Signature of Carrier-Induced Ferromagnetism in Ti$_{1-x}$Co$_x$O$_{2-\delta}$: Exchange Interaction Between High-Spin Co$^{2+}$ and the Ti 3d Conduction Band

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X-ray photoemission spectroscopy measurements were performed on thin-film samples of rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ to reveal the electronic structure. The Co 2p core level spectra indicate that the Co ions take the high-spin Co$^{2+}$ configuration, consistent with substitution on the Ti site. The high spin state and the shift due to the exchange splitting of the conduction band suggest strong hybridization between carriers in the Ti 3d $t_{2g}$ band and the $t_{2g}$ states of the high-spin Co$^{2+}$. These observations support the argument that room temperature ferromagnetism in Ti$_{1-x}$Co$_x$O$_{2-\delta}$ is intrinsic.

Reports of ferromagnetism at room temperature in anatase and rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ have attracted considerable attention to the class of diluted magnetic semiconductors (DMS) which exhibit colossal magnetoresistance and the anomalous hall effect among their physical properties. The maximum Curie temperature of known DMS materials is around 160 K, making reports of room temperature ferromagnetism an intrinsic effect due solely to the substitution of Co on the Ti sites or an extrinsic effect due to the presence of clustered metallic Co.

Early reports of room temperature ferromagnetism in both anatase and rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ have been made by Matsumoto et al. and others. The study of anatase combinatorial libraries concluded that the Co ions occupy the Ti cation sites and that Ti$_{1-x}$Co$_x$O$_{2-\delta}$ can be viewed as a diluted magnetic (wide-gap) semiconductor. On the other hand, it has been claimed that the ferromagnetism is attributable to Co nanoclusters in the Ti$_{1-x}$Co$_x$O$_{2-\delta}$ thin films rather than the substituted Co ions. The origin of ferromagnetism in both anatase and rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ remains the subject of intense debate.

Very recently, anomalous Hall effect measurements on systematically produced rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ films with different carrier doping levels have confirmed room temperature ferromagnetism in this material, strongly suggesting that the ferromagnetism is intrinsic and not the result of Co clustering. At the same time as the anomalous Hall effect measurements were reported a magnetization study of highly reduced rutile thin film samples revealed the co-occurrence of superparamagnetism and anomalous Hall effect, casting doubt on the reliability of the anomalous Hall effect for determining whether ferromagnetism in Ti$_{1-x}$Co$_x$O$_{2-\delta}$ is intrinsic or extrinsic. Determination of the effects of the Co impurity on the electronic structure and the electronic configuration of the Co impurity in Ti$_{1-x}$Co$_x$O$_{2-\delta}$ is thus very important for understanding the origins of the room temperature ferromagnetism in this potential DMS.

This letter reports the results of x-ray photoemission spectroscopy (XPS) measurements of the electronic structure of rutile phase Ti$_{1-x}$Co$_x$O$_{2-\delta}$ thin films. These films show Co ions uniformly substituted on the Ti cation sites without detectable clustering, supporting the idea that the observed room temperature ferromagnetism is an intrinsic property of these films.

Rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ thin films were taken from the same batches as the samples studied in Ref. where room temperature ferromagnetism was observed. These films were deposited by laser molecular beam epitaxy on TiO$_2$-buffered sapphire substrates, with $\delta$ controlled by varying the oxygen partial pressure from $10^{-4} \text{ to } 10^{-8}$ torr. This contrasts with the highly reduced films grown in high vacuum which show Co clustering. Further details of sample fabrication may be found in Ref. A JEOL JPS-9200 spectrometer, with the Al Kα line ($h\nu = 1486.6$ eV) as the x-ray source, was used to measure XPS spectra with an energy resolution of 0.6 eV under a base pressure of the order of $1 \times 10^{-10}$ Torr. Binding energies were calibrated to the Au 4f core level peaks of a gold reference sample and the intensity of all spectra shown has been normalised by peak height unless otherwise stated. To remove the effects of band bending a Nd:YAG pulsed laser was used at an energy of 3.5 eV (355 nm) with frequency 30 Hz. The maximum incident energy density at the sample surface used was 200 $\mu$J/cm$^2$ per pulse and
and Co nanoclusters \[11, 12, 13\] which show Co 2\textsuperscript{+} are significantly different from those of metallic Co. E\textsubscript{1}igration and satellite structure of the Ti signature of well-substituted Co ions at the film surface. Second, there is no discernible clustered Ti that the local electronic structure of Co impurities in peak binding energies with Co concentration, showing There is little variation of the spectral lineshapes and derived from O 2\textsuperscript{+} below the Fermi level to the valence states which are de-

