controlled via the sign of the strain – 110-type for tensile strain and 112-type for compressive strain. Such an understanding of the evolution of magnetic structure and the ability to manipulate the magnetism in this model multiferroic have significant implications for eventual utilization in applications. In particular, researchers are interested in utilizing the electric field control of antiferromagnetism in materials like $BiFeO_3$ to enable electric field tunable magnetism for memories, logics, sensing and more.

3.3. Role of domain walls in $BiFeO_3$

Recent observations are helping to answer questions surrounding the wide spectrum of magnetic responses observed in $BiFeO_3$ thin films. There is now a growing consensus that epitaxial films (with a thickness less than ~100 nm) are highly strained and thus the crystal structure is more akin to a monoclinic phase rather than the bulk rhombohedral structure. In films >100 nm, depending on the film–substrate lattice mismatch, films can relax to the bulk-like distorted rhombohedral structure and give rise to magnetic properties consistent with the weak canting of the antiferromagnetic moments. Furthermore, a systematic dependence of the ferroelectric domain structure in the film as a function of the growth rate has been observed [50]. Films grown very slowly (for example by MBE, laser MBE, or off-axis sputtering) exhibit a classical stripe-like domain structure that is similar to ferroelastic domains in tetragonal $Pb(Zr_x,Ti_{1-x})O_3$ films. Due to symmetry considerations, two sets of such twins are observed. These twins are made up of 71° ferroelastic domain walls, which form on the {101}-type planes (which is a symmetry plane). In contrast, if the films are grown rapidly (as was done in the original work of Wang et al. [28]) the domain structure is dramatically different (likely arising from a change in the growth mechanism from a step-flow or layer-by-layer process to an island growth process). It now resembles a mosaic-like ensemble that consists of a dense distribution of 71°, 109°, and 180° domain walls. It should be noted that 109° domain walls form on {001}-type planes (which is not a symmetry plane for this structure). Preliminary measurements reveal a systematic difference in magnetic moment between samples possessing different types and distributions of domain walls. The work of Martin et al. [50] suggests that such domain walls could play a key role in many observations of enhanced magnetic moment in $BiFeO_3$ thin films.

This hypothesis emerges from the work of Přívratská and Janovec [51,52], where detailed symmetry analyses were used to arrive at the conclusion that magnetoelectric coupling could lead to the appearance of a net magnetization in the middle of antiferromagnetic domain walls. Their idea was that domain walls represent a special kind of inhomogeneity where a lowering of the translation symmetry to two dimensions confines the appearance of new effects to a layer – the symmetry of the layer can be described by a so-called layer group. Such layer groups exclude some symmetry elements that may exist in the bulk of a domain (i.e. rotation and inversion axes that are not perpendicular or parallel to the domain wall) or may allow for invariance under operations that interchange domains on the two sides of the wall. Such operations cannot exist in the bulk of domains and thus result in an enhancement of symmetry. Thus the symmetry difference between the bulk of a domain and the domain wall is generally not a simple symmetry lowering and thus not only can induce an appearance of new effects in the domain wall that do not exist in the bulk of a domain, but also can result in the disappearance of some properties that exist in the bulk of the domain. The work of Janovec and colleagues focused on the possible appearance of spontaneously magnetized domain walls joining antiferromagnetic domains, especially in multiferroic/magnetoelectric crystals, while other prior studies suggested the possibility of electric polarization in domain walls in magnetically ordered crystals. [53] In the end, this work showed that this effect is allowed for materials with the $R3c$ space group (i.e. that observed for $BiFeO_3$). Although this analysis raises the possibility of an enhanced moment, the group-symmetry arguments do not allow for any quantitative estimate of that moment.

The idea that novel properties could occur at domain walls in materials presented by Přívratská and Janovec is part of a larger field of study of the morphology and properties of domains and their walls that has taken place over the last 50 years, with increasing recent attention given to the study novel functionality at domain walls [54–56]. For instance, recent work has demonstrated that spin rotations across ferromagnetic domain walls in insulating ferromagnets can induce a local polarization in the walls of otherwise non-polar materials (incommensurate magnetic ordering results from competing exchange interactions and the resulting spin density wave can induce a Lifshitz invariant coupling that induces a uniform electric polarization that breaks the inversion symmetry) [16,56], preferential doping along domain walls has been reported to induce two-dimensional superconductivity in WO_{3-x} [57] and enhanced resistivity in phosphates [58], while in paraelectric (non-polar) $SrTiO_3$ the ferroelastic domain walls appear to be ferroelectrically polarized [59]. Taking this idea one step further, Daraktchiev et al. [60,61] have proposed a thermodynamic (Landau-type) model with the aim of quantitatively estimating whether the walls in $BiFeO_3$ can be magnetic and if so, to what extent they might contribute to the observed enhancement of magnetization in ultrathin films. One can develop a simple thermodynamic potential incorporating two order parameters expanded up to P^6 and M^6 terms (the transitions in $BiFeO_3$ are found experimentally to be first order, and the low-symmetry ($\pm P_0$, 0) phase is described here) with biquadratic coupling between the two order parameters (biquadratic coupling is always allowed by symmetry, and therefore always present in any system with two order parameters). The authors also note that there is no published data on the Landau coefficients for $BiFeO_3$, no esti-