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MULTIFERROICS A whirlwind of opportunities

Mostovoy, Maxim

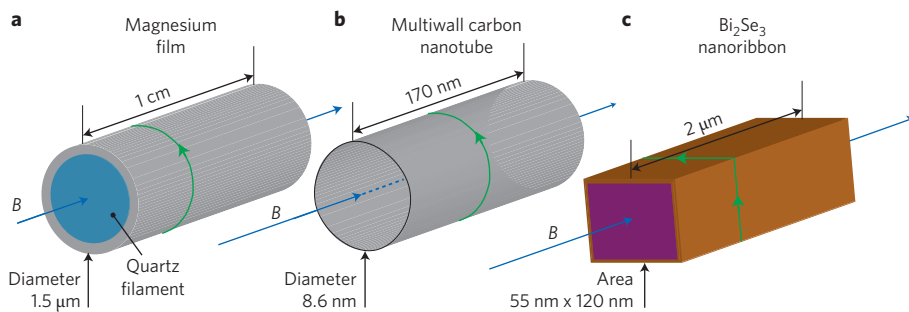[Link to publication in University of Groningen/UMCG research database](#)

Figure 2 | The similarity between different experiments on tube-like geometries. **a**, Geometry of the Sharvin and Sharvin experiment[7], in which a magnesium film was evaporated onto a quartz filament. **b**, Experiment on a carbon nanotube[9], where electron motion is confined to the cylindrical surface of the tube. **c**, The new experiment reported by Peng, Lai and co-workers[2], whereby a significant contribution to transport stems from the gapless surface states of the Bi_2Se_3 nanoribbon.

however, there is no need for an insulating core and a conducting surface, because the material itself has these characteristics. The interpretation of the new experiment is that the thin nanoribbon geometry reduces the bulk conductivity caused by crystal defects to an extent that allows the signature of the Aharonov–Bohm-type oscillations of surface states to be observed, if a magnetic field is applied along the ribbon axis. The observation of the fundamental h/e period surprisingly indicates the absence of strong self-averaging in these experiments. Peng, Lai and colleagues argue that in the Bi_2Se_3 nanoribbons the topological protection helps to bring about the fundamental period of the Aharonov–Bohm interference at small magnetic fields,

rather than the more robust $h/2e$ period seen in the magnesium cylinders, and in carbon nanotubes.

Present research on topological insulators is still at an early stage, but has the potential to have a bright future. Perhaps nature will provide us with even more materials belonging to this class. Improving the quality of the available materials represents a significant challenge. Nanoribbons made of three-dimensional topological insulators could be natural competitors of today's core–shell nanowires grown epitaxially with great precision and high quality. But two-dimensional topological insulators will also contribute to future research: edge-channel transport in the two-dimensional

heterostructure HgTe/HgCdTe, which is a zero magnetic-field topological insulator, has been demonstrated recently[11], and Aharonov–Bohm-type oscillations have been seen in this material. Two-dimensional topological insulators have also been proposed in single- and double-layer graphene. Visionary proposals see applications in spintronics, valleytronics or even topological quantum computation, for example with the exotic fractional quantum Hall state at filling factor 5/2 (ref. 12). Although the realization of these goals will be highly challenging, it will no doubt spark a great variety of new basic research on nanoscale structures at the interface between physics, materials science and electronic engineering. ❐

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MULTIFERROICS

A whirlwind of opportunities

The formation of vortices in multiferroic hexagonal manganites, where the sign of electric polarization changes six times around the vortex core, points towards the origin of composite multiferroic domain walls.

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Multiferroic materials with their coexisting ordered states of electric and magnetic dipoles may find use in many technological applications — such as magnetoelectric random-access memory — that excel by virtue of their low power consumption[1]. One of the key milestones on the way to achieving this goal was the demonstration of remarkable control of electric polarization by an applied magnetic field in a number of compounds in which the electric dipoles are induced by ordered electron spins[2].

