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# Hall effect in cobalt-doped $TiO_{2-\delta}$

J. S. Higgins,* S. R. Shinde, S. B. Ogale, T. Venkatesan, and R. L. Greene
*Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland 20742-4111, USA*

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We report Hall effect measurements on thin films of cobalt-doped $TiO_{2-\delta}$. Films with a low carrier concentration ($10^{18}$–$10^{19}$/cm$^3$) yield a linear behavior in the Hall data while those having a higher carrier concentration ($10^{21}$–$10^{22}$/cm$^3$) display anomalous behavior near zero field. In the entire range of carrier concentrations, n-type conduction is observed.

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In the field of spintronics, one of the major foci is the attempt to inject spin-polarized current into existing semiconductor technology, ultimately at room temperature (RT). A possible method is the use of magnetic semiconductors, unfortunately the Curie temperatures ($T_c$) of these materials are significantly lower than RT, resulting in little practical relevance. Another possibility is to take existing semiconductor materials and dope them with magnetic impurities, called diluted magnetic semiconductors (DMS). The idea is to retain the parent compound's semiconducting properties while adding ferromagnetism to the system. $Ga_{1-x}Mn_xAs$, the most extensively studied DMS, exhibits $T_c$s as high as 160 K,[1] which, while higher than most, is still too low for practical purposes.

Recently, oxide DMS systems have shown ferromagnetism above RT. One promising oxide is $Ti_{1-x}M_xO_2$ ($M$ = magnetic dopant).[2] However, evidence shows that in the anatase Co:$TiO_{2-\delta}$ system, clustering of cobalt atoms occurs above a certain doping level (2–3%), and it is believed that the observed high-temperature ferromagnetism in such samples is manifested in these clusters.[3–5] Under specific growth and annealing conditions, samples without any obvious clusters have also been shown to exhibit ferromagnetism with a $T_c$ close to 700 K. However, whether the ferromagnetism in this system is carrier-induced or extrinsic still remains an unresolved issue. In this context, studies of the Hall effect, optical magnetic circular dichroism (O-MCD), and electric-field effect measurements have been suggested to be the clarifying experimental windows. In this work, we report our observations on the Hall effect in the Co:$TiO_{2-\delta}$ system. While our work was in progress, two groups reported on electronic transport properties in oxide DMS systems. Toyosaki *et al.*[6] reported an anomalous Hall effect in rutile Co:$TiO_{2-\delta}$, and Wang *et al.*[7] found similar effects in rutile Fe:$TiO_{2-\delta}$. These results are suggested to imply that the observed ferromagnetism influences the electronic transport in this material.

We grew thin films of anatase and rutile $Ti_{1-x}Co_xO_{2-\delta}$ ($x=0,0.02$) via pulsed laser deposition. The low cobalt concentration was chosen such that cobalt clusters would be less likely to occur. We used stoichiometric ceramic targets and deposited films through a Hall bar shadow mask onto $LaAlO_3$ substrates (for anatase films) and R-$Al_2O_3$ $(1\bar{1}02)$ substrates (for rutile films). The substrate heater temperature was 700 °C and the laser energy density was 1.8 J/cm$^2$ at 3 Hz. Magnetization measurements were made using a quantum design SQUID magnetometer and transport measurements were made using a quantum design physical property measurement system (PPMS).

Initially, we studied anatase Co:$TiO_{2-\delta}$ films. In order to obtain the anatase structure, we grew films on $LaAlO_3$ in an oxygen environment of $10^{-4}$–$10^{-8}$ Torr. At higher pressures ($P_{O2} \geqslant 10^{-6}$ Torr), the films grew in (001) anatase form and showed RT ferromagnetic behavior.[4] However, in Hall measurements, we did not observe an anomalous Hall effect (AHE). At lower pressures, the anatase structure was compromised and gave x-ray diffraction (XRD) scans different from the (001) anatase films. From the peak positions, it appeared to us that the film was rutile $TiO_2$. Hall measurements on this film exhibited a small, nonlinear behavior near zero field (not shown). These results prompted further investigation into highly oxygen deficient rutile films.

We used two approaches to increase oxygen vacancies in rutile Co:$TiO_{2-\delta}$, as the conduction electrons originate from these vacancies. Sample 1 was grown in vacuum with a base pressure of $2\times10^{-8}$ Torr. Sample 2 was deposited using a 5% hydrogen-argon mixture at 1 mTorr of pressure. X-ray diffraction (XRD), in Fig. 1, shows that sample 1 grew in the rutile (101) structure.[7,8] Sample 2 showed similar XRD patterns.

