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Electronic Transport in the Oxygen Deficient Ferromagnetic Semiconducting $TiO_{2-\delta}$

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$TiO_{2-\delta}$ films were deposited on (100) Lanthanum aluminates $LaAlO_3$ substrates at a very low oxygen chamber pressure $P \approx 0.3$ mtorr employing a pulsed laser ablation deposition technique. In previous work, it was established that the oxygen deficiency in these films induced ferromagnetism. In this work it is demonstrated that this same oxygen deficiency also gives rise to semiconductor titanium ion impurity donor energy levels. Transport resistivity measurements in thin films of $TiO_{2-\delta}$ are presented as a function of temperature and magnetic field. Magneto- and Hall- resistivity is explained in terms of electronic excitations from the titanium ion donor levels into the conduction band.

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INTRODUCTION

Today, material research is focused toward a technology base whereby miniature devices operating at high speed, over a wide range of frequencies and exhibiting multifunctional properties can be developed routinely and efficiently[1, 2, 3]. Titanium dioxide TiO_2 is a well known wide band gap oxide semiconductor belonging to the group IV-VI semiconductors. It is described in terms of a model structure of Ti^{4+} and O^{2-} ions. It has large dielectric constant and dielectric anisotropy with various crystal structures. TiO_2 is known to be an n-type semiconductor with a large energy gap in the range 3 volt $< \Delta/e <$ 9 volt depending on sample preparation[4, 5, 6, 7, 8, 9, 10, 11]. Previously[12], thin $TiO_{2-\delta}$ films of thickness in the range 200 nm $< t <$ 400 nm were deposited on substrates of (100) of lanthanum aluminate $LaAlO_3$. Bulk TiO_2 does not order magnetically at room temperature. However, spontaneous magnetization in $TiO_{2-\delta}$ films[12] occurred in the temperature range 4 °K $< T <$ 880 °K. The spontaneous magnetization was attributed to the oxygen deficiency induced during the growth of the films. It was argued that oxygen deficiency caused an imbalance in the ionic charge neutrality of the film thereby creating electron donor impurity ions of Ti^{2+} and Ti^{3+} in addition to the usual Ti^{4+} ions. Ferromagnetism, i.e. net magnetic moments in the Ti^{2+} and Ti^{3+} ions, was a result of superexchange interactions between these ions via the oxygen ions. Calculations indicate that of all possible superexchange permutations, double exchange may be the most predominant interaction in view of the filled electron bands of the oxygen ions[13]. It is well known[14, 15] that such double exchange favors ferromagnetism.

Our purpose is to argue that the *same* magnetic ions and oxygen deficiency that gave rise to magnetism in $TiO_{2-\delta}$ films also play a vital role in the electronic *transport properties*. Specifically, the existence of donor Ti^{2+} and Ti^{3+} donor ions in our films allow for electronic excitations into conduction bands. The number of carriers in the conduction band varies only mildly with magnetic field and more strongly with temperature. Indeed, the measurements reported here of the Hall resistivity is approximately linear in the magnetic field and the the magneto-resistivity is only very mildly field dependent. The magneto- and Hall- resistivity have very similar temperature dependence reflecting the variation of the number of mobile electron transport carriers with temperature. Measurements of transport properties of TiO_2 films as well as the theoretical analysis are discussed in the next section. The films were deposited employing a pulsed laser ablation deposition (PLD) technique at an oxygen pressure $P \approx 0.3$ mtorr. Final arguments are presented in the concluding section.