Another promising route towards magnetoelectric switching relies on the unusual properties of defects in multiferroic orders[3]. In particular, in the hexagonal manganite $YMnO_3$, nonlinear optical studies show that ferroelectric domain walls are firmly locked with the magnetic domain walls[4] forming composite multiferroic domain walls. This observation is very surprising at first because the sign of electric polarization is independent of the orientation of the magnetic spins and vice versa.

Writing in *Nature Materials*, Taekjib Choi and colleagues now report[5] the discovery of a missing component that is crucial to the understanding of this domain-wall clamping. The authors combine transmission electron microscopy (TEM), which enables them to observe the six different structural domains of $YMnO_3$, with conductive atomic force microscopy (CAFM), which they use to measure the polarization of the ferroelectric domains. These experiments reveal that the ferroelectric and structural domains

coincide, so that the electric polarization always changes sign at the structural boundaries. Most interestingly, fascinating 'cloverleaf' defects appear in which all six structural domains forming 60° wedges merge (Fig. 1). As structural and ferroelectric domains coincide the electric polarization changes its sign six times along a loop encircling the defect.

These findings represent a very elegant proof of the 'geometric' nature of ferroelectricity in YMnO$_3$ (refs 6,7). In contrast to conventional ferroelectrics such as BaTiO$_3$, the shifts of positive and negative ions inducing electric polarization are not the main driving force of the ferroelectric transition in YMnO$_3$. Instead, the polarization is a by-product of a very different kind of lattice distortion — that is, trimerization. In hexagonal YMnO$_3$ both manganese and yttrium ions form triangular layers. A difference in the ionic radii of yttrium and manganese results in a distortion of the atomic lattice whose periodic modulation makes the unit cell three times larger.

The periodic lattice modulation has six different phases rotated by 60° with respect to each other. Each phase corresponds to one of the six structural domains. By itself this periodic modulation carries no electric dipole. However, the anharmonicity of the lattice makes the trimerized state ferroelectric, inducing an electric polarization normal to the triangular layers. Corresponding to these six phases there are three positive polarization states, denoted as α+, β+ and γ+, and three corresponding negative states, denoted as α−, β− and γ−.

These six structural domains represent the minima of free energy of the system, rotated by 60° angles, as depicted in Fig. 2a. In this picture, the domain walls separating the structural domains are trajectories beginning in one minimum and ending in another. The lowest-energy domain walls connecting two neighbouring minima are depicted by the dashed line in Fig. 2a. As is evident from the alternating sign of polarization of neighbouring domains, such domain walls flip the electric polarization.

The cloverleaf defects are therefore vortices where around the defect the phase angle goes successively through all six phases. This leaves only two possible domain sequences: α+, β−, γ+, α−, β+, γ− (vortex) and α+, γ−, β+, α−, γ+, β− (antivortex). Therefore, the electric polarization changes sign at each domain wall (Fig. 2b,c). Such vortices are stable topological defects that cannot be unwound by local lattice distortions. Indeed, as

Choi and colleagues also observe, a strong electric field applied along the direction of the positive polarization reduces the size

