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Controlled transformation of paramagnetism to room-temperature ferromagnetism in cobalt-doped titanium dioxide

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Samples of $Co_{0.1}Ti_{0.9}O_{2-\delta}$ (anatase) prepared by the sol–gel technique are found to be paramagnetic at room temperature, with the magnetic susceptibility following Curie–Weiss law in the investigated range of 2–370 K. However, transformation from paramagnetism to room-temperature ferromagnetism (RTFM) is observed by hydrogenation of the sample at 573 K. The increase in the hydrogenation time from 1 to 6 h increases the remanance, and the Curie temperature $\simeq 470$ K is determined by extrapolation. X-ray photoelectron spectroscopy and transmission electron microscopy of the hydrogenated samples failed to detect Co nanoparticles, suggesting that the observed RTFM in the hydrogenated samples may be intrinsic. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1622991]

The recent reports[1–4] of room-temperature ferromagnetism (RTFM) in transparent semiconducting $Co_xTi_{1-x}O_{2-\delta}$ thin films for $x \geqslant 0.01$, for both anatase and rutile phases, have attracted a great deal of attention in part because of the application of such magnetic semiconductors in spintronics. However the cause of this RTFM remains controversial since more recent reports[5–8] have indicated the presence of Co nanoparticles in the thin films prepared by sputtering and pulsed laser depositions. This raises the serious possibility that the observed RTFM could be due to undetected Co nanoparticles, which because of the high Curie temperature of bulk $Co (T_c \simeq 1388$ K) could easily account for the observations. In a recent report from our laboratory,[9] it was observed that $Co_{0.1}Ti_{0.9}O_{2-\delta}$ anatase films prepared by a different technique, for example, spray pyrolysis are paramagnetic at room temperature. The temperature dependence of the magnetic susceptibility χ of this sample followed Curie–Weiss behavior, $\chi = \chi_0 + C/(T-\theta)$, with $\theta \simeq -5$ K and only for $T < 5$ K was a hysteresis loop observed. In the work presented here, we report that $Co_{0.1}Ti_{0.9}O_{2-\delta}$ (anatase) powder prepared by the sol–gel technique is also paramagnetic at room temperature and follows a similar Curie–Weiss law. However, by controlled hydrogenation of this sample at 573 K, the paramagnetic $Co_{0.1}Ti_{0.9}O_{2-\delta}$ is transformed into a ferromagnet with Curie temperature $T_c \simeq 470$ K, without any observable change in the crystal structure as revealed by x-ray diffraction. X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) studies of the hydrogenated sample failed to detect the presence of any Co nanoparticles. Details follow.

The sample of $Co_{0.1}Ti_{0.9}O_{2-\delta}$ was prepared by mixing (reacting) appropriate amounts of titanium isopropoxide (Aldrich) and cobalt nitrate (Aldrich) in ethanol. The solution was dried in an oven and the powder obtained was heated to

750 K for 1 h which yielded a dark-green sample. X-ray diffraction (XRD) of this powder confirmed the anatase form of TiO_2, with only a trace amount of rutile phase (Fig. 1). Part of this powder was used for magnetic measurements and the remainder used for 1, 3 and 6 h of hydrogenation carried out at 573 K. The hydrogen reduction setup consisted of a tubular furnace kept inside a continuously vented hood. The sample, contained in an open glass boat, was placed inside the tubular furnace and H_2 gas was passed over the sample at 573 K with the help of a gas flow control unit. Temperature and magnetic field variations of the magnetization, M, of these four samples were then measured using a commercial superconducting quantum interference device (SQUID) magnetometer. These results are presented below.