Both films display a relatively high conductivity ($\rho_{300\,K} = 2.53$ mΩ cm and 13.4 mΩ cm for sample 1 and sample 2, respectively), shown in Fig. 2. As the temperature decreases, the resistivity of sample 2 increases in an activated manner

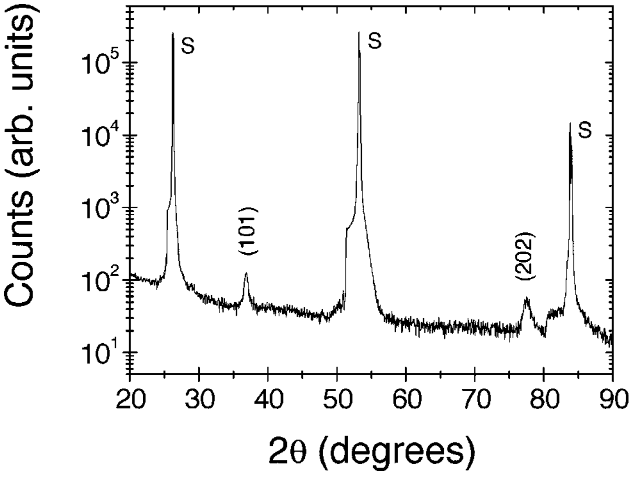

FIG. 1. XRD scan of sample 1. The scan for sample 2 is nearly identical. The peaks labeled "S" are substrate peaks.

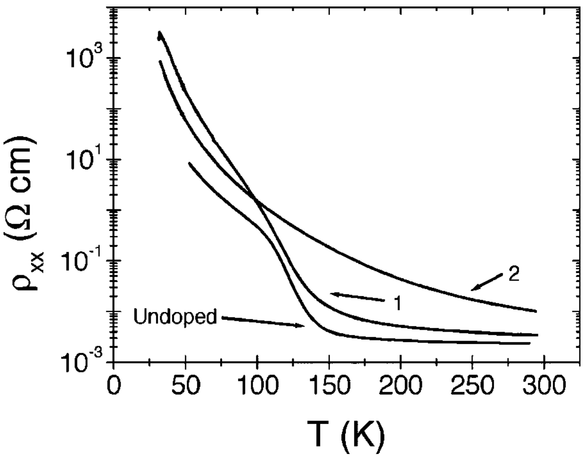

FIG. 2. Resistivity curves for sample 1, sample 2, and an undoped film.

whereas sample 1 shows an elbow near 140 K. Similar behavior was observed by Toyosaki *et al.*[6] and Wang *et al.*[7] for their films in which an AHE was observed. The resistivity of sample 1 is not an expected result due to the elbow, whereas sample 2 displays a temperature dependence similar to bulk $TiO_{2-\delta}$. The temperature behavior of sample 1, however, matches more closely with the Magnéli phase of this material ($Ti_nO_{2n-1}$).[9] This different phase of Ti-O orders in the rutile structure of $TiO_{2-\delta}$, so XRD scans may not be able to differentiate between the Magnéli phases and the rutile $TiO_2$ phase. We also grew an undoped film in the same manner as sample 1. The resistivity of this sample has a temperature dependence similar to sample 1. Therefore, the temperature behavior of the resistivity of our $TiO_{2-\delta}$ films is influenced by the oxygen deficiency rather than the magnetic dopant (cobalt).

The Hall effect arises from the Lorentz force deflecting charges moving in a perpendicularly oriented magnetic field. This establishes an electric field transverse to the current. Typically this effect is linear in field. However, in magnetic materials, the magnetic moment associated with the atoms gives rise to an additive term in the Hall equation,[10,11]

$$\rho_{xy}=\frac{E_y}{J_x}=R_0B+R_A\mu_0M_S, \qquad (1)$$

where $\rho_{xy}$ is the Hall resistivity, $E_y$ is the electric field perpendicular to the current and magnetic field, $J_x$ is the current density, $R_0$ is the ordinary Hall coefficient, $R_A$ is the anomalous Hall coefficient, $\mu_0$ is the permeability of free space, and $M_S$ is the field-dependent spontaneous magnetization of the material. This anomalous Hall term is conventionally attributed to asymmetric scattering processes involving a spin-orbit interaction between the conduction electrons and the magnetic moments in the material. At low magnetic fields, the behavior of $\rho_{xy}$ is dominated by the field dependence of $M_S$. Once the material's magnetization is saturated, the $\rho_{xy}$ field dependence is linear and due to the ordinary Hall effect. In many materials, $R_A$ shows a strong temperature dependence, which usually correlates with the electrical resistivity.