MAGNETO-TRANSPORT MEASUREMENTS

Pulsed laser ablation deposition (PLD) techniques were employed with a weakly paramagnetic magnetic TiO_2 target. Thin films of oxygen deficient $TiO_{2-\delta}$ were produced on (100) lanthanum aluminate $LaAlO_3$ substrates. During the PLD process, the substrate temperature was fixed at $T = 700$ °C while varying the oxygen pressure in the range 0.3 mtorr $< P <$ 400 mtorr. Films deposited at $P \approx 0.3$mtorr exhibited spontaneous magnetization and were therefore selected for measurements of magneto-transport film properties. The thickness of the films were in the range 200 nm $< t <$ 400 nm. The details of the magnetic and crystallographic characteri-

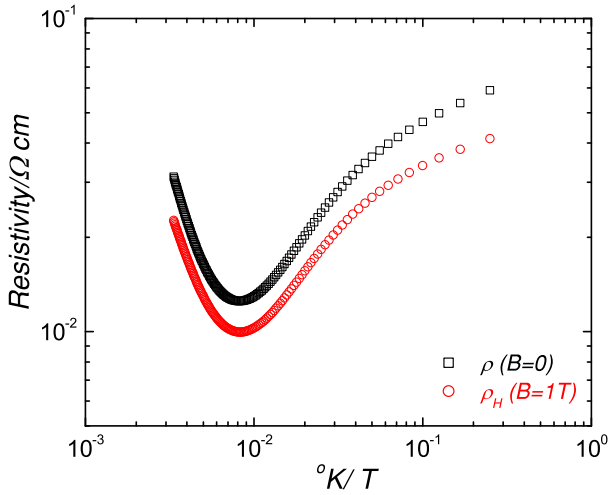

FIG. 1: Plotted on logarithmic scales are the magneto-resistivity ρ at zero magnetic field intensity and the Hall resistivity ρ_H at $B = 1$ Tesla versus inverse temperature. The temperature variations are quite similar, i.e. the Hall angle $\theta_H = \arctan(\rho_H/\rho)$ is fairly uniform in temperature.

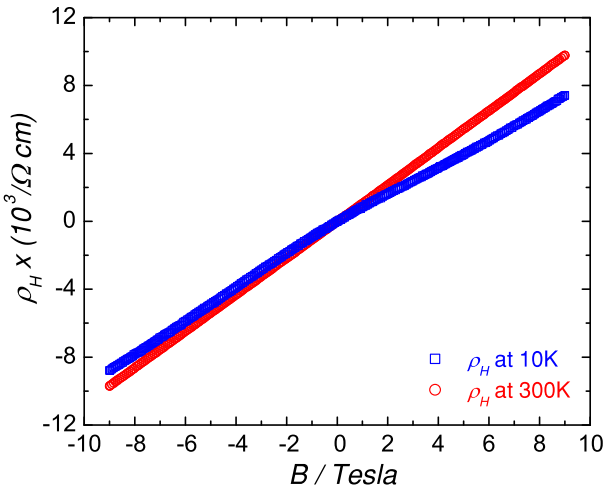

FIG. 2: Shown are plots for a film deposited at 0.3 mtorr of the Hall resistivity ρ_H for two temperatures, $T = 10\ ^oK$ and $T = 300\ ^oK$. In the high temperature regime, the linear behavior in magnetic field $\rho_H = (B/ne)$ is accurately obeyed. In the low temperature regime there are experimental deviations from linear behavior.

zation as well as other impurities and contaminants in the films were previously reported[12].

For steady currents and with the magnetic intensity $\mathbf{H}$ directed normal to the film, the resistance matrix R in the plane of the film may be written as[16]

$$\mathsf{R} = \begin{pmatrix} R_{xx} & R_{xy} \\ R_{yx} & R_{yy} \end{pmatrix} = \frac{1}{t}\begin{pmatrix} \rho & -\rho_H \\ \rho_H & \rho \end{pmatrix} \tag{1}$$

wherein ρ and ρ_H represent, respectively, the magneto-resistivity and the Hall resistivity. The resistance matrix R of the $TiO_{2-\delta}$ films was measured by a conventional four-terminal technique using a gold-plated resistance sample puck from the quantum design physical property measurement system (PPMS). In that the ferromagnetic moment per unit volume is small on the scale of applied magnetic intensities, $|\mathbf{M}| \ll |\mathbf{H}|$, the magnetic field intensity may be identified with the magnetic induction $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M})$, i.e. $\mathbf{B} \approx \mu_0\mathbf{H}$. As a consequence of such a weak magnetization $\mathbf{M}$, the anomalous Hall resistivity is negligible. The original Hall expression for ρ_H is sufficiently accurate. The magneto-resistivity is here described by the Drude model. Altogether, we may analyze the data in terms of the simple conventional expressions

$$\rho_H = \frac{B}{ne} \quad \text{and} \quad \rho = \frac{m}{ne^2\tau}\ , \tag{2}$$

wherein n is the density per unit volume of carriers in the conduction band.

