Antiferromagnetic Superexchange and Oxygen Vacancies in Co-Doped V_2O_5 Nanoparticles: A DFT+U and Experimental Study

J.Granados,[1] J.D.Rueda,[1] C.F. Eugenio,[1] A.Cardona,[1] M.A.Macías,[1] R.J.Gonzalez,[1] J.G.Ramirez,[1] and Y.R.Hernandez[1]

[1] *Universidad de los Andes*

Vanadium pentoxide (V_2O_5) nanoparticles are promising candidates for photocatalysis and neuromorphic computing due to their sensitivity to thermal processing and defect engineering. This study investigates the synthesis and characterization of V_2O_5 nanoparticles doped with low concentrations of Cobalt, with a specific focus on the critical role of calcination temperature (400–500 °C).

Experimentally, we observe a significant reduction in the optical band gap as calcination temperature increases. Raman spectroscopy and X-ray diffraction analyses reveal that the lattice parameters and vibrational modes associated with the vanadyl oxygen (O1) fluctuate between 425 and 450 °C. Magnetic characterization using Vibrating Sample Magnetometry (VSM) demonstrates temperature-dependent ferromagnetic and paramagnetic contributions in the undoped samples, whereas Co-doping is observed to suppress the net magnetization compared to the undoped, calcined baseline. To investigate the local magnetic environment, we performed DFT+U calculations on a 96-atom supercell, which indicate that Cobalt atoms preferentially integrate into lattice positions neighboring oxygen vacancies rather than occupying the vacancy sites.We attribute the observed optical shifts and structural fluctuations to the structural relaxation associated with the formation of oxygen vacancies. Accordingly, the magnetic signals in the undoped nanoparticles are identified as arising from these intrinsic defects. Finally, based on the specific lattice configuration identified by DFT, the suppression of magnetization in the doped samples is explained by an antiferromagnetic (AFM) superexchange coupling between the Co dopants and the vacancy-induced V^{4+} polarons.

References:

[1] Correal, S., Hernández-Gómez, D., Esquivel, A.S. et al. Tuning electronic and magnetic properties through disorder in V2O5 nanoparticles. Sci Rep 13, 6752 (2023).