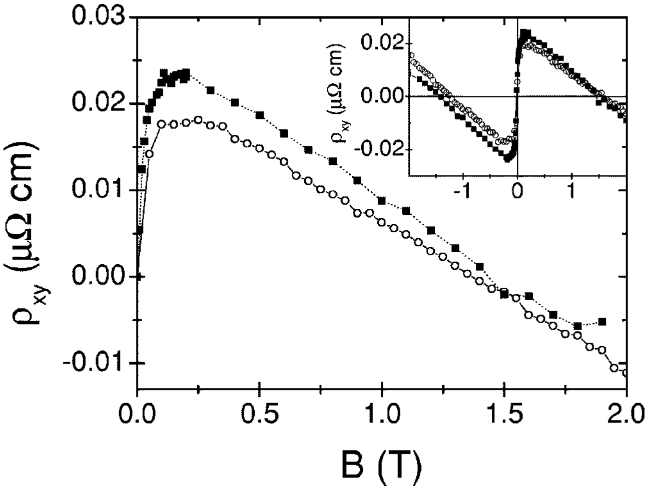

FIG. 3. Hall resistivity for sample 1. Closed symbols are taken at 300 K and open symbols are taken at 200 K. The respective resistivities are 2.54 mΩ cm and 3.22 mΩ cm.

The field dependence of $\rho_{xy}$ for sample 1 is shown in Fig. 3, measured at 300 K and 200 K. The data were obtained by a simple subtraction in order to eliminate any magnetic-field effects which are an even function of field, i.e., magnetoresistance (MR) ($\rho_{xy}=\frac{1}{2}[\rho_{xy}(H^+)-\rho_{xy}(H^-)]$). The inset shows the data before MR subtraction. These data show a sharp increase in $\rho_{xy}$ at low fields and a linear behavior at higher fields, as expected for ferromagnetic materials. The magnetic hysteresis loop for sample 1, measured with the field perpendicular to the film plane, is shown in Fig. 4(a). For comparison, the Hall data is expanded and replotted in Fig. 4(b). The field at which the magnetization saturates ($\sim$0.1 T) coincides well with the low-field behavior of the Hall data. Therefore, the rapid increase in $\rho_{xy}$ at low field can be interpreted as an AHE. It is important to note that the negative slope of the high-field Hall data indicates *n*-type carriers. This is in contrast with earlier reports,[6,7] but is expected for $TiO_{2-\delta}$. The negative slope at high fields gives an effective carrier concentration of $3.3\pm0.2\times10^{22}/\mathrm{cm}^3$ at 300 K and $3.56\pm0.02\times10^{22}/\mathrm{cm}^3$ at 200 K. The Hall data for sample 2 are shown in Fig. 5. The inset shows the data after

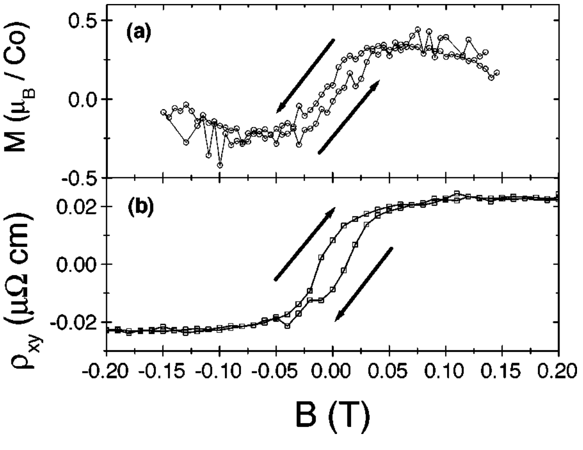

FIG. 4. (a) Magnetic hysteresis loop at 300 K for sample 1. (b) Expanded view of the Hall resistivity for sample 1 at 300 K.

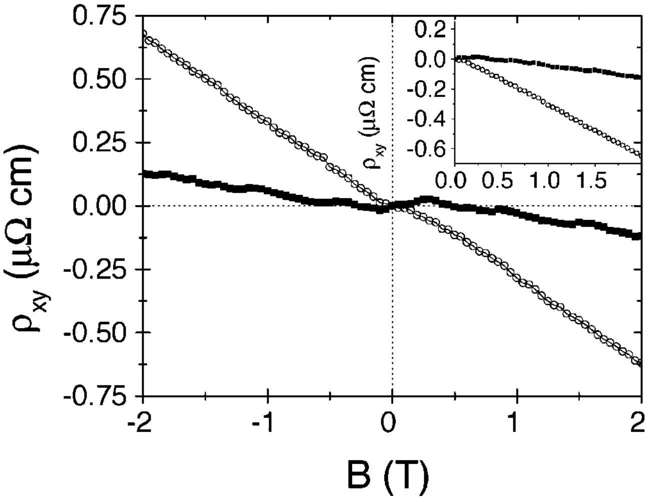

FIG. 5. Hall resistivity for sample 2 at 300 K (closed symbols) and 200 K (open symbols). The resistivities are 13.4 mΩ cm and 57.2 mΩ cm, respectively.