In FIG. 1 is shown measurements of ρ at zero magnetic intensity and ρ_H at $\mu_0 H = 1.0$ Tesla is plotted as a function temperature T. One notes that the temperature variations of ρ and ρ_H are quite similar as they are in other semiconductors[17, 18] The Hall angle θ_H, as defined by

$$\tan\theta_H = \frac{\rho_H}{\rho} \equiv \frac{eB\tau}{m} \equiv \omega_c\tau\ , \tag{3}$$

is experimentally fairly uniform in temperature.

The hall resistivity ρ_H as a function of magnetic field were measured at fixed temperature with applied field sweeps in the range -9 Tesla $< \mu_0 H < +9$ Tesla. The data for a high and low temperature are plotted in FIG. 2. For high temperatures, the experimental data is in excellent agreement with the linear magnetic field behavior for ρ_H in Eq.(2). For low temperatures, the agreement with the linear behavior in magnetic field is only fair. Nevertheless, it is experimentally clear that the carriers are n-type and the carrier densities may be determined by

$$n = \frac{B}{e\rho_H}, \tag{4}$$

quite accurately for high temperatures and somewhat less accurately for low temperatures. The resulting variation of the density of carriers n with temperature T is shown in FIG. 3.

The two striking features of the resulting inferred density of carriers are as follows: (i) The density of carriers does not appear to vanish in the low temperature limit $T \to 0$. In fact, there appears to be a low density of carriers in the ground state $TiO_{2-\delta}$ system of approximately

$$n_0 \approx \frac{8.1 \times 10^{16}}{\text{cm}^3} \tag{5}$$

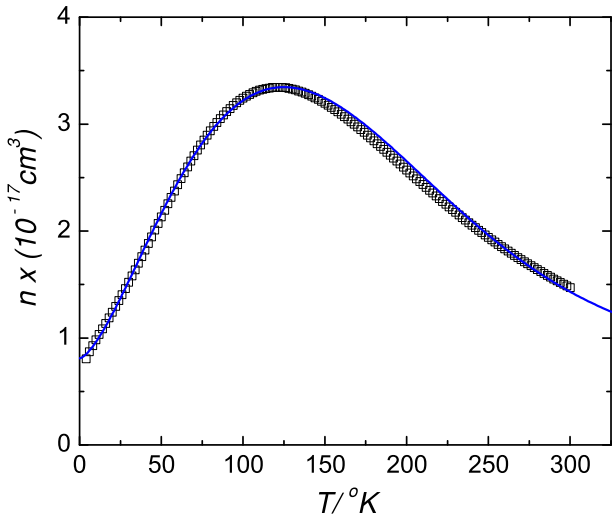

FIG. 3: Shown are the inferred density of carriers n as a function of temperature taken from Hall resistivity data in a fixed magnetic field of $B = 1$ Tesla. Also shown (solid curve) is the fit to Eqs.(5) and (6) with $\xi = 0.0065$ and $\theta = 125\ ^oK$.

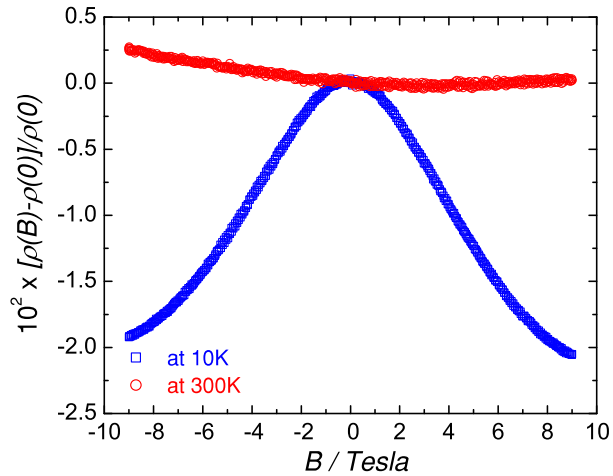

FIG. 4: The fractional change f of the magneto-resistance in Eq.(8) is plotted as the function of magnetic field. The blue squares and red circles represent, respectively, the measurements taken at temperatures $T = 10\ ^oK$ and $300\ ^oK$.