The feature at 2 eV in Fig. 4 is indicative of the formation of an impurity band derived from the Co 3d orbitals and this observation implies that the donor level of the Co impurity is located just above the valence band maximum of TiO\textsubscript{2} in the dilute limit. These donor levels grow with Co doping and finally form the Co 3d impurity band. Although it is impossible to see the acceptor level using photoemission spectroscopy, the energy difference between the donor and acceptor levels is approximately given by the charge transfer energy obtained from cluster model analysis of the Co 2p spectra. The Co impurity band is located 2 eV below the Fermi level for \(x = 0.10\) and the entire band is shifted to lower binding energy by around 0.5 eV, as estimated later from Ti 2p and O 1s core level spectra. The donor level is thus located 2.5 eV below the Fermi level in the dilute limit. As this value is comparable to the charge-transfer energy of 4 eV, it is expected that the acceptor level of the Co impurity is located just above the valence band minimum. In addition, since the TiO\textsubscript{2} octahedra are edge sharing in the rutile structure, direct hopping between the substituted Co 3d \(t_{2g}\) orbital and the neighbouring Ti 3d \(t_{2g}\) orbital is expected to be large. These effects the effective pulse width was 6 ns.

\(\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}\) valence band spectra for \(x = 0, 0.01, 0.05\) and 0.10 are shown in Fig. 1 and corresponding Co 2p spectra are presented in Fig. 2. The pure TiO\textsubscript{2} valence band spectrum shows a band gap extending 3 eV below the Fermi level to the valence states which are derived from O 2p and Ti 3d states. Co substitution shifts the valence band to lower binding energy by up to 0.5 eV at \(x = 0.10\) and causes a broad peak to appear in the spectra at around 2 eV, the intensity of which increases with Co concentration. The Co 2p core level spectra exhibit a main Co 2p\textsubscript{3/2} peak at 780.1 eV, accompanied by a relatively weak satellite peak around 786 eV, with the Co 2p\textsubscript{1/2} peak appearing at 795.6 eV (\(\Delta E = 15.5\) eV). There is little variation of the spectral lineshapes and peak binding energies with Co concentration, showing that the local electronic structure of Co impurities in \(\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}\) is largely independent of \(x\).

Both the Co 2p and valence band spectra show the signature of well-substituted Co ions at the film surface. First, the Co 2p\textsubscript{3/2} binding energy, Co 2p\textsubscript{3/2}−2p\textsubscript{1/2} separation and satellite structure of the \(\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}\) spectra are significantly different from those of metallic Co and Co nanoclusters [11, 12, 13] which show Co 2p\textsubscript{3/2} at 778.3−778.5 eV, \(\Delta E = 15.0\) eV and lack any satellite structure. Second, there is no discernible clustered metallic Co component in either the valence band (cf. the dotted line in Fig. 1) or Co 2p spectra, to an estimated detection threshold of 0.5 at. %. For the observed moment of just over 1 \(\mu_B/\text{Co}\) in the \(x = 0.05\) and 0.10 films to be due to metallic Co clusters would require 65% of the total Co to cluster [14]. Such a large amount of clustered cobalt should be clearly visible in Figs. 1 and 4. Nevertheless, the possibility of a well-substituted surface with metallic Co clusters segregated to the bulk of the film can not be categorically excluded by a surface-sensitive technique like XPS. The possibility of CoO at the film surface is excluded by the large differences in the valence band (cf. the dashed line in Fig. 1) and Co 2p line shapes. In particular, while the Co 2p main peak of CoO is wide due to lattice effects, that of \(\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}\) is rather narrow because the Co ions are isolated in \(\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}\).
FIG. 3: Comparison of the Co 2p spectra from CoO [10], SrCoO₃ [14], LiCoO₂ [16] and CoS₂ [12] (solid lines) with that of Ti₀.₉Co₀.₁O₂₋₀.₅ (dots). The solid line through the Ti₀.₉Co₀.₁O₂₋₀.₅ spectrum shows the result of a cluster model calculation for CoO₆.

will enhance the exchange coupling between the Co 3d spins and the carriers in the Ti 3d conduction band [15].

Interstitial dopant substitution is a possibility in the rutile structure and to determine whether Co substitutes on the Ti site, rather than interstitially, it is necessary to determine the electronic state of the Co ion. Figure 3 shows a comparison of the measured Co 2p spectrum for x = 0.10 (dots) with the results of cluster model calculations (the solid line superimposed on the experimental data). An integral background has been added to the calculated spectrum. The cluster model calculations were performed for CoO₆ clusters and the best agreement with the measured spectrum was found for Co in the high spin Co²⁺ state, with parameters Δ = 4.0 eV, U = 6.5 eV and (pΔσ) = −1.1 eV. As interstitially substituted Co is predicted to take the low spin state [3], the observation of a high spin Co²⁺ state in the films indicates that the Co atoms are predominantly substituted on the Ti site.

