

Supplementary Material

Cobalt Doping Effects in Zinc Oxide: A Combined Experimental and Ab Initio Approach

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1. Assessing Half-Metallic Behavior in ZnO-Cd-Co Supercell: Theoretical Prediction vs. Experimental Observations

The discrepancy between the theoretical prediction of a half-metallic behavior and the experimental observation of ZnO-Cd-Co as a semiconductor may be attributed more to limitations or approximations in the computational approach rather than being solely attributed to an actual physical effect. This error in band theory prediction is intrinsic to the approximations to the exchange and correlation potential. This is expected from the potentials used (standard LDA/GGA) since they fail to properly describe energy gap on metallic oxides (with and without impurities).

Even if the approximation does not hold exactly a rigorous description of the localization effects. The predicted values for the EFG on Cd site on ZnO-Cd and ZnO-Cd-Co are in a good agreement with Perturbed Angular Correlation (PAC) measurements for pure and Co doped ZnO, where they show a very similar EFG on the Cd site. This indicates that our theoretical prediction is adequate, even though Co doping in the ZnO-Cd changes the DOS, hybridization between O with Zn and O with Co are not significantly distinct, e.g. Cd-O-Zn and Cd-O-Co bindings are similar.

For clarification purposes, Figure S1 illustrates the DOS of selected atoms based on their crystal positions relative to Cd. Notably, the distant Oxygen from Cd and Co exhibits densities similar to those observed in the ZnO pure cell (which presents semiconductor behavior like ZnO-Cd), indicating a small defect-defect interaction despite two impurities in the supercell. Conversely, O_{Cd-Co} predominantly exhibits its p sublevels within the characteristic band of pure ZnO (Figure S2 and Figure S3), hybridized with specific states introduced by Cd and Co, suggesting that the Oxygen atom plays an important role in bridging these two impurities (smaller graph in Figure S1).