at liquid helium temperatures. This suggests that the electron chemical potential is placed very slightly into the conduction band by the Ti^{2+} donors. The double exchange mechanism lowers that part of the conduction band containing electrons with spins parallel to those localized spins producing the magnetization[19]. These effects allow for the low density of ground state carriers. (ii) The density of carriers as a function of temperature exhibits a clear maximum. We attribute this maximum in the number of carriers to the decrease of the magnetization M to values below the saturation value M_s as the temperature is raised. Theoretically, one finds from spin wave theory that $\lim_{T\to 0}[1-(M(T)/M_s)]/T^{3/2} = A_0$. For the temperature range here of experimental interest, we find that $M(T) \approx M_s[1 - A_1 T^{5/2}]$. If the rise in the carrier band lowest energy state is proportional to the the deviation of the magnetization from saturation[20], i.e. if $\Delta E \propto (M_s - M)$, then a reasonable phenomenological expression for the density of carriers, both in the ground state and in the thermally excited states, is

$$n(T) = n_0 + \frac{\xi}{\lambda_T^3} \exp\left[-\left(\frac{T}{\theta}\right)^{3/2}\right] , \qquad (6)$$

wherein the electron thermal wavelebgth

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_BT}} , \qquad (7)$$

ξ is a dimensionless constant and θ is derived from the Boltzman factor $\exp(-\Delta E/k_BT)$ on the right hand side of Eq.(6). That the density of carriers is the sum of ground state and thermally activated terms is at the heart of our phenomenology. As can be seen from the data in FIG. 3, the model gives rise to a good fit to the experimental data.

Finally in FIG. 4, the magneto-resistivity is plotted as a function of magnetic field in both the high and low temperature regimes. One may view the fractional change in magneto-resistivity,

$$f(B,T) = \frac{\rho(B,T) - \rho(0,T)}{\rho(0,T)} , \qquad (8)$$

as a measure of how strongly the carrier density n and the carrier lifetime τ vary with magnetic field. In the high temperature regime, the fractional change in the magneto-resistivity is quite small $|f_{high}| < 0.003$. In the low temperature regime the fractional change in magneto-resistivity is again fairly small $|f_{low}| < 0.022$. Altogether, the magnetic field variations of the magneto-resistivity obeys $|f| < 2.2\%$ in all regimes. That the deviations are small provides experimental support for the Hall-Drude model of electronic transport in Eq.(2) for the oxygen deficient $TiO_{2-\delta}$ ferromagnetic semiconductor.

CONCLUSION

Measurements of the magneto- and Hall- resistivity have been measured in oxygen deficient $TiO_{2-\delta}$ magnetic semiconductor films. The data can be understood on the basis of the Hall-Drude model of resistivity from mobile carriers. The anomalous magnetic moment contribution to the Hall resistivity is small in most regimes since the ferromagnetic moment resides mainly on the dilutely distributed ions Ti^{2+} and Ti^{3+} and the magnitude is small $|\mathbf{M}| \ll |\mathbf{H}|$. The Drude relation time τ is

only weakly dependent upon the magnetic field **B** and the temperature T so that both the Hall resistivity ρ_H and the normal resistivity ρ vary similarly with temperature. The experimental data can thereby be described in terms of a temperature dependent mobile carrier density $n(T)$. Apart from an expected Zeeman internal magnetic field splitting of the conduction band wherein the carrier spins align themselves parallel to the spins of the local ionic ferromagnetic moments, there also appears to be a small but finite mobile carrier density that persists even in the $T \to 0$ limit. The theory of such quantum ground state carriers in double ferromagnetic exchange semiconductors is worthy of further investigation.

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