Magnetic properties of Co-doped TiO$_2$ anatase nanopowders

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Abstract

This letter reports on the magnetic properties of Ti$_{1-x}$Co$_x$O$_2$ anatase phase nanopowders with different Co contents. It is shown that oxygen vacancies play an important role in promoting long-range ferromagnetic order in the material studied, in addition to the transition-metal doping. Furthermore, the results allow ruling out the premise of a strict connection between Co clustering and the ferromagnetism observed in the Co:TiO$_2$ anatase system.
Among the oxide based diluted magnetic semiconductor materials with potential use in the development of spintronic devices, Co-doped TiO$_2$ has attracted particular interest due to its ferromagnetic (FM) behavior well above RT for low Co doping concentrations ($T_c > 650$K)\textsuperscript{1,2,3}. Since the first report of RT ferromagnetism in the Co:TiO$_2$ system\textsuperscript{4,5} the synthesis of both anatase and rutile Co:TiO$_2$ FM films was achieved using a wide variety of deposition techniques\textsuperscript{2,3}. Magnetic moments of such films ranging from $0.16 \, \mu_B/\text{Co}$ to values as high as $2.3 \, \mu_B/\text{Co}$ have been reported\textsuperscript{2,3}. Such a wide spread of magnetic moments has raised concerns about the intrinsic nature of the FM properties of the Co:TiO$_2$ films, namely due to the possibility of existing Co secondary phases\textsuperscript{6,7,8} heterogeneities or even contamination\textsuperscript{1,9}. On the other hand, the presence of oxygen vacancies has been pointed out as a possible factor influencing the FM behaviour of the films\textsuperscript{1,10,11}; it has never been clearly shown whether it induces Co clustering and/or promotes magnetic ordering. Moreover, claims that undoped reduced TiO$_{2-\delta}$ thin films are ferromagnetic at RT\textsuperscript{12,13} has raised the question if the transition-metal doping plays any fundamental role in the FM properties observed in the Co:TiO$_2$ system. While the mechanism for ferromagnetism has not yet been definitively clarified, these controversial results have prompted many speculations that the growth conditions of the samples and/or the subsequent annealing conditions can be one of the important factors that determine their FM properties.

The main purpose of the present work is to bring further insight into the origin of the ferromagnetism observed in the Co:TiO$_2$ system by studying the effect of oxygen vacancies on the magnetic properties of highly pure Co-doped TiO$_2$ anatase nanopowders and to establish or refute the premise of a strict connection between Co clustering and the ferromagnetism observed in this material. The use of nanopowders allows circumventing the non-equilibrium conditions normally used for thin film growth and to prevent any source of contamination. The Co:TiO$_2$ nanoparticles were synthesised near equilibrium conditions by the hydrothermal process recently described by our group\textsuperscript{14}. The synthesis approach allows preparing highly pure and stable anatase Co:TiO$_2$ nanoparticles with grain sizes in the range 20-30 nm and doping concentrations up to 10 at.\%, the Co being homogeneously distributed in substitutional sites of the anatase matrix, as previously shown\textsuperscript{14}. Samples of pure TiO$_2$ anatase and with four different Co contents ($x = 0.03$, $0.07$, $0.08$ and $0.10$) were selected for this study. Co concentrations were determined by coupled plasma-optical emission spectrometry (ICP-OES). Heat treated samples were annealed at 500 $^\circ$C for 3 h in a reducing
atmosphere (N$_2$ + 5% H$_2$) at atmospheric pressure. The magnetic properties of the as-prepared Ti$_{1-x}$Co$_x$O$_2$ samples and of the reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ heat treated samples were compared. Their structure and phase purity were studied by XRD with Cu-K$_\alpha$ radiation. Magnetization measurements were performed using a SQUID magnetometer. Isothermal magnetization curves were obtained for fields up to 3 T for temperatures between 4 and 300 K. For all the samples the magnetization was measured as a function of temperature, after both zero-field-cooling (ZFC) and field-cooling (FC) procedures. AC susceptibility was measured using a Maglab 2000 magnetic characterization system. The in-phase, $\chi'$, and out-of-phase, $\chi''$, linear susceptibilities were measured at different frequencies, from 95 to 9995 Hz in the 2-300 K temperature range, with an AC driving field of 1 Oe.

All the XRD patterns recorded over undoped TiO$_{2-\delta}$ and Ti$_{1-x}$Co$_x$O$_{2-\delta}$ annealed samples match the TiO$_2$ anatase phase, confirming that the anatase structure was preserved after the heat treatment, whatever the Co content considered in this study. No traces of rutile or brookite secondary phases were observed. Furthermore, there is no sign of Co phases throughout the whole range of Co contents investigated, even when the diffracted intensity is plotted on a square root scale. Therefore, XRD patterns seem to provide evidence for the high homogeneity of doping and for the absence of secondary phases in the reduced samples. Nevertheless, the existence of very small cobalt clusters can not be ruled out since they are hardly detectable by XRD.

