

Magnetolectric effects in composite of nanogranular Fe/TiO_{2-δ} films

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Employing a new experimental technique to measure magnetolectric response functions, we have measured the magnetolectric effect in composite films of nanogranular metallic iron in anatase titanium dioxide at temperatures below 50 K. A magnetolectric resistance is defined as the ratio of a transverse voltage to bias current as a function of magnetic field. In contrast to the anomalous Hall resistance measured above 50 K, the magnetolectric resistance below 50 K is significantly larger and exhibits an even symmetry with respect to magnetic field reversal $H \rightarrow -H$. The composite films are unique in terms of showing magnetolectric effects at low temperatures, <50 K, and anomalous Hall effects at high temperatures, >50 K. © 2008 American Institute of Physics.

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Present research in new functional materials, such as magnetolectric (ME) or multiferroic (MF) materials, have drawn a great deal of attention because of their potential applications in electronics and nanoelectronic device technologies.¹⁻⁷ Properties of ME and MF materials have been recently reviewed.^{1,5-7} The effects are a consequence of the coupling between electric and magnetic fields in materials. ME and MF materials have multipurposes or multifunctional applications. Relatively, few multiferroic materials exist in natural phases, such as TbMnO₃,^{1,2} BiFeO₃,^{1,3,8} and HoMnO₃.⁴ Composite bulk materials combining piezoelectric and magnetostrictive materials have been suggested as possible ME or MF materials.^{1,7} As suggested by previous authors, strain in the composite is induced by the magnetostrictive component upon the application of an external magnetic field which gives rise to an electric field, since the composite is also partially piezoelectric.^{1,7} Synthesis of composite materials having ME or MF properties are now of great laboratory interest,^{1-4,7,9} especially in a thin film configuration.

In our previous work,^{10,11} oxygen deficient anatase structure titanium dioxide TiO_{2-δ} films on (100) lanthanum aluminate (LaAlO₃) exhibited both ferromagnetic and semiconducting properties at room temperature. In order to enhance the saturation magnetization at room temperature in these semiconducting films, we have incorporated nanogranular (NG) metallic iron (Fe) spheres in highly epitaxial oxygen deficient anatase TiO_{2-δ}. Details of the growth of the composite films by pulsed laser deposition have been presented in Ref. 12. The resulting composite films¹² gave rise to some intriguing phenomenon that the composite films exhibited strong carrier spin polarization of anomalous Hall effects at $T > 200$ K, where the carrier density was measured to be $n > 10^{22}/\text{cm}^3$.

A standard technique^{13,14} for measuring the ME effect in films is to monitor the electric polarization via voltage measurements across the film thickness in the presence of an external magnetic field \mathbf{H} . This technique may be indirect if the ME film material is, for example, deposited on a non-magnetic substrate. We have devised a simple direct scheme by which the ME effect is measured in film materials by

placing electrodes in the plane of the film rather than across the film. We utilize the same measurement technique as devised in Hall measurements whereby a bias current is applied in the film plane bisecting the two electrodes. Whereas in the measurement of the Hall, voltage \mathbf{H} is applied normal to the film planes, in the measurements of ME voltage \mathbf{H} may be applied in any direction as shown in Figs. 1(a) and 1(c). From the measured I - V characteristics at fixed \mathbf{H} , one may deduce the magnetization as a function of electric fields which is indeed the ME effect. There is a basic difference between the Hall measurement and the ME measurement technique as devised here and they are as follows. (i) Experimentally, the Hall voltage can be measured only for \mathbf{H} applied normal to the film plane, whereas in our present tech-

