Optical band edge shift of anatase Ti$_{1-x}$Co$_x$O$_{2-\delta}$

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We report on the optical properties of magnetic cobalt-doped anatase phase titanium dioxide Ti$_{1-x}$Co$_x$O$_{2-\delta}$ films for low doping concentrations, $0 \leq x \leq 0.02$, in the spectral range $0.2 \leq \hbar\omega < 5$ eV. For well oxygenated films ($\delta \ll 1$) the optical conductivity is characterized by an absence of optical absorption below an onset of interband transitions at 3.6 eV and a blue shift of the optical band edge with increasing Co concentration. The absence of below band gap absorption is inconsistent with theoretical models which contain midgap magnetic impurity bands and suggests that strong on-site Coulomb interactions shift the O-band to Co-level optical transitions to energies above the gap.

Dilute magnetic semiconductors (DMS) offer a possible system to realize control of the charge transport by using the spin degrees of freedom or "spintronics".[1] DMS consist of magnetic impurities doped in a semiconducting host (e.g., Mn-doped GaAs). Such materials undergo a ferromagnetic phase transition below the Curie temperature, T_c which is typically $T_c \approx 100$ K.

Therefore the recent discovery of ferromagnetism with $T_c > 300$ K in cobalt-doped TiO$_2$ has generated considerable interest in this system and similar dilute magnetic oxides.[2] High-temperature magnetization measurements using vibrating sample magnetometry[3] find a $T_c \gtrsim 1180$ K for $x = 0.07$ Ti$_{1-x}$Co$_x$O$_{2-\delta}$, nearly that of bulk Co ($T_c = 1404$ K). Such a large T_c, suggests that cobalt appears in clusters rather than substitutionally and that the resulting magnetism is due to clustered Co rather than a new dilute magnetic oxide. Indeed several groups report direct observation of cobalt clusters from transmission electron microscopy.[3,4,5] In a careful study of doping dependence, Shinde *et al.*[3] find a limited solubility of cobalt in Ti$_{1-x}$Co$_x$O$_{2-\delta}$ above a concentration of $x \sim 0.02$ with Co clustering beginning thereafter. Low-doped systems, $x \leq 0.02$, exhibit a $T_c \approx 700$ K and show no evidence of Co clusters. The existence of such a high T_c for a dilute magnetic system showing no Co clustering remains puzzling. Thus, further measurements to elucidate the electronic structure and resolve the nature of the magnetism are warranted.

In this paper, we present measurements of the optical absorption of well-characterized thin films of anatase Ti$_{1-x}$Co$_x$O$_{2-\delta}$ for low Co concentrations. Interband absorption above the band gap at 3.6 eV dominates the optical spectra. We discuss the implications of these results related to band structure calculations and compare our measured band edge shift to other optical studies.

Thin film samples of Ti$_{1-x}$Co$_x$O$_{2-\delta}$ with $x = 0, 0.01$, and 0.02 were grown on SrLaGaO$_4$ (SLGO) substrates using pulsed laser deposition. Additionally, a pure TiO$_2$ film was grown on LaAlO$_3$ (LAO) for comparison. Films were deposited to ~ 1500 Å thickness with an oxygen partial pressure of 10^{-5} Torr corresponding to ($\delta \ll 1$). 4-probe dc resistance measurements exhibit insulating behavior with room temperature resistivity $\rho_{295K} \gtrsim 10\ \Omega\,$cm. X-ray diffraction (XRD) measurements[3] of both pure and doped TiO$_2$ films show peaks corresponding to those observed in bulk anatase TiO$_2$. Values of the in-plane and out-of-plane (d_{004}) lattice constants obtained from XRD are discussed later in the paper.

Room temperature transmission $\mathcal{T}(\omega)$ and reflection $\mathcal{R}(\omega)$ measurements of near-normal incidence light at frequencies from 0.25 to 5 eV are performed using a Fourier-transform spectrometer.[6,7] By numerically inverting the Fresnel formulas[8] for $\mathcal{T}$ and $\mathcal{R}$, we obtain the complex index of refraction $\tilde{n} = n + i\,k$ without the need for Kramers-Kronig analysis.[6,7] From $\tilde{n}(\omega)$, we may derive other optical constants, e.g. the optical absorption $\alpha(\omega)$ or the complex optical conductivity $\tilde{\sigma}(\omega)$.