of the domains with negative polarization to a minimum, but it cannot wipe them out entirely[5]. The cloverleaf defects are
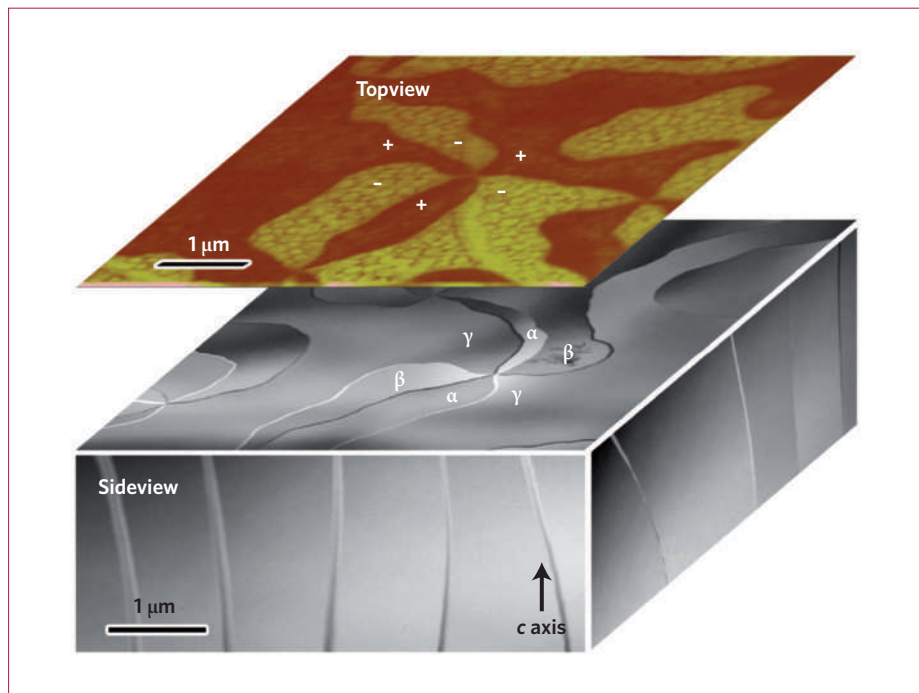

Figure 1 | Cloverleaf defect in hexagonal YMnO$_3$. The combination of TEM (bottom grey-scale layer) and CAFM (top coloured layer) measurements shows six crystallographic domains joining at a defect line with positive and negative polarization (+ and – signs in the CAFM image, respectively) alternating around the defect.
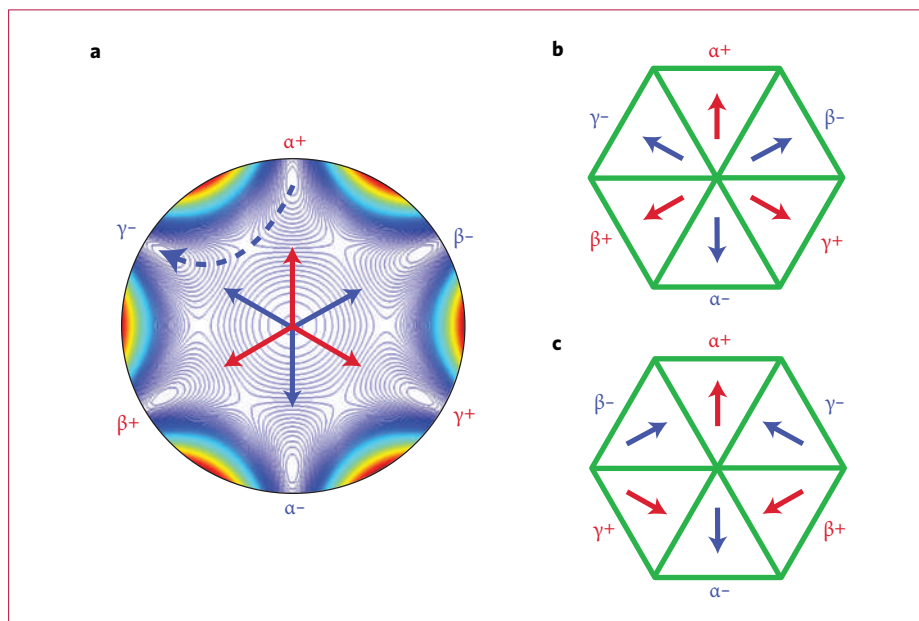

Figure 2 | Structural domains in YMnO$_3$. **a**, Contour plot of the free energy of hexagonal YMnO$_3$, where the six minima correspond to six structural domains. The arrows in the direction of the minima (coloured blue and red) indicate the direction describing these states. The red and blue arrows also encode the sign of electric polarization. The dashed arrow connecting two neighbouring minima is a lowest-energy domain wall. **b,c**, The vortex (**b**) and the antivortex (**c**) configurations correspond to the cloverleaf defect shown in Fig. 1.

discrete analogues of magnetic vortices and vortices in superconductors and superfluid helium. They are similar to discrete-vortex solitons recently observed in nonlinear photonic lattices[8,9].