The temperature variation of χ for the as-prepared samples (prior to hydrogenation) is shown in Fig. 2 where the solid line is fit to Curie–Weiss law: $\chi = \chi_0 + C/(T-\theta)$. This variation is similar to the one reported for the sample prepared by spray pyrolysis.[9] Note that the temperatures in Fig. 2 are plotted on a log scale in order to show details of the χ vs T behavior at lower temperatures. From the Curie constant $C = 2.6 \times 10^{-3}$ emu K/g Oe and $C = N\mu^2/3k_B$ (with N the number of magnetic ions/g, k_B the Boltzmann constant and μ the magnetic moment), $\mu = 4.1\mu_B$ for the Co^{2+} ion is obtained. This magnitude of μ is consistent with the high spin state of Co^{2+}, assuming that Co^{2+} substitutes for the Ti^{4+} ions in the anatase unit cell for 10% Co doping, with the balance of the charge compensated by $O_{2-\delta}$. In the inset of Fig. 2, the linear variation of M vs H at $T = 300$ K is shown, confirming paramagnetism.

After hydrogenation at 573 K, the sample acquires RTFM. The hysteresis loops were measured for samples hydrogenated for 1, 3 and 6 h, taking a new sample for hydrogenation each time. For the 6 h sample, Fig. 3 shows the temperature variation of the remanance M_r (M at $H=0$) from 5 to 350 K for the 1, 3 and 6 h samples and in the inset the hysteresis loop measured at 350 K for the 6 h sample is shown. (Measurements for $T > 350$ K could not be made because of experimental limitations). These variations of M_r vs

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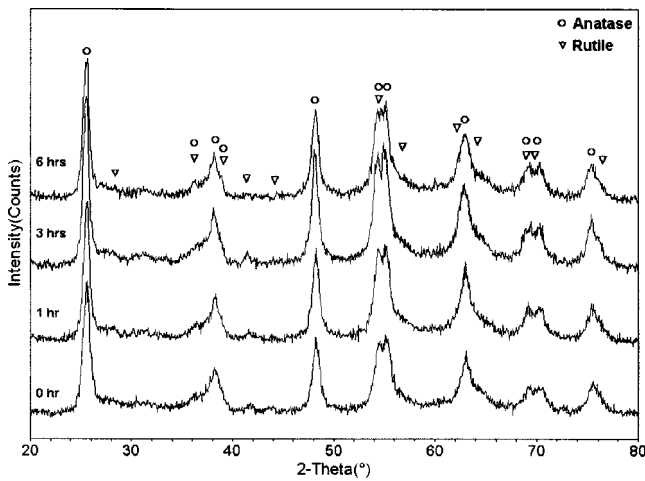
FIG. 1. X-ray diffraction patterns of the as-prepared (0 h) sample of $Co_xTi_{1-x}O_{2-\delta}$ and the sample hydrogenated for 1, 3 and 6 h at 573 K. The expected line positions for the anatase and rutile phases are shown.

FIG. 3. Temperature variation of remanance M_r of the sample hydrogenated for 1, 3 and 6 h at 573 K. The dotted lines are extrapolations, indicating $T_c \simeq 470$ K where M_r goes toward zero. In the inset, the hysteresis loop for the 6 h sample at 350 K is shown.