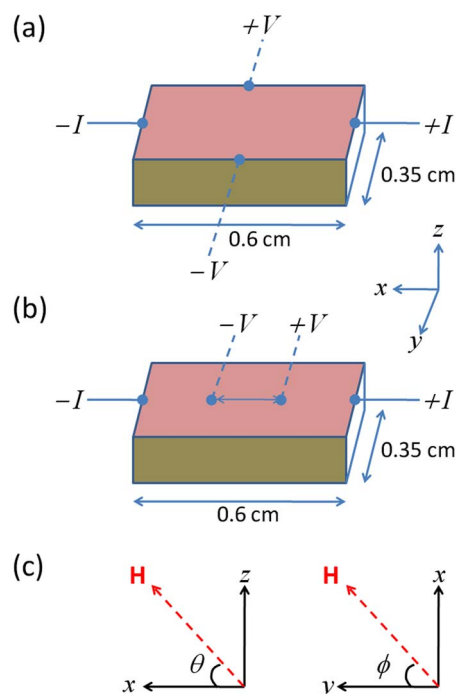


FIG. 1. (Color online) Schematics of transport measurements. (a) Magneto-electric resistance $R_{xy}(\mathbf{H})$. (b) Magnetoresistance $R_{xx}(\mathbf{H})$. (c) Direction of applied magnetic field, $0 \leq \theta \leq 90$ and $0 \leq \phi \leq 90$.

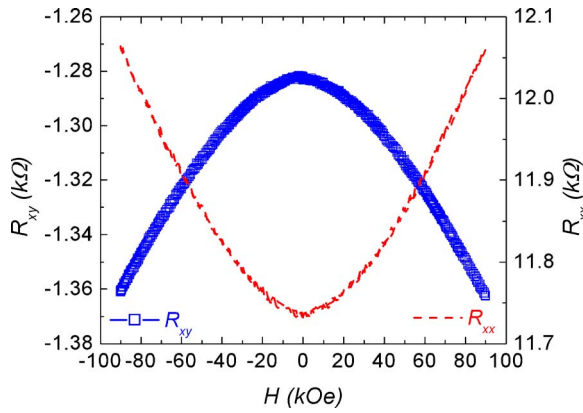


FIG. 2. (Color online) Magnetoresistance $R_{xx}(\mathbf{H})$ (dashed line) and magnetoelectric resistance $R_{xy}(\mathbf{H})$ (solid symbols) measured in function of magnetic field at temperature $T=4$ K.

nique \mathbf{H} may be applied in any direction. For example, for \mathbf{H} applied in the film plane, the electrodes in the film plane would not detect any Hall voltage as shown Figs. 1(a) and 1(c). (ii) Theoretically, for a fixed current I , the Hall voltage is an odd function of \mathbf{H} and the ME voltage is an even function of \mathbf{H} .

We now report magnetoelectric effects in our composite films for $T < 50$ K. We measured both R_{xx} and R_{xy} as a function of magnetic field \mathbf{H} , where R_{xx} is defined as the normal resistance measured by colinear four point probe technique and R_{xy} is measured using conventional Hall transport measurement technique. Sample dimensions for the transport measurements were $0.6 \times 0.35 \times 0.19 \times 10^{-4}$ cm³, and schematics of the transport measurements are shown in Fig. 1. The transverse voltage V_{\perp} was measured perpendicular to the bias current I . We define the ME resistance R_{xy} as $R_{xy}(\mathbf{H}) = V_{\perp} / I$. In Fig. 2, we plot the measured $R_{xy}(\mathbf{H})$ as a function of \mathbf{H} . The bias current I was fixed as the magnetic field was varied from -90 kOe $< \mathbf{H} < +90$ kOe. The bias current was applied in the film plane. Figure 2 shows that the measured $R_{xy}(\mathbf{H})$ is an even function of \mathbf{H} , where \mathbf{H} was applied normal to the film plane. It is argued below that the measured voltage is due to the ME effect of the film rather than the Hall effect, since $R_{xy}(\mathbf{H})$ is an even function of \mathbf{H} . Indeed, when we apply \mathbf{H} in the film plane, where there is no possibility of Hall voltage to be measured in the film plane, $R_{xy}(\mathbf{H})$ nevertheless behaves similarly to Fig. 2.