Historically, the spectral dependence of the band edge is characterized using the absorption coefficient, $\alpha = 4\pi\,\omega\,k$, where ω is the frequency in cm^{-1} and k is the extinction coefficient ($k = \text{Im}\{\tilde{n}\}$). At photon energies above the band gap E_g, $\alpha \propto (\hbar\omega - E_g)^{1/2}$ for a direct gap while $\alpha \propto (\hbar\omega - E_g)^2$ for an indirect gap.[9] Band structure calculations[10] predict a direct gap at energies just lower than the onset of indirect transitions. In a detailed study of the absorption edge of single crystal anatase TiO$_2$, Tang *et al.*[11] report a band edge with $E_g = 3.420$ eV and tentatively assigns the transition to a direct gap. Consistent with the behavior of a direct gap, we plot α^2 versus frequency in Fig. 1. Linear fits to the high-frequency part above the band edge onset are extrapolated to zero absorption, giving the direct band gap energy E_g. Pure TiO$_2$ exhibits $E_g = 3.6$ eV, slightly larger than the value obtained by Tang *et al.*[11] With increased Co concentration x, the band edge shifts to higher frequencies, showing
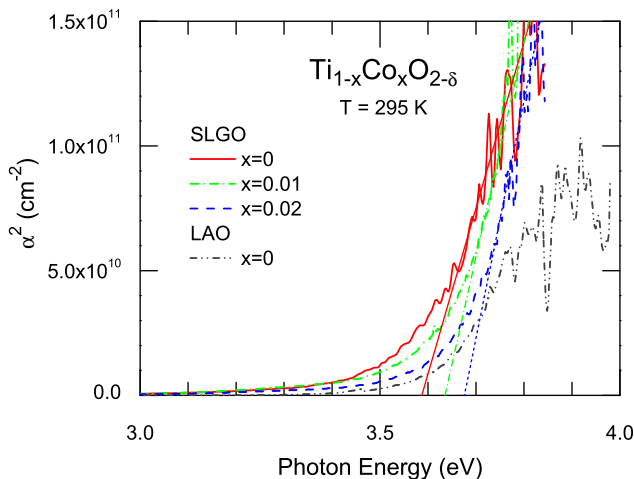
FIG. 1: Frequency dependence of the square of the absorption coefficient α at room temperature for Co concentrations $x = 0$, 0.01, and 0.02. Straight lines represent linear fits. An undoped TiO_2 sample grown on a $LaAlO_3$ substrate is shown for comparison.

FIG. 2: Frequency dependence of the real part of the optical conductivity σ_1 at room temperature for Co concentrations $x = 0$, 0.01, and 0.02. Inset expands the region just below the band edge. Band theory calculations from Yang $et\ al.$[12] are shown for $x = 0$ and $x = 0.125$.

a maximum shift of 100 meV for $x = 0.02$. Apart from a band edge tail, there appears no evidence for strong absorption at frequencies below the gap. Additionally, we compared our results to linear fits of $\sqrt{\alpha}$ consistent with an indirect gap and found that while the indirect band edge is approximately 0.4 eV lower in energy, the shift of E_g with doping remains unaffected. The exact nature of the gap (direct or indirect) remains uncertain.

While α well characterizes the band edge onset, the optical conductivity better suites to compare experimental results to predictions of band theory. In particular, the real part of the optical conductivity is given by $\sigma_1(\omega) \propto 2\,n\,k\,\omega$, where n and k are the real and imaginary part of the complex index of refraction respectively and ω is the frequency. Figure 2 shows the frequency dependence of σ_1 at room temperature for several Co concentrations. Throughout the mid-infrared (mid-IR) to visible frequency range (0.25 to 3 eV), σ_1 remains essentially zero, consistent with the negligible dc conductivity ($\sigma_{dc} \lesssim 0.1\ \Omega^{-1}\,cm^{-1}$). At frequencies larger than 3 eV, σ_1 increases rapidly corresponding to the increase in absorption as seen in Fig. 1. To further elucidate the minimal midgap conductivity, we expand the scale in the inset of Fig 2. Although no strong conductivity in the spectral range $1 \leq \hbar\omega \leq 3$ is observed, σ_1 increases slightly near the edge, although non-monotonically, with the addition of Co. Such an increase may result from the Co levels in the gap or disorder effects on the Urbach tail[11] of the fundamental absorption edge.

