Magnetoelectric Effects on Composite Nano Granular Fe/TiO$_{2-\delta}$ Films

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Employing a new experimental technique to measure magnetoelectric response functions, we have measured the magnetoelectric effect in composite films of nano granular metallic iron in anatase titanium dioxide at temperatures below 50 K. A magnetoelectric resistance is defined as the ratio of a transverse voltage to bias current as a function of the magnetic field. In contrast to the anomalous Hall resistance measured above 50 K, the magnetoelectric resistance below 50 K is significantly larger and exhibits an even symmetry with respect to magnetic field reversal \( H \rightarrow -H \). The measurement technique required attached electrodes in the plane of the film composite in order to measure voltage as a function of bias current and external magnetic field. To our knowledge, the composite films are unique in terms of showing magnetoelectric effects at low temperatures, \(< 50 \text{ K}, \text{ and anomalous Hall effects at high temperatures, } > 50 \text{ K.} \)

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Present research in new functional materials, such as magnetoelectric (ME) or multiferroic (MF) materials, have drawn a great deal of attention because of their potential applications in electronics and nano electronic device technologies\[1, 2, 3, 4, 5, 6, 7\]. Properties of ME and MF materials have been recently reviewed\[1, 2, 3, 4\]. The effects are a consequence of the coupling between electric and magnetic fields in materials. ME and MF materials have multi purposes or multi functional applications. Relatively few multiferroic materials exist in natural phases, such as TbMnO$_3$,\[1, 2\] BaFeO$_3$,\[1, 3, 4\] HoMnO$_3$,\[4\]. Composite materials combining dielectric and ferromagnetic materials have been suggested as possible ME or MF materials\[1, 2, 3, 4\]. Synthesis of composite materials having ME or MF properties are now of great laboratory interest\[1, 2, 3, 4, 5, 6\].

In our previous work\[10, 11\], oxygen deficient anatase structure titanium dioxide TiO$_{2-\delta}$ films on (100) lanthanum aluminates LaAlO$_3$ were deposited. The films 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 nano granular (NG) metallic iron (Fe) spheres in highly epitaxial oxygen deficient anatase TiO$_{2-\delta}$. The resulting composite films gave rise to some intriguing phenomena that the composite films exhibited strong carrier spin polarization of anomalous Hall effects (AHE) at \( T > 200 \text{ K} \), where the carrier density was measured to be \( n > 10^{22}/\text{cm}^3 \).

We now report magnetoelectric effects in the films for \( T < 50 \text{ K} \). These were measured by a conventional four probe Hall transport measurement technique. The transverse voltage, \( V_\perp \), was measured perpendicular to the bias current \( I \). We define the ME resistance, \( R_{xy} \), as \( R_{xy} = (V_\perp)/I \). In FIG. 1, we plot the measured \( R_{xy}(H) \) as a function of \( H \). The bias current \( I \) was fixed as the magnetic field was varied from \(-90 \text{ kOe} < H < +90 \text{ kOe}\). The bias current was applied in the film plane. FIG. 1 shows that the measured \( R_{xy}(H) \) is an even function of \( H \), where \( H \) 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 \( R_{xy}(H) \) is an even function of \( H \). Indeed, when we apply \( H \) in the film plane, where there is no possibility of Hall voltage to be measured in the film plane, \( R_{xy}(H) \) nevertheless behaves similarly to FIG. 1. Thus, for temperatures below 50 K, the composite films are characterized by a magnetoelectric effect and above 50 K by an anomalous Hall effect\[12\].

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 \( H \). This technique may be indirect if the ME film material is, for example, deposited on a nonmagnetic 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 \( H \) is applied normal to the
film planes, in the measurements of ME voltage \( \mathbf{H} \) may be applied in any direction. 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: (i) Experimentally, the Hall voltage can be measured only for \( \mathbf{H} \) applied normal to the film plane, whereas in our present technique \( \mathbf{H} \) 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. (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 \( \mathbf{H} \).

In previous work[12] the magnetoresistance \( R_{xx}(T, \mathbf{H}) \) and the Hall resistance \( R_{xy}(\mathbf{H}) \) of the composite films were measured for temperatures 4 K < \( T \) < 300 K. For \( T > 50 \) K, the anomalous Hall resistance \( (R_{xy}(\mathbf{H})) \) and 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 of \( R_{xy}(\mathbf{H}) \) dependence on \( \mathbf{H} \) was parabolic as shown in FIG. 1. Plots of \( R_{xx}(\mathbf{H}) \) show positive MR in that range of temperatures (below 50 K). We suggest that this behavior of \( R_{xy}(\mathbf{H}) \) at low temperatures may be due to ME effects in the composite films. \( R_{xy}(\mathbf{H}) \) in FIG. 1 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, 16] 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 read[1, 17]

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

\[
dF = -SdT - \mathbf{P} \cdot d\mathbf{E} - \mu_0 \mathbf{M} \cdot d\mathbf{H},
\]

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

\[
\mathcal{A}_{ij}(\mathbf{E}, \mathbf{H}, T) = -\frac{\partial^2 F(\mathbf{E}, \mathbf{H}, T)}{\partial E_i \partial H_j} = \mathcal{A}_{ij}(-\mathbf{E}, -\mathbf{H}, T),
\]

wherein \( \mathcal{A} \) is the ME pseudoscalar coupling coefficient and \( \mathcal{A}_{ij} = \epsilon j \mu_0 \) is the vacuum impedance. One may associate a uniform magnetization \( \mathbf{M} \) with a surface current per unit length \( \mathbf{K} \) via

\[
\mathbf{K}_{\text{magnetic}} = \mathbf{M} \times \mathbf{n},
\]

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

\[
\delta \mathbf{K}_{\text{ME effect}} = g \delta \mathbf{E} \times \mathbf{n}, \quad \text{where} \quad g = \frac{\alpha}{R_{\text{vac}}},
\]

In the experimental four probe configuration on the film surface,

\[
\begin{pmatrix}
\delta E_x \\
\delta E_y
\end{pmatrix} =
\begin{pmatrix}
R_{xx} & R_{xy} \\
R_{yx} & R_{yy}
\end{pmatrix} \begin{pmatrix}
\delta K_x \\
\delta K_y
\end{pmatrix}
\]

where \( R_{yx} = -R_{xy} \), yields the central result for the experimental method; i.e.

\[
\alpha = R_{\text{vac}} g = \frac{R_{xy}}{R_{xx}^2 + R_{xy}^2}.
\]

FIG. 2 exhibits typical \( \alpha(\mathbf{H}) \) data at \( T = 4 \) K obtained from \( R_{xx} \) and \( R_{xy} \) versus \( \mathbf{H} \). The theoretical fitting plot of \( \alpha(\mathbf{H}) \) was obtained according to

\[
\alpha(\mathbf{H}) \approx \alpha(0) + \eta H^2.
\]

The fit between theory and experiment appears satisfactory.

In summary, magnetoelectric resistances of nano granular Fe in TiO\(_{2-x}\) 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 $R_{xy}(H)$ and $R_{xx}(H)$ for temperatures below 50 K. Thermodynamic arguments were presented to explain the ME measurement technique, see FIG. 2. In view of the fact that in our composite films of nano granular metallic Fe spheres embedded in anatase TiO$_2$ we have a magnetostrictive material (nano granular Fe spheres) and piezoelectric materials (TiO$_2$), 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 seems to suggest that there may be potential for spintronics and/or multifunctional nano electronic applications.

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