mates of domain-wall magnetization, and no analytical expression of domain wall magnetization as a function domain-wall thickness, coupling, and the all-important Landau coefficients (which determine the accuracy of such phenomenological models). The authors recommend rigorous measurement of the Landau coefficients for $BiFeO_3$ and suggest that this could greatly increase our understanding of these and other topics.

Regardless, when one goes from $+P$ to $-P$, it is energetically more favorable for the domain wall energy trajectory not to go through the center of the landscape ($P = 0$, $M = 0$), but to take a diversion through the saddle points at $M_0 \neq 0$, thus giving rise to a finite magnetization (Fig. 4). The absolute values of the magnetic moment at the domain wall will depend on the values of the Landau coefficients as well as the boundary conditions imposed on the system, namely whether the material is magnetically ordered or not. Analysis of the phase space of this thermodynamic potential shows that it is possible for the net magnetization to appear in the middle of ferroelectric walls, even when the domains themselves are not ferromagnetic (Fig. 4b). The authors of this model note, however, that it is presently only a "conceptual model" which does not take into account the exact symmetry of $BiFeO_3$, so it cannot yet quantitatively estimate how much domain walls can contribute to the magnetization. The exact theory of magnetoelectric coupling at the domain walls of $BiFeO_3$ also remains to be formulated.

Recently, a holistic picture of the connection between processing, structure, and properties has brought to light the role of magnetism at ferroelectric domain walls in determining the magnetic properties in $BiFeO_3$ thin films. By controlling domain structures through epitaxial growth constraints and probing these domain walls with magneto-transport and high-resolution transmission electron microscopy, He et al. [62] have demonstrated that certain types of ferroelectric domain walls (i.e. 109° walls) can possess exotic magnetic properties in $BiFeO_3$. Building off the work of Martin et al. [50], they were able to demonstrate that samples possessing 109° domain walls show significantly enhanced circular dichroism that is consistent with collective magnetic correlations, while samples with only 71° domain walls show no measurable circular dichroism. In summary, it appears that certain domain walls can give rise to enhanced magnetic behavior in $BiFeO_3$ thin films.

Seidel et al. [63] undertook a detailed scanning probe-based study of domain walls in $BiFeO_3$ and discovered a new and previously unanticipated finding: the observation of room temperature electronic conductivity at certain ferroelectric domain walls. The origin of the observed conductivity was explored using high-resolution transmission electron microscopy and first-principles density functional computations. The results showed that domain walls in a multiferroic ferroelectric, such as $BiFeO_3$, can exhibit unusual electronic transport behavior on a local scale that is quite different from that in the bulk of the material. Using a model (110)-oriented $BiFeO_3/SrRuO_3/SrTiO_3$ heterostructure with a smooth surface (Fig. 5a), the researchers were able to switch the $BiFeO_3$ material is such a way that enabled them to create all the different types of domain walls possible in $BiFeO_3$ (i.e. 71°, 109°, and 180° domain walls) in a local region (Fig. 5b and c). Conducting atomic force microscopy (c-AFM) measurements (Fig. 5d) revealed conduction at 109° and 180° domain walls. Detailed high-resolution transmission electron microscopy studies (Fig. 5e) revealed that this conductivity was, in part, structurally induced and can be activated and controlled on the scale of the domain wall width – ~2 nm in $BiFeO_3$. From the combined study of conductivity measurements, electron microscopy analysis, and density functional theory calculations, two possible mechanisms for the observed conductivity at the domain walls have been suggested: (1) an increased carrier density as a consequence of the formation of an electrostatic potential step at the wall; and/or (2) a decrease in the band gap within the wall and corresponding reduction in band offset with the c-AFM tip. It was

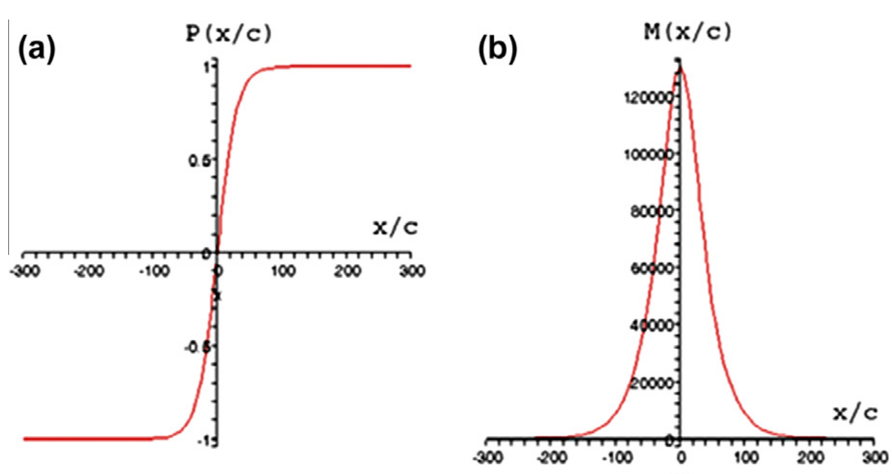

Fig. 4. Shape of ferroelectric polarization and magnetism across a domain wall in $BiFeO_3$. (a) Ferroelectric polarization goes to zero at the center of the domain wall. (b) A net magnetization appears at the center of the domain wall, even though the domains themselves do not possess a net moment (adapted from Refs. [60,61]).