T' twins ($\gamma_{T/T}$) and mixed phase microstructure ($\gamma_{T/R}$).

Returning to the experiments, we show next the PFM and AFM derived periodicities for both T'/T' twins and mixed phase boundaries. Figure 5 displays the periodicities of both strain relieving entities as a function of the square root of thickness (with intercept = 0), as a linear fitting of this plot would indicate that the scaling mechanism is following Kittel’s law. As there are distinct thickness regions with different behaviors, we isolated the four thinnest films to calculate the periodicity of T'/T' twin walls. Using a similar line of reasoning, the four thickest films were isolated to calculate the periodicity of the phase boundaries. In this way, we identify two separate regimes to which we applied our energy analysis, each following a dense domain wall model. Rationale for using only these four end points in each case is provided later.
Figure 5. Periodicity against square root of film thickness of both T-like twin domain walls (top) and mixed phase boundaries (bottom) in the sample series of BFO//LAO (001). The linear fit for each data set indicates these strain relieving entities follow Kittel’s scaling law \( \omega \propto d^{1/2} \).

We denote the linear fit gradients as \( M_{T/T} \) (orange fit, \( \approx 4.03 \times 10^{-4} \)) and \( M_{T/R} \) (red fit, \( \approx 2.93 \times 10^{-4} \)) for the T-like domain walls and mixed phase boundaries, respectively. The gradients are related to the energy terms through the following equations, where \( 2\pi \) is a shape factor [41] typically used in Kittel expressions:

\[
M_{T/T} = 2\pi \left( \frac{\gamma_{T/T}}{U_{T/T}} \right)^{1/2}
\]

\[
M_{T/R} = 2\pi \left( \frac{\gamma_{T/R}}{U_{T/R}} \right)^{1/2}
\]

The elastic energy term \( U_{T/T} \) was derived from the elastic misfit between the substrate and both the a and b lattice parameters:
\[ \varepsilon_{a_T} = \frac{a_T - a_{\text{sub}}}{a_T} \]  
\[ \varepsilon_{b_T} = \frac{b_T - a_{\text{sub}}}{b_T} \]  
\[ U_{T/T} = \frac{Y}{1-\nu} \left( \varphi \varepsilon_{a_T}^2 + \left[ 1 - \varphi \right] \varepsilon_{b_T}^2 \right) \]  

where \( a_T \) and \( b_T \) are the in-plane lattice parameters, \( a_{\text{sub}} \) is the substrate lattice parameter of 3.791 Å, \( Y \) is the Young’s modulus (186 GPa, calculated from reference [31]), \( \nu \) is the Poisson’s ratio (0.35; Ref. [42]), and \( \varphi \) is the phase fraction of \( a \) oriented domains in the region of T-like phase, which, if assuming equal T’/T’ domain populations, we take \( \varphi = 1/2 \).

Similarly, the energy \( U_{T/R} \) was calculated by consideration of the average in-plane (IP) elastic misfit strains in the region of mixed phase striations:

\[ \varepsilon_{I_P_T} = \frac{I_{P-T} - a_{\text{sub}}}{I_{P_T}} \]  
\[ \varepsilon_{I_P_R} = \frac{I_{P-R} - a_{\text{sub}}}{I_{P_R}} \]  
\[ U_{T/R} = \frac{Y}{1-\nu} \left( \varphi \varepsilon_{I_P_T}^2 + \left[ 1 - \varphi \right] \varepsilon_{I_P_R}^2 \right) \]  

where \( I_{P_T} \) and \( I_{P_R} \) are the average in-plane lattice parameters for the T-like and R-like striations, and in this case \( \varphi \) is the ratio of T-like to R-like phases in the areas containing striations, which we assume will reduce to \( \varphi = 1/2 \), given previous literature [25] identifying the phases of each portion of these needle-like structures.

