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PERSPECTIVE

Interface/surface magnetoelectric effects: New routes to the electric field control of magnetism

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In this perspective paper, we discuss possible ways to control magnetism using electric-field. Special focus is given to interface/surface magnetoelectric effects, which will become important when the thickness of magnetic films drops to nanoscale. We show that significantly different mechanisms may lead to interface/surface magnetoelectric effects, providing great flexibility to apply such effects. As a result, we propose several protype devices utilizing these novel magnetoelectric effects, and strongly advocate experimental endeavors to realize such devices.

Keywords magnetoelectric effect, multiferroic, electric-field controlled magnetism

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Magnetoelectric effect, which describes the coupling between electric and magnetic fields in matter [1], provides an alternative way to control the magnetic or dielectric properties of materials. Many applications based on magnetoelectric effect have been proposed, including energy and frequency converter, transformer and gyrator, field sensor, modulator, signal amplifier, *etc* [2]. The biggest impetus of the research on magnetoelectric effect, however, probably comes from the field of data storage and processing. Actually, the *Holy Grail* in magnetoelectric and multiferroic [3,4] studies is the magnetization switching or even magnetization reversal by the electric field at room temperature. The electric field approach has an apparent advantage over the traditional magnetic field or the more advanced spin-current method, as it requires much lower power to switch the magnetization [5] and might bring revolutions into the information processing industry.

At the first glance, the electric field control of magnetization reversal, i.e., 180 ° switching of the magnetization, seems to be a *mission impossible*. This is based on the fact that the constant electric field does not break the time-reversal symmetry, which seems to be necessary to reverse the magnetization. With the deeper understanding on the magnetoelectric couplings in the materials, however, it is now being realized that the electric field induced magnetization reversal is achievable, at least theoretically. The key to the magnetization reversal by the electric field is that the magnetization must be strongly coupled to the polarization, so that the polarization reversal will inevitably result in the magnetization reversal. Several mechanisms may lead to such a phenomenon, which include the cases when the ferroelectric polarization is induced by the magnetic ordering as in magnetic twist due to the Dzyaloshinskii–Moriya (DM) interaction [6–8], or the electric dipole moments of the system are intrinsically related to the spin orientation as in the case of permanent electric dipole moment of the electron [9], or the magnetization is induced by and parallel to the applied electric field as in topological magnetoelectric effect [10]. We also cannot rule out the possibility in the case of strong spin–orbit coupling, where the spin orientations are intimately coupled to the lattice, hence they are forced to rotate with the rotations of ferroelectric polarizations. There has been no experimental report on such a case, but we expect that it could occur if magnetism is introduced into ferroelectric polymers (see Fig. 1), which is possible since both ferromagnetism [11] and ferroelectricity [12] could be individually found in polymers. Note that here the magnetic field can still reverse the magnetization without changing the ferroelectric polarization, which is different from the case of electric dipole moment of the electron [9].

Nevertheless, even the magnetization reversal has been hardly achieved experimentally. It is still exciting to see that the magnitude of the magnetocrystalline energy

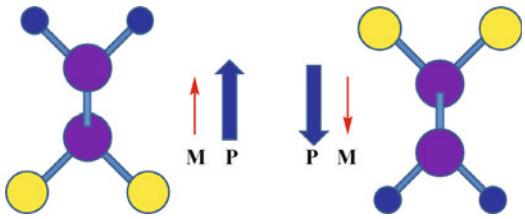

Fig. 1 Ferroelectric polarization induced magnetization reversal in a hypothetical multiferroic polymer or macro polar molecules. The magnetization (**M**, red narrow arrow) is strongly coupled to the lattice due to spin–orbit interaction, and the electric polarization (**P**, blue wide arrow) is naturally determined by the intrinsic dipoles of the constituent of the polymer. Therefore, the reversal of **P** will coherently reverse **M**.

(MAE) can be affected by an electric field, as in this way it could significantly decrease the required magnetic field to reverse the magnetization, forming the so called *electric field assisted magnetic recording* technology [13].

Here we will introduce several novel magnetoelectric effects, which might be useful to the realization of room temperature electric field control of magnetism in the future. As is to be shown in detail later, these effects mainly occur at the surfaces or interfaces of the materials, and they demonstrate significantly different mechanisms from traditional magnetoelectric effects, therefore greatly enriching our understanding on the interactions between electric and magnetic fields in materials.