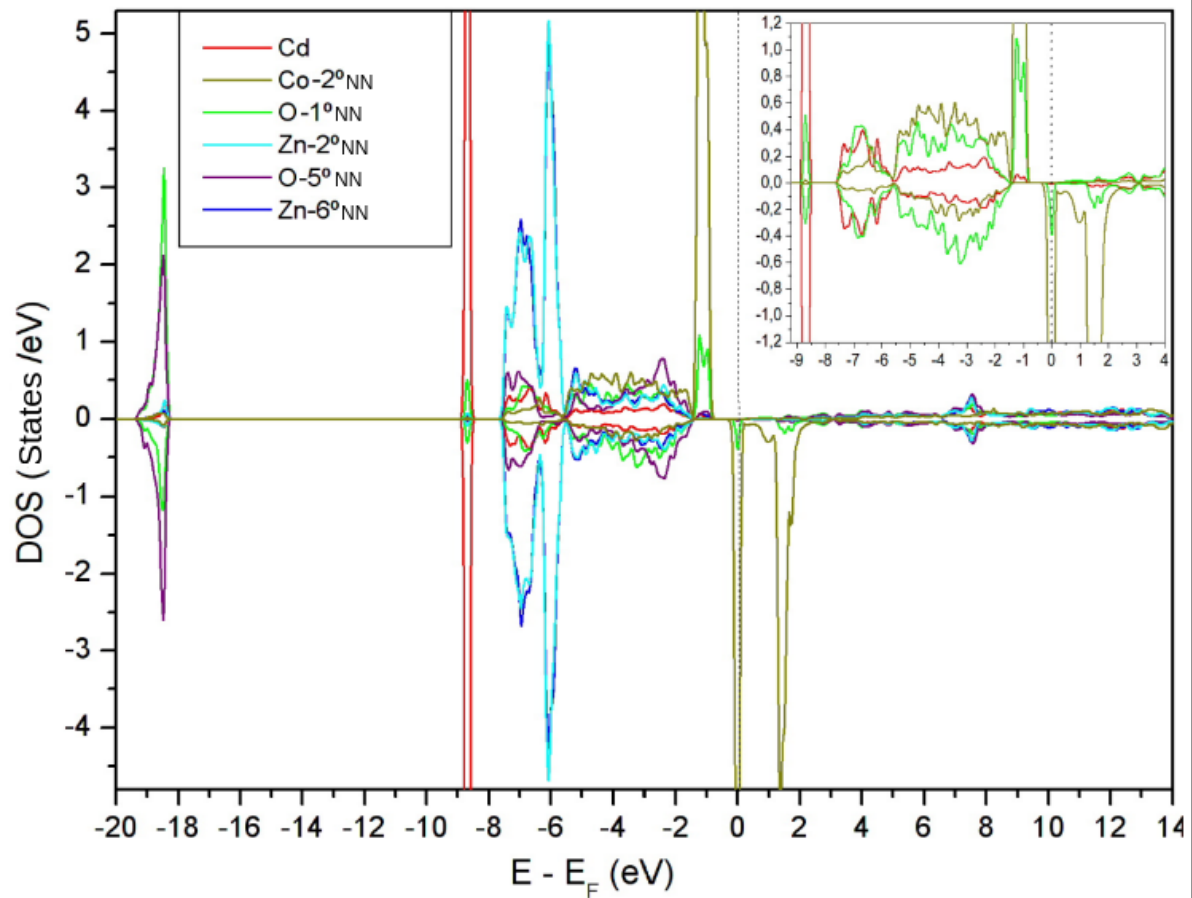


Figure S1. Calculated project DOS on some ions for ZnO-Cd-Co SC, predicted by GGA-PBE functional. The Co, Zn and O ions nearest neighbors (NN) to Cd are included for comparison purposes. The Fermi level is indicated by the vertical dot line at 0 eV.