Comparison with XPS spectra obtained from CoO, LiCoO₂, CoS₂ and SrCoO₃ [16, 17, 18, 19], which exhibit a variety of Co electronic states, is also helpful. These spectra, with binding energies normalised at the Co 2p₃/₂ peak, are included in Fig. 3 and show high spin Co²⁺ (CoO [10]), low spin Co³⁺ (LiCoO₂ [16]), low spin Co²⁺ (CoS₂ [18]) and low or intermediate spin Co⁴⁺ (SrCoO₃ [17, 19]). The CoO spectrum shows the strongest resemblance to the Ti₁₋ₓCoₓO₂₋ₓ spectrum, arguing that the valence state of the Co cations in Ti₁₋ₓCoₓO₂₋ₓ is the divalent high-spin ground state seen in CoO [10]. This observation confirms the conclusion drawn from comparison of the rutile Ti₁₋ₓCoₓO₂₋ₓ spectrum with cluster model calculations.

It is worth noting that while general agreement exists regarding the Co²⁺ oxidation state in both rutile and anatase Ti₁₋ₓCoₓO₂₋ₓ, there is widespread disagreement over whether the spin state is high [3, 6, 20] or low [1, 2, 21]. Most conclusions of a low spin state have been drawn from the low average magnetic moment observed in magnetization measurements. It may be difficult, however, to deduce the spin state from the magnetization due to the effects of disorder. For example, it has been suggested that interstitially substituted Co will strongly suppress the spin moment of the Co ions on the Ti site and thus the average Co magnetic moment [3].

The high spin Co²⁺ state has a partially unoccupied t₂g orbital. This unoccupied Co 3d t₂g orbital is expected to strongly hybridize with the Ti 3d t₂g orbital, permitting direct t₂g−t₂g hopping as shown in Fig. 4. Such direct hopping should enhance the exchange coupling between the Co ions, increasing the magnetic moment [15]. Indeed, the rutile phase shows a higher average magnetic moment in magnetisation measurements [3] compared to the anatase phase [1], consistent with this expectation.

Figure 4 shows Ti 2p and O 1s core level spectra for all Ti₁₋ₓCoₓO₂₋ₓ films studied (x = 0, 0.01, 0.05 and 0.10). To remove the effect of band bending at the surface, the spectra were measured under laser irradiation at 3.5 eV. Photoexcitation is known to induce a surface photovoltage which cancels band bending at the surface. Consistent with this we observed a small increase in binding energy with photoexcitation in all samples, including
pure TiO$_2$, signalling the removal of this extrinsic binding energy shift. The pure TiO$_2$ film shows a sharp, symmetric peak at a binding energy just under 530.4 eV, while the $x = 0.01$, 0.05 and 0.10 core level peaks are somewhat broadened (particularly the $x = 0.10$ sample) and are shifted by 0.13, 0.18 and 0.50 eV to lower binding energy. This binding energy shift is attributed to a chemical potential shift due to the exchange splitting of the conduction band $\delta$. The implications of this binding energy shift—the degeneracy of the Co impurity acceptor level and the conduction band minimum—were discussed earlier.

In conclusion, we have studied the electronic structure of Ti$_{1-x}$Co$_x$O$_{2-\delta}$ ($x = 0.01$, 0.05 and 0.10) using x-ray photoemission spectroscopy. The electronic state of Co in rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ is high spin Co$^{2+}$, indicating substitution of the Co ions on the Ti sites. There is no discernible metallic Co signal in the XPS spectra. The valence band spectra show the evolution of a broad impurity band derived from the Co 3$d$ orbitals located 2 eV below the Fermi level. A cluster model analysis of the Co 2$p$ core-level spectrum gives a charge transfer gap of 4 eV, while the magnitude of the exchange splitting of the conduction band is estimated to be as large as 0.5 eV from the residual Ti 2$p$ and O 1$s$ core level binding energy shift relative to pure TiO$_2$. Taking into consideration the charge transfer energy and the binding energy shift due to the exchange splitting, the acceptor level of the Co impurity is found to be almost degenerate in energy with the conduction band minimum. The degeneracy and direct $t_{2g}$ hopping, arising from hybridization between carriers in the Ti 3$d$ $t_{2g}$ band and the $t_{2g}$ states of the high-spin Co$^{2+}$, are expected to enhance the exchange coupling between the carriers and the Co 3$d$ spins and give the high Curie temperature observed in Ti$_{1-x}$Co$_x$O$_{2-\delta}$. These results are consistent with the view of rutile Ti$_{1-x}$Co$_x$O$_{2-\delta}$ as a diluted magnetic (wide-gap) semiconductor.

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