The value of T’/T’ domain wall (or phase boundary) energy, \( \gamma_{T/T} \) (or \( \gamma_{T/R} \)) is extracted from the linear fits in Figure 5:
\[ \gamma_{T/T(R)} = \frac{U_{T/T(R)} M_{T/T(R)}}{4\pi^2} \]  

(13)

From this analysis, the average energy for forming T’/T’ twin domain walls is \( \approx 0.11 \pm 0.02 \) Jm\(^{-2}\), while for forming mixed phase T’/R’ boundaries it is \( \approx 35.19 \pm 0.06 \) Jm\(^{-2}\). These values, as expected, are consistent with the experimental observation of a critical thickness at which mixed phases form – only at this thickness does the film overcome the cost of forming phase boundaries to relieve strain, whereas the more energetically favorable method of partial strain relief (forming T’/T’ twins) occurs at all the thicknesses (above \(~ 15 \) nm) across our sample range.

**CONCLUSIONS**

We conclude with a brief discussion on the caveats of our empirical approach. Recall that our treatment uses two key quantitative results from experiments: 1) a strain energy term related to the order parameter, and 2) a periodicity discontinuity, which we ascribe to the system changing the type of interface nucleated in order to reduce the elastic energy. As there is no change of phase in the out of plane PFM signal, it appears these domains do not form to minimize depolarization field. Therefore, we disregard the electrostatic energies and assume the T’/T’ twin walls form in order to minimize the internal self-strain energy arising from the monoclinic distortion of the T-like unit cell. This explains why we exclusively treat the free energy in-elastic energy terms.

Next, we point out that we have not accounted for the curvature of the domain walls. This would require incorporating a gradient term (in the vicinity of the wall) in the strain energy expression, only possible experimentally by precise mapping of the atomic level displacements as a function of the distance from the wall. To the best of our knowledge, such information
would only be possible using aberration corrected transmission electron microscopy wherein the sample preparation removes the initial mechanical boundary conditions and hence adds an additional layer of complication which is outside the scope of the paper. Therefore, we only fitted the first four data points to the T’/T’ twin walls as we are certain with only for these four samples the strain state is only governed by T’/T’ twins and not the mixed phase system formation. In the same vein, only the last four data points are fitted to extract the energy for the T’/R’ interphase boundaries. It is only in these last four samples that we truly find the dense domain state, which allows us to reasonably disregard the gradient terms. [31,43]

In summary, we have explored the energetics of formation of T’/T’ and interphase boundaries in the mixed-phase BiFeO₃ thin film system. Combining XRD, AFM, and PFM techniques, we characterized a series of BFO//LAO (001) films with thicknesses ranging 15-120 nm. From the XRD data we extracted the lattice parameters for both the T-like and mixed phase regions, allowing the estimation of elastic strain energies. The periodicities of the T’/T’ twin ferroelastic domain walls and mixed phase T’/R’ striations were determined through PFM and AFM analyses, respectively. The energy of formation for domain walls and interphase boundaries were calculated to be \( \gamma_{T/T} \approx 0.11 \pm 0.02 \text{ Jm}^{-2} \) and \( \gamma_{T/R} \approx 35.19 \pm 0.06 \text{ Jm}^{-2} \) respectively. Our results strengthen our understanding of these strain relieving microstructures and provide numerical guidelines for the engineering of new exotic phases in tailor-made and dimensionally confined multiferroic systems.
ASSOCIATED CONTENT

Supporting Information.

The following file is available free of charge.

Additional lattice parameter ratios calculated from x-ray diffraction reciprocal space maps; mixed phase lattice parameters as a function of thickness; atomic force microscopy images of mixed phase films and highlighted phase interfaces; effective lattice parameter of film series calculated from the combination of x-ray diffraction and atomic force microscopy data (PDF)

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Notes

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

This research was partially supported by the Australian Research Council Centre of Excellence in Future Low-Energy Electronics Technologies (Project No. CE170100039) and funded by the Australian Government. D.S. and V.N. acknowledge the support of the Australian Research Council through Discovery Grants. S.R.B. acknowledges current funding from the Canada First Research Excellence Fund, and partial funding from the UNSW Science PhD Writing Scholarship. S.R.B. and O.P. thank AINSE Limited for providing financial assistance (Award - PGRA). The authors thank Ekhard Salje, Alina Schilling and Marios Hadjimichael for helpful discussions.

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