DC magnetization vs. temperature ($M$-$T$) curves obtained at a constant applied field of 0.5 T for the as-prepared and reduced samples are shown in figure 1. As can be seen from figure 1a, the $M$-$T$ curves for both the as-prepared undoped TiO$_2$ and reduced undoped TiO$_{2-\delta}$ samples follow a paramagnetic pattern behaviour, their $M$ values vanishing for $T > 50$ K. These particular results should be seen as a validation of the synthesis and heat treatment procedures used for nanoparticle preparation as free-contamination methods. $M$-$T$ curves for the as-prepared Ti$_{1-x}$Co$_x$O$_2$ (Fig. 1b) and reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ (Fig. 1c) nanopowders show that only the doped reduced samples exhibit $M \neq 0$ at RT. For these samples, the $M$-$T$ curves seem to result from a superposition of a paramagnetic component at low temperature and a FM-like one, the rather flat contribution suggesting that the FM component has a Curie temperature considerably higher than 300 K. The isothermal magnetization ($M$-$B$) curves obtained at several temperatures confirmed the FM-like behaviour of the reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ samples, their magnetization reaching near the saturation mag-
netization value, $M_s$, at $B = 3$ T (not shown). Figure 2 shows these $M$-$B$ curves obtained at 300 K for $B \in [-0.5, 0.5]$ T, the hysteresis loops being clearly resolved. $M_s$ values between 0.09 and 0.63 $\mu_B$/Co and high coercivities, $H_c$, ranging between 256 and 622 Oe were deduced at RT (Fig. 2, inset). No obvious relation between $M_s$ or $H_c$ and Co content was found, probably due to different oxygen vacancy concentrations induced in the samples, which are difficult to control using post-annealing processes. From the results described above two important points are worth noting here. First, it can be inferred that both cobalt and oxygen vacancies play an important role in the ferromagnetic properties observed in the Co:TiO$_2$ system studied. Second, they clearly contradict the claims that undoped TiO$_2$ may be ferromagnetic at RT by only promoting oxygen vacancies in its structure.

To gain a deeper insight into the origin of the magnetism of our reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ samples we have performed field-cooled (FC) and zero-field-cooled (ZFC) measurements of the magnetization dependence on temperature at various low applied fields (100, 50 and 10 mT). A clear branching in the ZFC-FC curves was observed for all doping concentrations, both curves tending to join not far from 300 K, and the magnetization remaining non-zero (not shown). Figure 3 shows the ZFC-FC plots acquired at $B = 10$ mT for samples with different Co content. As can be seen, samples with $x = 0.03$ (Fig. 3a), 0.07 (Fig. 3b) and 0.10 (Fig. 3d) exhibit ZFC-FC curves with similar trends, not showing any additional features usually associated with superparamagnetism (SPM) or spin-glass-like (SG) systems. Thus, the branching of the ZFC-FC curves of these samples can only be attributed to a FM-like behaviour. Cooling the samples under a magnetic field would favour the growth of domains in the direction of the applied magnetic fields and hence it would result in a higher value of magnetization as compared to the ZFC magnetization. In the case of zero-field-cooling, domain growth would be random in direction and dictated by a magneto-crystalline anisotropy. Moreover, this FM-like behaviour is consistent with the significant coercivity values measured for the samples at 300 K (Fig. 2, inset).

A different behaviour was found for the sample with $x = 0.08$ (Fig. 3c). The shape of the $M_{ZFC}(T)$ curve at 10 mT shows a well defined broad peak centred at 5.58 K which may be associated with a freezing/blocking temperature, $T_B$. From the inset of figure 3c it can be seen that $T_B$ shifts towards a lower temperature with increasing applied field and tend to vanish, which is consistent with clustering SPM or glassy-like type behaviour, probably due the existence of Co aggregates. The fact that the branching (irreversibility) between
the $M_{ZFC}$ and $M_{FC}$ curves persists for temperatures much higher than $T_B$ seems to result from the superposition of a SPM/SG contribution with a dominant FM component. The existence of a prevailing long-range FM ordered state is consistent with the high coercivity of 383 Oe measured for the Ti$_{0.92}$Co$_{0.08}$O$_{2-\delta}$ sample at 300 K.