T are typical of a ferromagnet, with $T_c \simeq 470$ K determined from extrapolating the M_r data to zero (Fig. 3) at higher temperatures. The primary effect of increasing the hydrogenation time from 1 to 6 h is to increase M_r, demonstrating a similar source of the RTFM for the three samples. This is further confirmed by the temperature variation of the coercivity which also tends toward zero at $T_c \simeq 470$ K (Fig. 4). Thus it appears that with the increase in hydrogenation time, more of the sample is transformed into a ferromagnet. Again, it is noteworthy that this hydrogenation does not appear to affect the crystal structure since no significant differences are observed in the XRD patterns of the four samples (Fig. 1). From the widths of the XRD lines, the average particle size of the anatase phase is $\simeq 10(2)$ nm, without any major changes upon hydrogenation. Although in the extrapolation of Figs. 3 and 4, similar T_c is implied for the 1, 3 and 6 h samples, the extrapolations are clearly very approximate since M_r and H_c are often nonlinear on approach to T_c.
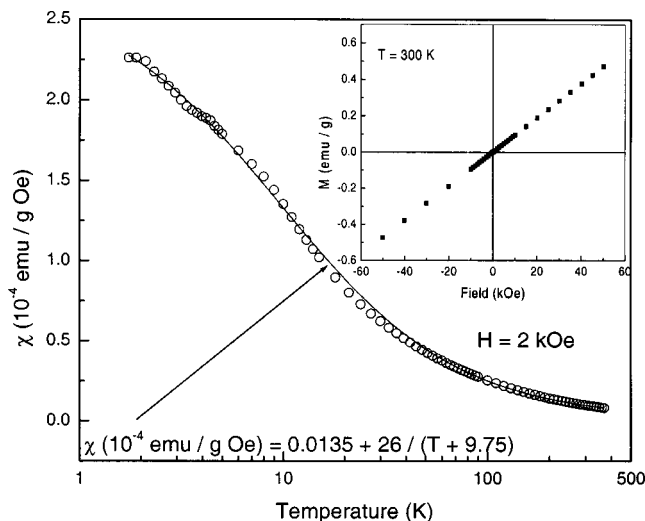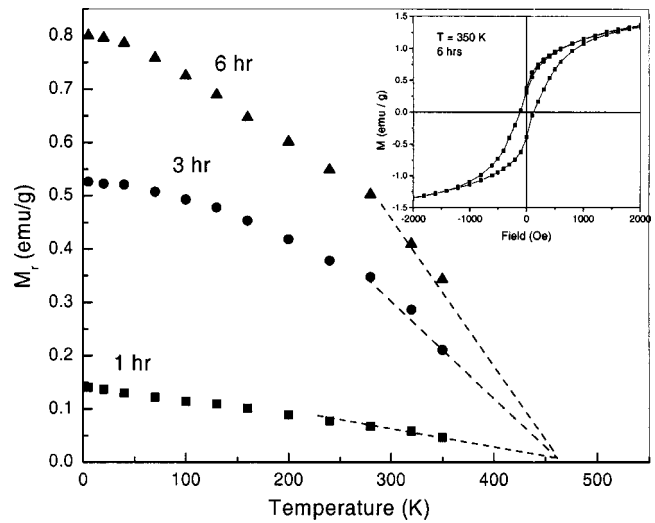
Thus an increase in T_c with an increase in hydrogenation time is not ruled out for the data in Figs. 3 and 4.

In light of the recent reports on the presence of Co nanoparticles in Co/TiO_2 films prepared by sputtering in different partial pressures of oxygen,[5,8] we carried out several experiments in addition to XRD to check for Co nanoparticles in our samples. XPS analysis of the as-prepared and the 6 h hydrogenated samples indicated that neither Ti nor Co is in a metallic state. For the hydrogenated sample, Ti $2p$ peaks were observed at 457.5 and 463.2 eV and Co $2p$ peaks at 779.5 and 795.2 eV. The corresponding values for the as-prepared samples were 458.1 and 463.8 eV for Ti $2p$ and 780.5 and 796.2 eV for Co $2p$. These magnitudes indicate 2+ and/or 3+ states of Co and 2+ and/or 4+ states for Ti (the metallic Co $2p$ peak position should be at 778.3 eV). High resolution TEM studies of the hydrogenated samples clearly showed particles of about 10 nm whose energy dispersive x-ray (EDX) spectra yielded the presence of Co, Ti
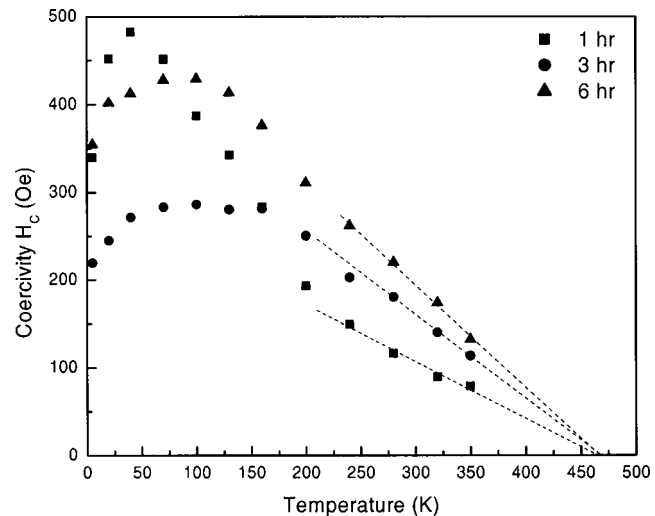