In previous work,¹² the magnetoresistance $R_{xx}(T, H)$ and the Hall resistance $R_{xy}(T, \mathbf{H})$ of the composite films were measured for temperatures $4 \text{ K} < T < 300 \text{ K}$. For $T > 50$ K, the anomalous Hall resistance [$R_{xy}(\mathbf{H})$] and negative magnetoresistance $R_{xx}(\mathbf{H})$, respectively, were measured. $R_{xy}(\mathbf{H})$ was measured to be an odd function of \mathbf{H} at temperatures above 50 K. However, for temperature below 50 K and for \mathbf{H} in the plane as well as normal to the film plane $R_{xy}(\mathbf{H})$ dependence on \mathbf{H} was parabolic, as shown in Fig. 2. Plots of $R_{xx}(\mathbf{H})$ show positive magnetoresistance in that range of temperatures (below 50 K). Thus, for temperatures below 50 K, the composite films are characterized by a magnetoelectric effect and above 50 K by an anomalous Hall effect.¹²

We suggest that this behavior of $R_{xy}(\mathbf{H})$ at low temperatures may be due to ME effects in the composite films. At any temperature there are two contributions to the measurement of R_{xy} : (i) voltage due to the ME effect and (ii) Hall

voltage. The Hall voltage scales with carrier density and roughly with temperature. The temperature dependence of the density with temperature has been measured by us.¹² Clearly, the Hall voltage is relatively small compared to ME voltage, since the carrier density is also small at low temperatures. $R_{xy}(\mathbf{H})$ in Fig. 2 demonstrates both broken time reversal and broken parity conservation symmetry as in a ME system. Note that the product symmetry (parity multiplied by time reversal) is unbroken. Previous theoretical studies^{15–17} of the ME effect are recalled to explain the behavior of $R_{xy}(\mathbf{H})$. In order to derive a relationship between $R_{xy}(\mathbf{H})$ and the ME effect, let us first consider free energy per unit volume F . The thermodynamic laws read¹⁷

$$F(\mathbf{E}, \mathbf{H}, T) = F(-\mathbf{E}, -\mathbf{H}, T),$$

$$dF = -SdT - \mathbf{P} \cdot d\mathbf{E} - \mu_0 \mathbf{M} \cdot d\mathbf{H}, \quad (1)$$

where \mathbf{P} is the electric polarization vector, \mathbf{E} the electric field vector, \mathbf{M} the magnetization vector, and \mathbf{H} the magnetic field vector. Note the symmetry condition

$$A_{ij}(\mathbf{E}, \mathbf{H}, T) = -\frac{\partial^2 F(\mathbf{E}, \mathbf{H}, T)}{\partial E_i \partial H_j} = A_{ij}(-\mathbf{E}, -\mathbf{H}, T),$$

$$A_{ij}(-\mathbf{E}, -\mathbf{H}, T) = \mu_0 \left(\frac{\partial M_j}{\partial E_i} \right)_{\mathbf{H}, T} = \left(\frac{\partial P_i}{\partial H_j} \right)_{\mathbf{E}, T},$$

$$\alpha_{ij}(\mathbf{H}, T) = c \lim_{E \rightarrow 0} A_{ij}(\mathbf{E}, \mathbf{H}, T) = \alpha_{ij}(-\mathbf{H}, T), \quad (2)$$

where c is light velocity and α_{ij} is the magnetoelectric tensor. If a small electric field $\delta \mathbf{E}$ is present in the plane of the film, then the magnetization change due to the electric field obeys^{15,17}

$$R_{\text{vac}} \delta \mathbf{M} = \alpha \delta \mathbf{E}, \quad (3)$$

where α is the ME pseudoscalar coupling coefficient and $R_{\text{vac}} = c\mu_0$ is the vacuum impedance. One may associate a uniform magnetization \mathbf{M} with a surface current per unit length \mathbf{K} via

