

Optical band-edge shift of cobalt-doped titanium dioxide

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Diluted magnetic oxides (DMO) offer a possible system to realize control of the charge transport by exploiting the spin degrees of freedom or "spintronics".[1] Cobalt-doped TiO_2 has generated interest as a DMO displaying room-temperature ferromagnetism, $T_c \geq 650$ K for low-doped materials. A recent study[2] reporting the importance of growth conditions on Co solubility confirms the existence of ferromagnetism in films showing no direct evidence of metallic Co clusters. The existence of such a high T_c for a diluted magnetic system remains puzzling. Thus, further measurements to elucidate the electronic structure and resolve the nature of the magnetism are warranted.

We report[3] measurements of the optical absorption of well-characterized thin films of anatase $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ exhibiting no evidence of clustering. Interband absorption above the direct band gap at 3.6 eV dominates the optical spectra. Figure 1 shows the frequency dependence of the absorption coefficient squared α^2 . Straight lines represent linear fits of α^2 to extract the direct band gap. The inset of Fig. 1 shows the shifts of the band edge with x . With increased Co concentration x , the band edge shifts to higher frequencies, showing a maximum shift of 130 meV for $x = 0.04$. Similar blueshifts occur in the photoluminescence (PL) spectra.[4]

Consideration of the real part of the optical conductivity σ_1 affords comparison of optical measurements with theoretical models. Figure 2 shows the frequency dependence of σ_1 at room temperature for several dopings. Apart from an Urbach band edge tail, there appears no evidence for absorption at frequencies in the gap. Band structure calculations[5] predict that the crystal-field split Co d -levels fall within the energy gap between the valence band

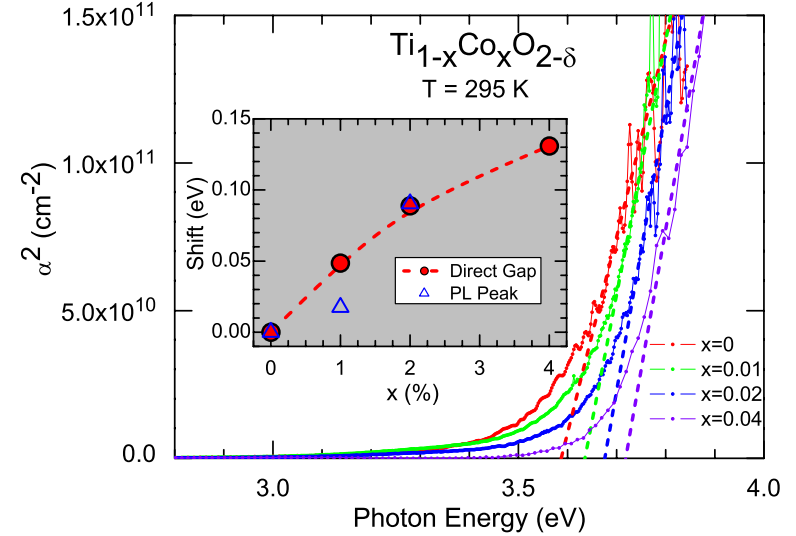


Fig. 1: Room temperature α^2 spectra for several Co concentrations. Inset shows shifts with x of the direct band edge (circles) and PL peak (triangles).

(O p -levels) and the conduction band (Ti d -levels). Figure 2 includes σ_1 (dashed curves) from band structure[5] and, in the inset, a schematic energy level diagram. The absence of below gap optical excitations in the measured conductivity may be understood either as evidence that the band calculations fail to capture the electronic structure of this material or that the on-site Coulomb energy U for adding another electron to the Co ion is large.

Our optical measurements have revealed a blue shift of the band edge with Co doping and an absence of mid gap absorp-

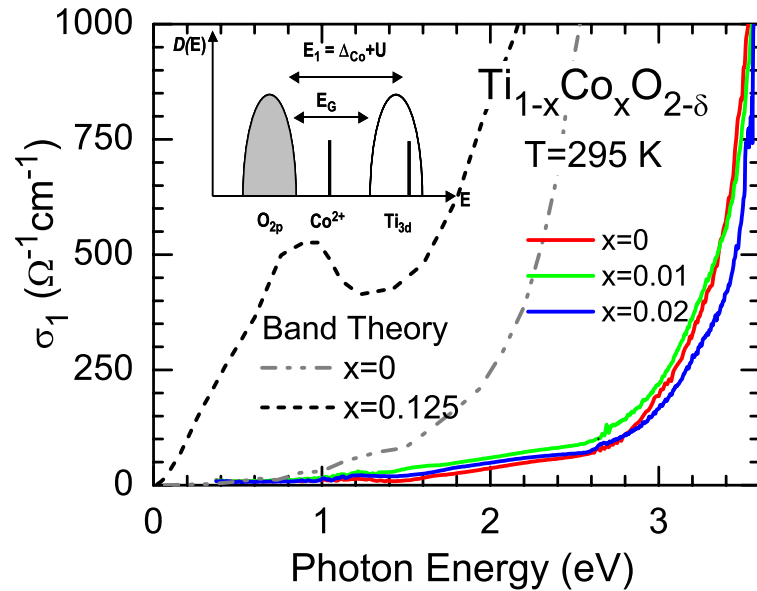


Fig. 2: Room temperature optical conductivity spectra for several Co dopings and band structure predictions[5] (dashed curves). Inset shows a schematic energy level diagram.

tion in $\text{Ti}_{1-x}\text{Co}_x\text{O}_{2-\delta}$. These observations remain inconsistent with theoretical models, which contain mid gap magnetic impurity bands, and imply strong Coulomb interaction effects on the optical processes involving the Co ions. Such strong interactions prove especially interesting as a requirement for the large exchange interaction and associated high ferromagnetic T_c observed in this material.

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