We first describe the magnetoelectric effects in the interface. The observation of interface magnetoelectric effect originates from the search for multiferroic composite materials since room temperature single phase multiferroic materials are rare. In 2006, Duan *et al.* [14] proposed a simple ferroelectric/ferromagnetic heterostructure ($Fe/BaTiO_3$, see left of Fig. 2). They found that for the perfect $Fe/BaTiO_3(001)$ interface, i.e., the epitaxial growth of the heterostructure, there exists strong atomic bonding between the TiO_2 and Fe layers, forming energy favorable interface structure. Interestingly, the Fe–TiO_2 bonding results in sizeable induced magnetic moments in Ti^{4+} ions, which are antiferromagnetically coupled with adjacent Fe ions. What is more interesting, since the induced magnetic moments are sensitive to the interfacial bonding strength, they can be controlled by the ferroelectric displacements in $BaTiO_3$ (Fig. 2, right).

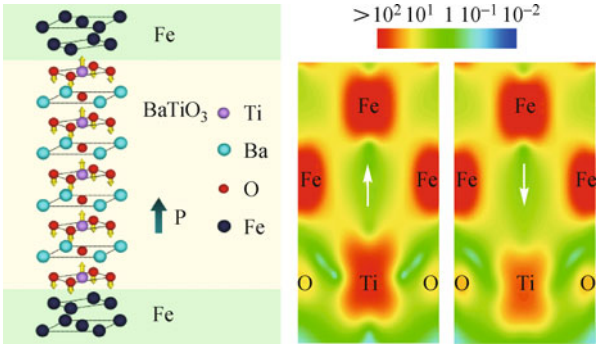

Fig. 2 *Left*: Atomic structure of $Fe/BaTiO_3$ multilayer. *Right*: Minority-spin charge density at the $Fe/BaTiO_3$ interface for two opposite polarizations in $BaTiO_3$. Reproduced from Ref. [14], Copyright © 2006 the American Physical Society.

As can be seen from the above description, this interface magnetoelectric effect is of quantum mechanical origin, and it is significantly different from the strain-mediated magnetoelectric effect which describes the coupling between elastic components of the ferromagnetic and ferroelectric constituents through the strain [2]. The major difference is that this new effect is sensitive to the direction of ferroelectric polarization, whereas the latter is not, which is confirmed by several experiments [15]. Similar results have been found in other structures like $Co_2MnSi/BaTiO_3$ [16] and $Fe_3O_4/BaTiO_3$ [17, 18].

The magnetization change in the interface is not the only consequence of the ferroelectric switching in such ferromagnetic/ferroelectric heterostructure. In a further study [19], Duan *et al.* found that the ferroelectric polarization also affects the orbital magnetic moments and in turn the MAE of Fe ions at the interface. To be specific, the polarization switch could alter the MAE of a Fe monoloayer by as large as about 50%. Considering the additional shape anisotropy which is thickness dependent, they claimed that it may be possible to design ferromagnetic films with the anisotropy switchable between in plane and out of plane using electric field. Apparently, the magnetoelectric control of MAE also could be helpful in the *writing* on high coercivity perpendicular media.

The influence of the ferroelectric polarization on the spin polarization at the interface results in another, maybe more important application of magnetoelectric effect, i.e., spin-dependent transport. In 2010, Garcia *et al.* [20] fabricated $Fe/BaTiO_3/La_{0.67}Sr_{0.33}MnO_3$ multiferroic tunnel junction. By controlling the ferroelectric polarization of $BaTiO_3$, they observed reversible changes of the tunnel resistance by about 30%. This provides direct evidence on the strong dependence of the tunneling magnetoresistance on the direction of the ferroelectric polarization.

Indeed, the interface magnetoelectric effect could have more general origin. In 2008, based on first-principles calculations, Rondinelli *et al.* [21] found that the external electric field leads to the accumulation of spin-polarized charges, and in turn the magnetic moments, at the interface between a dielectric (e.g., $SrTiO_3$) and a spin-polarized metal (e.g., $SrRuO_3$). The so called carrier mediated interface magnetoelectric effect, according to Rondinelli *et al.* [21], has nothing to do with the details of interfacial bonding, and hence is more common in the oxide interface.

In 2008, Duan *et al.* [22] realized that the spin accumulation at the ferromagnetic metal/dielectric interface due to external electric field is actually a consequence

of the spin-dependant screening effect [23]. Using first-principles simulations, they demonstrated that the external electric field itself can induce magnetic moments in the surfaces of the ferromagnetic metals, e.g., Fe, Co and Ni (Fig. 3). Since this magnetoelectric effect is limited to the metal surface, it was named *surface magnetoelectric effect*.