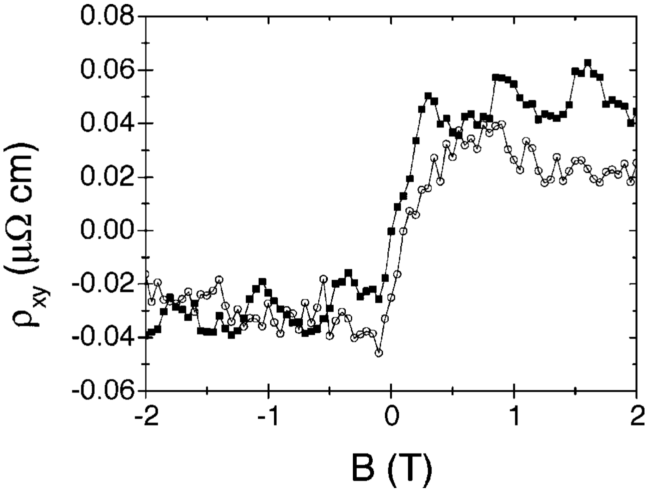

FIG. 6. Hall resistivity for sample 2 in which the normal Hall contribution is subtracted from the data. Closed symbols are taken at 300 K and open symbols are taken at 200 K.

MR subtraction. A small but noticeable effect can be seen around zero field. However, if we subtract the ordinary Hall component from the data (determined from high fields), a clear effect can be seen near the origin (Fig. 6). As in sample 1, sample 2 displays *n*-type behavior. The effective carrier concentration is $8.0 \pm 0.1 \times 10^{21}/\mathrm{cm}^3$ at 300 K and $1.837 \pm 0.005 \times 10^{21}/\mathrm{cm}^3$ at 200 K.

The rather large carrier concentration observed in these highly reduced samples raises some questions. It is known that oxygen vacancies contribute shallow donor states in $\mathrm{TiO}_{2-\delta}$. A pure rutile film of $\mathrm{TiO}_{2-\delta}$, grown by the same method as sample 1, gave a carrier concentration of $3.09 \pm 0.02 \times 10^{22}/\mathrm{cm}^3$ at RT, consistent with the cobalt-doped samples. This observed carrier density would then suggest the presence of approximately one oxygen vacancy for every unit cell ($\delta \sim 0.5$). This large carrier density, along with the resistivity behavior, suggests that Magnéli phases are present in films made using our growth conditions.

Our Hall measurements give clear evidence for an AHE in the heavily oxygen reduced samples. Is this effect intrinsic to the material, or is it a result of cobalt nanoclusters? First, the low-field data change behavior at nearly the same point that the magnetization of the sample saturates. The magnetic saturation in our films occurs at a field that is significantly lower than that for cobalt metal films ($H \sim 1.5$–2 T). Second, since the resistivities of each sample remain nearly the same for the two temperatures measured, we expect the AHE to remain relatively constant (in magnitude) for each sample, as is suggested by our measurements. While it is tempting to argue that the encouraging observation of the AHE in the cobalt doped $\mathrm{TiO}_{2-\delta}$ system *clearly* testifies to its carrier-induced or intrinsic ferromagnetic character, other material-related possibilities cannot be completely ruled out at this stage. Specifically, the question of cobalt clustering still lingers in view of the absence of a clear theoretical negation of the occurrence of the AHE for such cases. The structural and chemical microstructures formed in samples prepared under highly reduced conditions could be quite complex, especially in view of the known occurrence of Magnéli phases in the oxygen-reduced Ti-O system. Indeed, our preliminary transmission electron microscopy (TEM) observations on highly reduced samples show the presence of some ~10 nm clusters at the interface. Kim *et al.*[5] have also observed cobalt nanoclusters in their anatase Co:$\mathrm{TiO}_{2-\delta}$ films when the samples are grown in a low-pressure oxygen environment ($10^{-7}$ Torr). We propose to perform detailed studies on our samples to examine the relative proportion of dissolved and clustered cobalt to determine how the AHE could be interpreted in these terms.

In summation, we have investigated electronic transport measurements in the $\mathrm{Ti}_{0.98}\mathrm{Co}_{0.02}\mathrm{O}_{2-\delta}$ DMS system. All films displayed *n*-type behavior and an increase in carrier concentration with an increase in oxygen vacancies, which are expected behaviors in the parent compound $\mathrm{TiO}_{2-\delta}$. We have found that, among several films grown at different oxygen pressures and on different substrates, only the rutile films displaying high carrier concentrations exhibited an AHE. In spite of the observation of an AHE, it may be premature to conclude that ferromagnetism in Co:$\mathrm{TiO}_{2-\delta}$ is intrinsic.

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*Electronic address: sublime@glue.umd.edu

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