It is interesting to compare the optical conductivity and band edge shifts with photoluminescence (PL) spectra. PL studies[13,14,15] find a broad peak centered around 2.3 eV for anatase TiO_2. The peak in the PL spectrum is Stokes shifted 1.3 eV lower than the onset of inter-
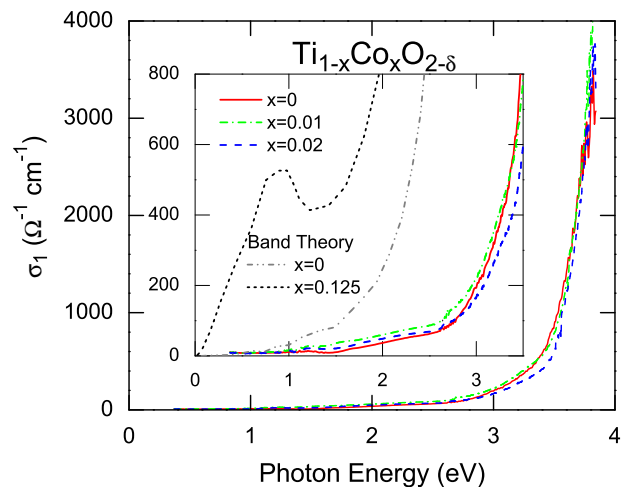
band transitions in the optical conductivity and the peak in the photoluminescence excitation spectrum.[15] Such a Stokes shift is consistent with that of a self-trapped exciton where the exciton loses energy nonradiatively to the lattice. With the addition of Co, the peak of the PL spectrum blue shifts,[13] similar to the shift observed in the band edge. Doping dependent shifts in the band edge and the PL peak are plotted together in Fig. 3 for comparison. The direct band gap energy increases monotonically with x, while the PL peak increases rather abruptly upon the addition of Co and saturates above $x = 0.02$. The saturation of the shift at higher doping concentrations is consistent with the limited solubility of Co in TiO_2 as reported earlier.[3]

Similar shifts of the band edge as observed here with Co doping are reported in a pressure-dependent optical study of single x-tal anatase TiO_2. Sekiya $et\ al.$[16] observe a blue shift of the band edge upon the application of hydrostatic pressure. For an applied pressure of 3.9 GPa, the edge shifts to higher energy by ~ 50 meV. We estimate the change in the TiO_2 lattice resulting from the hydrostatic pressure by introducing the bulk modulus, $B = -V\Delta P/\Delta V$, where V is the volume, ΔV is the change in volume, and P is the applied pressure. Taking the bulk modulus for anatase TiO_2, $B = 180$ GPa,[17] the applied hydrostatic pressure of 3.9 GPa introduces a volume decrease of 2%.

Given the blue shift of the band edge with increasing pressure or equivalently decreasing lattice size, we consider how substrate strain or the addition of cobalt may affect the lattice. Firstly the issue of substrate strain, the thin films studied suffer strain due to lattice mismatch with the substrates. For epitaxial films the initial layers grow coherently with the substrate but defects gradu-
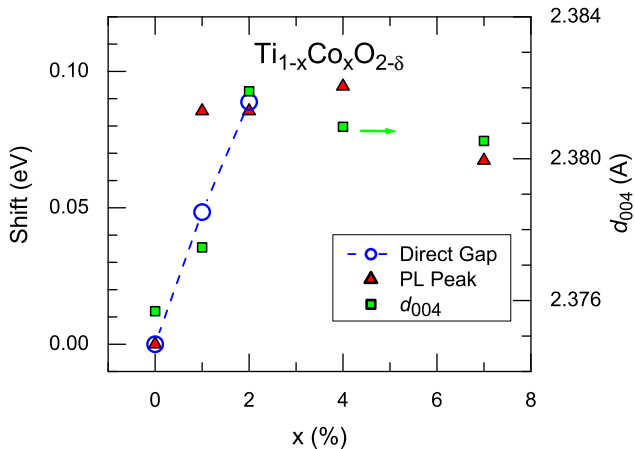
FIG. 3: Shifts with cobalt doping of the direct band edge (circles with a dashed line as a guide for the eye) and photoluminescence peak from Guha et al.[13] (triangles). For comparison the out of plane lattice constant,[3] d_{004}, for films grown on LaAlO$_3$ is plotted on a separate y-axis (squares).