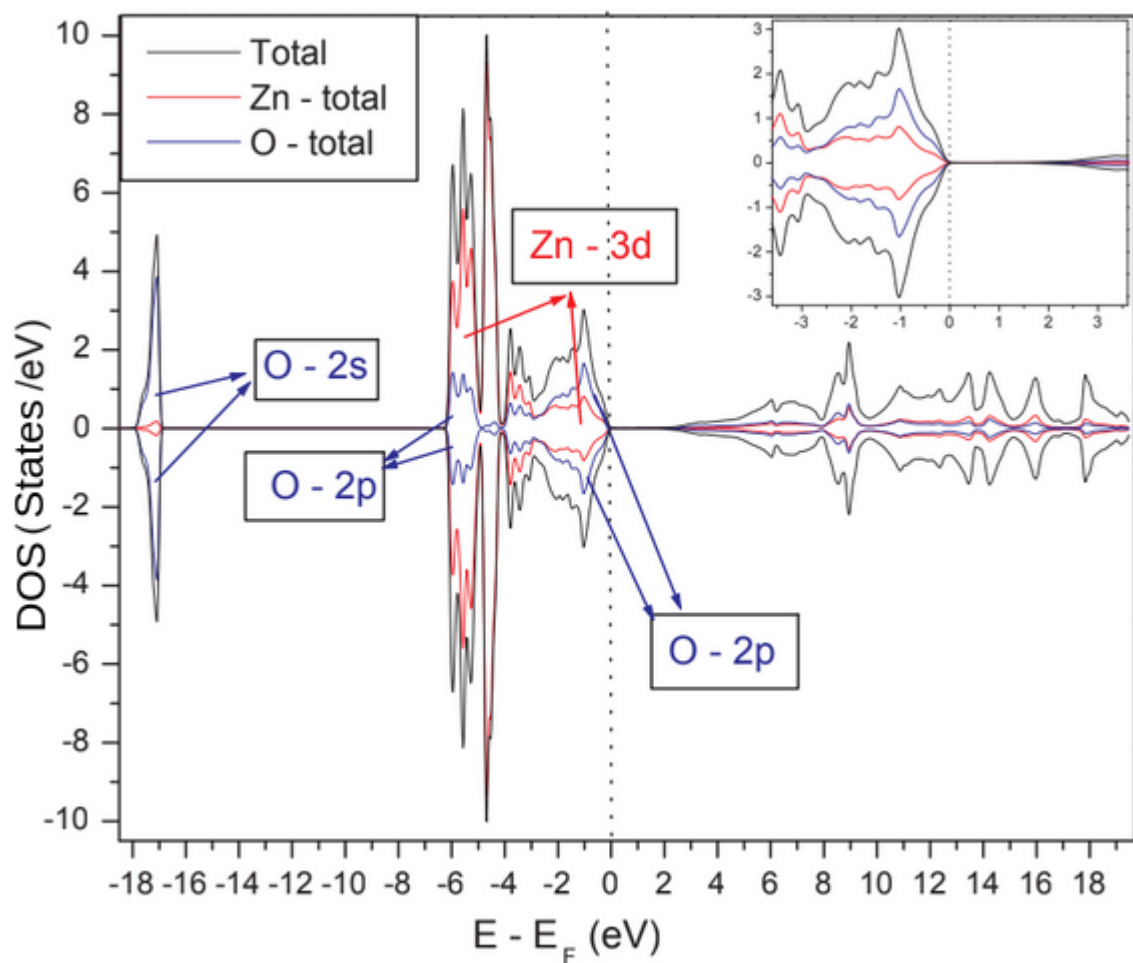
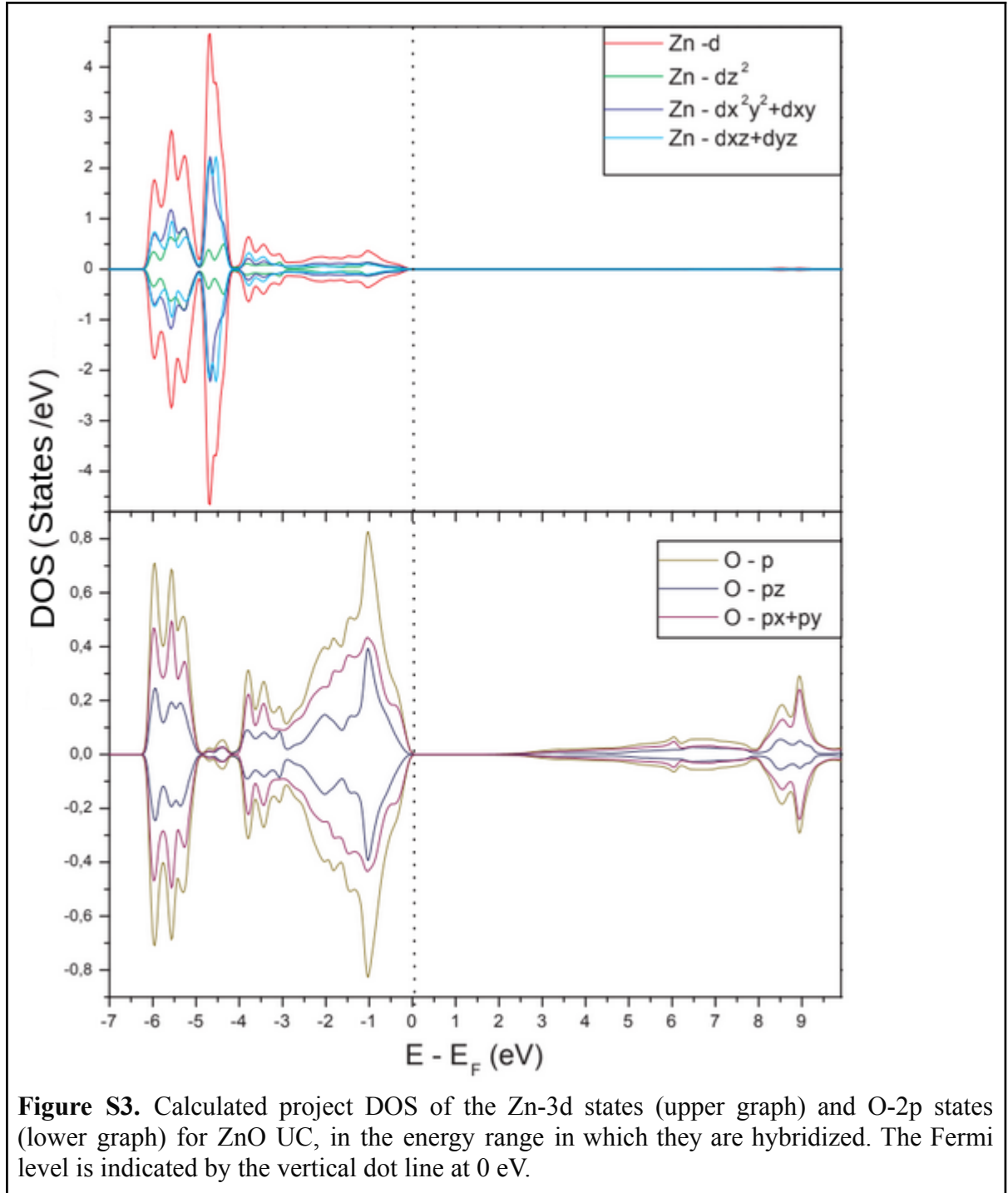


Figure S2. Calculated total DOS and project DOS of the Cd and Co ions for ZnO UC, predicted by GGA-PBE functional. In the smaller graphs, the states of each atom are identified. The Fermi level is indicated by the vertical dot line at 0 eV.



Furthermore, the standard DFT approach has been successfully applied in the prediction of the electric hyperfine properties for a broader range of oxide systems [18, 62-64], consolidating a benchmark set that validates the use of standard local or semilocal functionals.