In order to further elucidate the magnetic nature of the clusters detected in the reduced Ti$_{0.92}$Co$_{0.08}$O$_{2-\delta}$ sample, measurements of temperature dependent AC-susceptibility, $\chi_{AC}$, at different frequencies were performed. Figure 4 shows the temperature dependence of both the $\chi'(T)$ and the $\chi''(T)$ components of $\chi_{AC}$ for the Ti$_{0.92}$Co$_{0.08}$O$_{2-\delta}$ sample, taken for 5 different frequencies. Both components show a strong frequency dependence. In the $\chi'$ component, the peak position shifts to higher temperatures and peak height decreases as frequency increases (Fig. 4a, see arrow). On the other hand, for the $\chi''$ component, both the temperature and peak height increase with the increase of the frequency (Fig. 4b, see arrow), which is indicative of an intermediate relaxation process.$^{15,16}$ Peaks at $\sim$7 K were measured for $\chi'(T)$ and $\chi''(T)$ at frequencies of 95 and 9995 Hz, respectively. The peak positions agree well with the above referred feature of the ZFC-FC magnetization curves. In order to identify the dynamic behaviour of the freezing/blocking process observed in the sample, we calculated the empirical parameter$^{16}$

$$\Psi = \frac{\Delta T_B}{T_B \log_{10}(f)},$$

which represents the relative shift in $T_B$ per a frequency decade. $\Delta T_B$ stands for the difference between $T_B$ in the $\log_{10}(f)$ frequency interval. For the dependence observed in $\chi'$, $\Psi$ is found to be 0.04, higher than $\Psi$ observed in canonical SG systems ($0.001 \leq \Psi \leq 0.01$) but lower than $\Psi$ observed in SPM systems ($> 0.1$),$^{15}$ which is consistent with a cluster-glass behaviour and consequently confirms the presence of the Co-rich aggregates in the reduced Ti$_{0.92}$Co$_{0.08}$O$_{2-\delta}$ sample. The temperature dependence of AC-susceptibility for the other reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ samples was also measured in the same experimental conditions. The data clearly show a monotonic decrease of both $\chi'$ and $\chi''$ susceptibility components with the increase of temperature and no anomaly occurs (not shown). These facts reinforce the absence of any cluster formation in those samples, despite their strong FM behaviour.

In summary, we have shown that oxygen vacancies play an important role in promoting long-range FM order in bulk Co:TiO$_2$ anatase phase, in addition to the transition-metal
doping. Moreover, our results allow ruling out the premise of a strict connection between Co clustering and the ferromagnetism reported for this oxide. Despite the mechanism by which the oxygen vacancies promote ferromagnetism in Co-doped TiO$_2$ has not yet been definitively clarified, the FM order found in the reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ samples might be explained within the scope of the bound magnetic polaron (BMP) theory accordingly, when the concentration of shallow defects exceed the percolation threshold, defects such as oxygen vacancies can overlap many dopant ions to yield BMPs, which can result in FM coupling between dopant spins. A detailed study of the effect of different annealing conditions for samples with different Co content are expected to further elucidate the role of oxygen vacancies in the ferromagnetic properties of the Co:TiO$_2$ system. The work is in progress and it will be reported in a subsequent paper.

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FIG. 1: $M$-$T$ curves recorded at a constant applied field of 0.5 T for (a) as-prepared TiO$_2$ and reduced TiO$_{2-\delta}$ samples, (b) as-prepared Ti$_{1-x}$Co$_x$O$_2$ and (c) reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ samples.
FIG. 2: Hysteresis loops recorded at 300 K for different reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ samples. The inset shows the measured $M_s$ and $H_c$ values as a function of the cobalt content ($M_s$ - filled circles; $H_c$ - open circles).
FIG. 3: Field-cooled (FC) and zero-field-cooled (ZFC) magnetization curves recorded at $B = 10$ mT for different reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ nanopowder samples: (a) $x = 0.03$; (b) $x = 0.07$; (c) $x = 0.08$ and (d) $x = 0.10$. The inset in (c) shows the measured $T_B$ values as a function of the magnetic applied field for the sample with $x = 0.08$. 
FIG. 4: Temperature dependence of the (a) in-phase $\chi'$ and (b) out-of-phase $\chi''$ part of the AC susceptibility at various frequencies for the reduced Ti$_{0.92}$Co$_{0.08}$O$_{2-\delta}$ nanopowder sample. The solid arrows pass through the peak temperatures and are just guides for the eye.
XRD patterns of reduced TiO$_{2-\delta}$ and of different doped reduced Ti$_{1-x}$Co$_x$O$_{2-\delta}$ samples. The anatase diffraction lines are assigned. The bottom right-hand pattern shows the diffracted intensity plotted on a square root scale for the sample with $x = 0.08$. 