ally relax the induced strain allowing the films to grow more like bulk. Values of the in-plane lattice constant, a, for bulk TiO$_2$, LAO, and SLGO are listed in Table I. Both LAO and SLGO substrates have a larger in-plane

TABLE I: Lattice parameters.

	a (Å)	d_{004} (Å)
TiO$_2$ Bulk[a]	3.7851	2.3780
LaAlO$_3$ substrate	3.79	
SrLaGaO$_4$ substrate	3.84	
TiO$_2$ film on LaAlO$_3$		2.376 [b]
TiO$_2$ film on SrLaGaO$_4$		2.367 [b]

[a]Ref. 17
[b]X-ray diffraction measurement.

lattice parameter than bulk TiO$_2$, introducing a tensile strain in the films of approximately 0.12% and 1.5%, respectively. The tensile stress tends to expand the TiO$_2$ lattice in the plane. For materials with a typical Poisson ratio, an expansion in the plane results in a reduction of the out-of-plane lattice constant, d_{004}. Indeed XRD measurements of the TiO$_2$ films reveal such a decrease of d_{004}, as shown in Table I. The film on SLGO, with the larger in-plane tensile strain, exhibits a larger reduction in d_{004} relative to bulk TiO$_2$ ($\sim 0.45\%$) compared with the film on LAO ($\sim 0.08\%$). To explore the effects of lattice strain on the band edge, the absorption of a TiO$_2$ film grown on LAO is shown in Fig. 1. The band edge of the film on LAO with the smaller in-plane lattice is blue shifted ($\gtrsim 100$ meV) relative to the TiO$_2$ film grown on SLGO, consistent with the blue shift resulting from the application of hydrostatic pressure discussed above.

To address the effect of cobalt substitution on the shift

of the band edge, we examine the change in size of the lattice with doping. Cobalt appears in the doped TiO$_2$ system in the +2 formal oxidation state as determined from x-ray absorption spectroscopy.[4] The atomic radii of Co^{2+} and Ti^{4+} are 0.82 Å and 0.69 Å, respectively.[18] Substitution of the larger Co^{2+} for Ti^{4+} should expand the lattice. XRD measurements[3] of films grown on LAO (plotted in Fig. 3) show d_{004} increases with x, saturating at about $x = 0.02$. The increase of d_{004} supports the prediction of an increase in the size of the lattice with Co doping. For the films grown on SLGO, d_{004} remains relatively constant with Co, $d_{004} = 2.3674 \pm 0.0002$ Å. An increasing (films on LAO) or relatively constant (films on SLGO) lattice size with x should result in either a red shift or no shift of the band edge. Therefore, the observed blue shift with Co doping cannot be ascribed simply to a change of the lattice size.

In order to understand the observed blue shift of the band edge, we compare our conductivity to theoretical predictions of the electronic structure of both pure and Co-doped TiO$_2$. Band structure calculations[5,19] indicate the valence band derives primarily from oxygen p-levels, the conduction band derives from the Ti d-levels, and that the crystal-field split Co d-levels fall within the energy gap.[5] These midgap states would lead to below band gap optical absorption in a non-interacting electron picture of optical transitions. Using a first-principles density-functional approach, Yang et al.[12] calculates the dielectric function for Co-doped TiO$_2$. The resulting σ_1 for $x = 0.125$ and pure TiO$_2$ are shown in the inset of Fig. 2 for comparison.

The predicted increase in conductivity below the band gap results from transitions to cobalt levels. We may estimate the effective Co number density using optical sum rules.

$$S(\omega) = \frac{2}{\pi} \int_0^\omega \sigma_1(\omega') \, d\omega' = \frac{N_{eff} \, e^2}{m} , \qquad (1)$$

where N_{eff} is the effective carrier density, which in general will be somewhat less than the cobalt number density N, e is the electron charge, and m is the electron mass. The cobalt number density N as a function of x is given by $N = \frac{fx}{V}$, where $f = 4$ is the number of Ti per unit cell and $V = 136.85$ Å^3 is the unit cell volume. Estimating N_{eff} from the predicted conductivity using Eq. 1 and comparing to N, we find that approximately 0.75 of the total Co spectral weight appears in the predicted midgap absorption feature. In estimating the Co spectral weight from the experimental data we take the difference in σ_1 due to doping to be a constant $\sim 10 \ \Omega^{-1} \, \mathrm{cm}^{-1}$ (corresponding to the error in our measurement) over the frequency range from 1 to 3 eV. Substituting into Eq. 1, we find the experimental upper bound for $N_{eff} \sim 10^{20} \ \mathrm{cm}^{-3}$. Comparing this to the number density N we find the *upper* bound on the observed density of Co is roughly 0.15 times the expected total.