In addition to structural and electric properties, what are the magnetic properties of these domain walls and vortices? In bulk manganese, spins order non-collinearly with 120° angles between neighbouring spins. The spin orientation is also determined (up to an overall sign) by the lattice trimerization. Thus, the rotation of the lattice distortion at a structural domain not only flips the polarization, but also rotates the spins.

This explains the clamping of ferroelectric and antiferromagnetic domains found by Fiebig and colleagues[4]. Those 'loose' magnetic domain walls observed that are not locked to ferroelectric walls correspond to the 180° rotation of spins within one structural domain.

The 60° rotation of spins at domain boundaries implies that the cloverleaf defects are also magnetic vortices where lattice distortions and spins rotate together. It would be interesting to find out whether this amazingly complex interplay between structural, electric and magnetic properties of defects can lead to new magnetoelectric phenomena. ❑

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WEB DESIGNERS

MATERIAL WITNESS

In a new book challenging neo-Darwinian adaptationist theory[1], cognitive scientists Jerry Fodor and Massimo Piattelli-Palmarini point out that "lacking observations of spiders, nothing (least of all the theory of natural selection) could have predicted that there are creatures that have the spider's kind of adaptation to their niches. What happened is that somebody who knew that spiders make a living by eating flies looked carefully at their natural history and was thus able to figure out that spinning webs is how they do it."

Whatever you make of Fodor and Piattelli-Palmarini's attack on the biological orthodoxy, they are right to point out that the theory of natural selection makes few if any specific predictions about how nature will turn out. Certainly, it cannot predict that spiders make webs (as opposed to, say, catching flies by growing wings or coating surfaces with adhesive). And indeed natural history shows that spiders did not evolve silk to spin fly-catching webs, but must have originally used it, around 380 million years ago, in sheets for some other purpose, such as wrapping eggs[2] (as they still do today).

And yet it is hard to imagine any process but natural selection that could have produced such a remarkably 'engineered' structure

as the spider's web. The single silk thread is a masterpiece of materials processing, renowned for its combination of high tensile strength and elasticity. This is produced by control of the material's hierarchical structure during the spinning process, for which the spider has a sophisticated piece of apparatus called the spinneret. It involves careful control of liquid-crystalline ordering in the silk protein (fibroin) as the solution is progressively dehydrated, resulting in a composite of crystalline regions within a disordered matrix. The amino-acid sequence of the structural protein is varied depending on which function the strand serves. There has surely been some process of optimization to arrive at a biomaterial that we still struggle to mimic.

Physicists Yuko Aoyanagi and Ko Okumura of Ochanomizu University in Japan now show that the optimization doesn't stop there. They have developed a simple mechanical model of the canonical spider's web — the orb web, in which thin spiral threads bridge stronger radial threads — which shows that this hierarchical structure differs from common elastic materials in how it is affected by damage[3].

The researchers show that for typical values of the elastic moduli and cross-sectional area of radial and spiral threads, the force

PHILIP BALL

distribution in the threads is largely independent of the number and spacing of spiral threads, offering plenty of freedom in web design. And this distribution is virtually unchanged when spiral threads become damaged: it remains rather uniform throughout the web, with none of the stress concentration that develops near a crack and weakens other materials. So long as the radial threads are intact, the web is highly damage-tolerant.

As Aoyanagi and Okumura point out, these same principles are potentially valuable for human-built structures. And they reinforce the belief that whatever drives evolution, it is adept at finding 'good' solutions. ❑

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