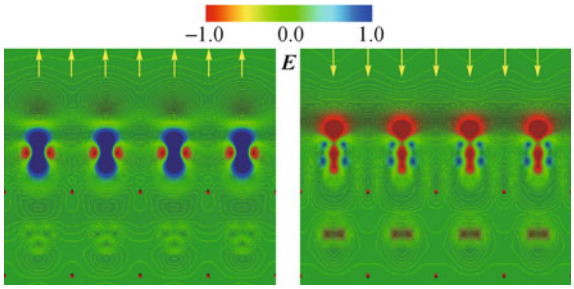

Fig. 3 Surface magnetoelectric effect of Fe film. *Left*: increase of the magnetization when the electric field is pointed away from the surface. *Right*: decrease of the magnetization when the electric field is pointed towards the surface (from Ref. [24].)

Considering that the surface is actually a special kind of interface (with a vacuum whose dielectric constant is 1), we can unify the carrier mediated interface magnetoelectric effect and the surface magnetoelectric effect by writing out their magnetoelectric coefficients as [22]

$$\alpha = \frac{\mu_0 \Delta M_s}{E} = -P_s \frac{\varepsilon \mu_B}{ec^2} \quad (1)$$

where ΔM_s is the induced magnetization per interface (surface); $P_s = \frac{n^\uparrow - n^\downarrow}{n^\uparrow + n^\downarrow}$ is the spin polarization rate of the conduction electron at the interface (surface); ε is the dielectric constant of the dielectric adjacent to the ferromagnetic metal; μ_B, e and c are Bohr magneton, electron charge and speed of light, respectively. Note that a positive electric field is defined to be pointed away from the metal film surface.

There are something interesting about Eq. (1). First, the spin polarization rate P_s at the interface (surface) is generally different from that of the bulk material. The majority spin electron in the bulk is not necessarily dominant at the interface (surface), therefore P_s can range from -1 to 1. The sign of the magnetoelectric coefficient α reflects the relative spin orientation of the dominant conduction electron at the interface (surface). Second, for a half metal whose spin polarization rate is 100%, in the vacuum, the surface magnetoelectric coefficient α is

$$\alpha_S = \pm \frac{\mu_B}{ec^2} = \pm \frac{\hbar}{2mc^2} \approx \pm 6.44 \times 10^{-14} \frac{\mathrm{G \cdot cm^2}}{\mathrm{V}} \quad (2)$$

This is a quite impressive result, as it suggests that the surface magnetoelectric coefficient of half-metals is a universal constant, independent of the specifics of atomic and electronic structure, as long as the orbital contribution to the surface magnetic moment can be neglected, and this is confirmed by a recent calculation done by Duan *et al.* on CrO_2 [25]. Third, dielectric constant ε plays a role in amplifying the interface (surface) magnetoelectric effect. In 2010, by studying the magnetoelectric effect of Fe/MgO structure, Niranjan *et al.* [26] found that the surface magnetoelectric coefficient of Fe is enhanced by a factor of 3.1, which is approximately the high frequency dielectric constant (ε_∞) of MgO (3.0).

The static electric field induced spin accumulation in the surface of the ferromagnetic metal leads to a new concept device named *spin capacitor*, which stores charges as well as spins [21, 27]. As the spin is the major source of magnetism in the materials, this effect indeed provides a way to generate magnetism using static electric field instead of alternating electric current.

To make the interface (surface) effect useful in application, one should use a large electric field, as even for an applied electric field as strong as 1 V/Å, the induced magnetic moment for a half metal is only about 0.005 $\mu_B/Å^2$. The other point is to avoid the magnetization cancelling effect when the two surfaces (interfaces) of the ferromagnetic metal feel an opposite electric field. Finally, one must adopt structures with large surface (interface)/bulk ratio to maximize the interface (surface) effect.

Here we propose two devices that could satisfy the above requirements and might be helpful to realize the static electric field generated magnetism. One of them adopts the so called interdigital capacitor structure [shown in Fig. 4(a)]. In this structure, ferromagnetic metal (e.g., Fe) and non-ferromagnetic metal (e.g., Cu) slabs are alternatively arranged and connected to negative and positive electrodes, respectively. In this way the top and bottom surfaces of the same ferromagnetic metal slab would experience the electric field of the same direction, doubling instead of cancelling the surface magnetoelectric effect. Indeed, if we replace the non-ferromagnetic metal by a ferromagnetic metal which has a different sign of the surface magnetoelectric coefficient from that of the first ferromagnetic metal, the effect will be further enhanced. In the extreme case when all slab surfaces are half metals and make positive contributions, we estimate that a voltage of 1 V can generate a magnetization of the magnitude of 10 emu/cm^3. Here we assume that all slabs and insulating layers are of the thickness of 1 nm, which is achievable experimentally, and the dielectric constant of the insulating layer (MgO) is chosen to be 10. If we choose large dielectric constant material such as $SrTiO_3$ ($\varepsilon \sim 300$), the induced magnetization can be 300 emu/cm^3, as compared with that of nickel and magnetite ($\sim$485 emu/cm^3).