The absence of below gap optical excitations in the

measured conductance may be understood either as evidence that the band calculations are not capturing the electronic structure of this material under the assumed charge state of the cobalt or that the on-site Coulomb energy, U, for adding another electron to the Co ion is large. In the second scenario the experiment implies $U \gtrsim 3$ eV.

Noting the absence of spectral weight associated with cobalt levels in the gap combined with the blue shift of the band edge, we examine the possible strong interaction effects on the optical transitions involving the Co ion. First we reject interpretations that consider the alloy within a rigid band picture. In this case a shift in the band edge results from uniform shifts of the conduction band due to the average Ti/Co potentials. Since the atomic potentials for Co are larger that those of Ti, the Ti/Co band would be lower than the pure Ti bands in TiO_2 resulting in a red shift of the band edge, contrary to observation. Indeed the rigid band approach is more appropriate for delocalized states. For the transition metal ions in $Ti_{1-x}Co_xO_{2-\delta}$ a localized picture is more appropriate. Therefore, we discuss the processes operating on the optical transitions involving the Co levels within a localized picture. A schematic view of the band structure is shown in Fig. 4. In pure TiO_2, the band edge E_g con-
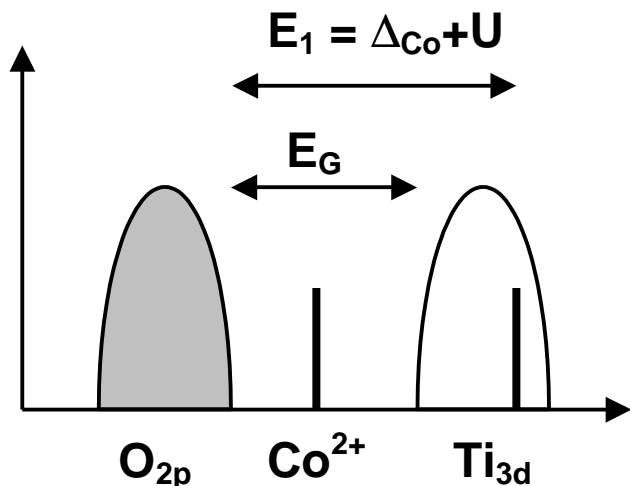

FIG. 4: Schematic energy level diagram.

sists of the energy difference between the filled O p-levels and the empty Ti d-levels with $E_g \approx 3.6$ eV (as discussed above). With the addition of cobalt, charge transfer transitions from the O p-levels to the empty localized Co^{2+} d-levels become possible. Allowed transitions from occupied Co levels to the Ti levels should be weaker since they involve a virtual transition through the O p-levels. The energy E_1 of the oxygen to cobalt transition is the sum of the charge transfer energy Δ_{Co} plus the on-site Coulomb energy U; $E_1 = \Delta_{Co} + U$. The observed absence of below band gap absorption indicates that E_1 is greater than the band gap in the alloy E'_g. This is reasonable since the U is estimated to be ~ 3 eV and the empty Co levels are ~ 2 eV above the oxygen band.[5]

We now turn our attention to the observed band edge shift, $\Delta E_g = \xi\, x$, where $\xi = 5$ eV. If the O and Ti band edges are not affected by the substitution of Co, this shift would be understood in terms of the reduction of the interband oscillator strength upon Ti dilution by Co and the extra absorption at E_1. However, this scenario leads not to a shift in the band edge but essentially to a change in the slope of α^2, contrary to observation. Therefore we conclude that O and Ti bands separate upon Co substitution. The large rate of separation ($\xi = 5$ eV) implies strong level repulsion that might occur for interstitial incorporation of the Co. This large band edge shift is especially interesting because it implies strong interactions which are also required to provide the large exchange interaction and associated high ferromagnetic T_c observed in this material.

In conclusion, optical measurements have revealed a shift of the band edge with Co doping and an absence of midgap absorption in anatase $Ti_{1-x}Co_xO_{2-\delta}$. The gap in the optical conductivity also implies strong Coulomb interaction effects on the optical processes involving the Co ions.

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