$$\mathbf{K}_{\text{magnetic}} = \mathbf{M} \times \mathbf{n}, \quad (4)$$

where \mathbf{n} is a unit vector normal to the surface. Equations (3) and (4) on the film surface yield a surface magnetoelectric conductance g according to

$$\delta \mathbf{K}_{\text{ME}} = g \delta \mathbf{E} \times \mathbf{n}, \quad (5)$$

where $g = \alpha / R_{\text{vac}}$. In the experimental four probe configuration on the film surface,

$$\begin{pmatrix} \delta E_x \\ \delta E_y \end{pmatrix} = \begin{pmatrix} R_{xx} & R_{xy} \\ R_{yx} & R_{yy} \end{pmatrix} \begin{pmatrix} \delta K_x \\ \delta K_y \end{pmatrix}, \quad (6)$$

where $R_{xy} = -R_{yx}$, yields the central result for the experimental method, i.e.,

$$\alpha = R_{\text{vac}} g = \frac{-R_{\text{vac}} R_{xy}}{R_{xx}^2 + R_{xy}^2}, \quad (7)$$

Figure 3 exhibits typical $\alpha(\mathbf{H})$ data at $T=4$ K obtained from $R_{xx}(\mathbf{H})$ and $R_{yx}(\mathbf{H})$ versus \mathbf{H} . The theoretical fitting plot of $\alpha(\mathbf{H})$ was obtained according to

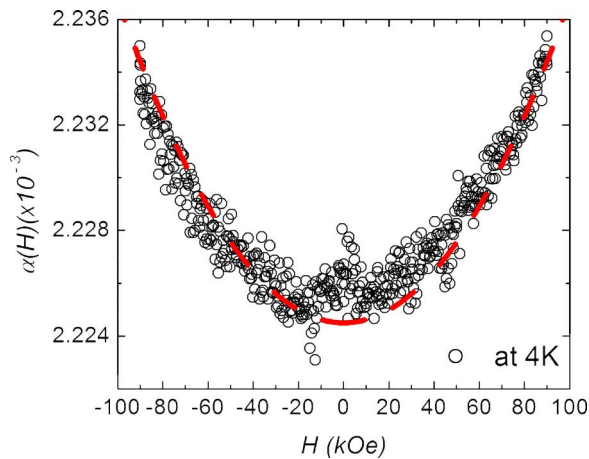


FIG. 3. (Color online) Magnetolectric coefficient, $\alpha(\mathbf{H})$ (symbols), data from magnetolectric conductivity. Dashed line shows fitting experimental ME coefficient with equation shown in Eq. (8).

$$\alpha(\mathbf{H}) \approx \alpha(0) + \eta H^2. \quad (8)$$

The fit between theory and experiment appear to be reasonable with $\alpha(0) \approx 2.22 \times 10^{-3}$ and $\eta \approx 2.22 \times 10^{-15}$ in unit of $(1/\text{kOe})^2$.

In summary, magnetolectric resistances of nanogranular Fe in $\text{TiO}_{2-\delta}$ composite were measured as a function of magnetic fields and temperatures below 50 K. The ME coupling was shown to be related to the measured resistance $R_{xy}(\mathbf{H})$ and $R_{xx}(\mathbf{H})$ for temperatures below 50 K. Thermodynamic arguments were presented to explain the ME measurement technique, see Fig. 3. In view of the fact that in our composite films of nanogranular metallic Fe spheres embedded in anatase $\text{TiO}_{2-\delta}$ we have a magnetostrictive material (nanogranular Fe spheres) and piezoelectric materials ($\text{TiO}_{2-\delta}$), the resultant composite mimics the effects of ME materials. Our result appears consistent with results observed in other

composite materials where magneto and ferroelectric material components were combined.^{1,6,7} The magneto transport properties of our composite seem to suggest that there may be potential for spintronics and/or multifunctional nanoelectronic applications.

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