FIG. 2. Temperature dependence of the magnetic susceptibility of the as-prepared sample of $Co_xTi_{1-x}O_{2-\delta}$. The solid line is fit to the equation shown. In the inset is the M vs H variation at 300 K.

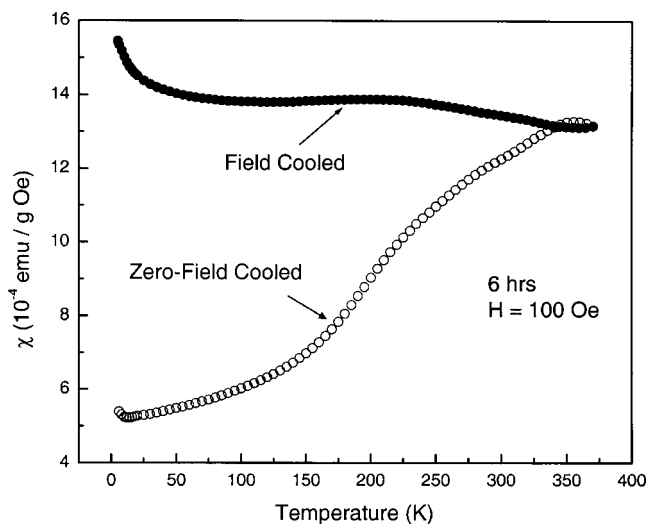FIG. 4. Same as in Fig. 3 except that the plot is for coercivity H_c.

FIG. 5. Temperature variation of the magnetic susceptibility of the 6 h sample under zero-field-cooled and field-cooled conditions.

change coupling between Co ions, and lead to intrinsic RTFM.[13] This indeed was the motivation for our hydrogenation experiments, since H_2 is likely to extract oxygen from the sample and produce oxygen holes. From our experiments described above, we were unable to detect the presence of Co nanoparticles, thus suggesting the intrinsic nature of RTFM in our hydrogenated samples. Additional experiments such as accurate measurements of electrical conductivity with time of hydrogenation would be useful to confirm these observations.

and oxygen, again ruling out the presence of metallic Co. Also, no exchange bias could be detected at 5 K in the 6 h sample when cooled from 300 to 5 K in $H = 20$ kOe, indicating the absence of a ferromagnetic/antiferromagnetic interface (e.g., Co/CoO) in the system.[10] Finally, we measured χ vs T for the 6 h sample under zero-field-cooled (ZFC) and field-cooled (FC) conditions (Fig. 5). The absence of a peak in χ for the ZFC cases, which is a signature for the blocking temperature, T_B, for Co as reported recently for thin films of Co/TiO$_2$ prepared by sputtering,[6] provides additional assurance of the absence of Co nanoparticles in our samples. The reported T_B values of Co nanoparticles of different sizes are $T_B \simeq 20$ K (3 nm), $T_B \simeq 50$ K (6 nm), $T_B \simeq 100$ K (8 nm) and $T_B \simeq 260$ K (11 nm).[11,12]

Theoretically, it has been suggested that oxygen holes near Co in $Co_x Ti_{1-x} O_{2-\delta}$ are essential to provide the ex-

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