The other strategy is to design a coaxial cylinder type spin capacitor [Fig. 4(b)]. In this geometry, the inner Fe rod has only one surface, therefore the net contribution to the magnetization due to surface magnetoelectric ef-

fect is also nonzero. Suppose both the radius of the inner Fe rod and the thickness of insulating layer are 1 nm, the induced magnetization is of the same magnitude of the previous interdigital capacitor. To generate net magnetization, however, the easy axis of the ferromagnetic rod should be parallel to the axial direction.

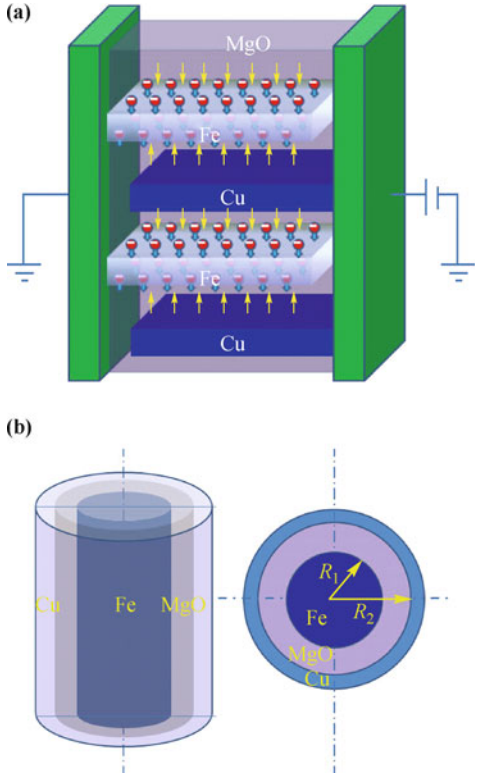

Fig. 4 Proposed new devices utilizing interface (surface) magnetoelectric effect. **(a)** Interdigital spin capacitor; **(b)** Coaxial cylinder spin capacitor.

If the dielectrics in above devices are replaced by ferroelectric materials [28], one would then expect *ferroelectric spin capacitors*, which might be important to the design of nonvolatile memory devices.

The applied electric field not only results in the change of magnetization on the surface of 3*d* transition metals, but also modifies their surface electronic structure [22, 29–31]. What is especially interesting is that the electron population of each 3*d* orbits will be altered, leading to the change of orbital momentum of transition metal ions. Accordingly the electric field can have direct influence on the MAE of the transition metal. This provides a nice explanation to the experimental work on FePt and FePd [32]. Recently, groups from Osaka University and Tohoku University have demonstrated that large voltage can induce magnetic anisotropy change in a few atomic layers of iron [33], which is a direct support for theoretical predictions.

In a more general sense, magnetoelectric effect can be described as the magnetic (dielectric) property of the material being affected by the applied electric (magnetic) field. In this way, there are many other interesting magnetoelectric effects, e.g., electric field control of exchange bias [34], magnetic ordering [35, 36], structural [37] and magnetic phase [38–40] transition, magnetic transition temperature [41], etc. In addition, when talking about electric field effect on the ferromagnetic metal surface, Rashba effect generally should not be ignored when the relativistic effect is strong [42].

Apparently, the electric field approach has been considered a promising way to control the magnetism [5, 43]. What may hinder the direct application of electric field is the dielectric breakdown, as the required electric field is usually extremely high. However, recent experimental progress shows that structures like *electric double layer transistors* could allow an electric field as high as 10 MV·cm^{-}1, which has paved the way for electric field manipulation of magnetism at room temperature [44].

This brief overview of the fascinating topic about magnetoelectric effect is by no means comprehensive. Details about the progress in this and other related field can be found in Refs. [45–47] among others. Yet, even from the above glimpse, we can already feel the rapid pulse of this exciting frontier. Indeed, due to the amazing achievement in both the computer simulations and the material growth technology, especially the state-of-the-art interface control, theory and experiment have never been so closely tied together. We have enough confidence that more and more intriguing and exciting phenomena will be revealed in the near future.

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