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Comment on "Intrinsic n-type Behavior in Transparent Conducting Oxides

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Ágoston *et al.* Reply: In a recent work we studied the oxygen vacancy in In_2O_3 , SnO_2 , and ZnO by means of hybrid-functional calculations within density functional theory [1]. In particular, our interpretation of the intrinsic electron donation mechanism in the transparent conducting oxide In_2O_3 has been questioned by Lany and Zunger [2]. In the following we reply to their comments.

Lany and Zunger argue that our results indicate a deep color center behavior of the oxygen vacancy in In_2O_3 , because the defect state of a shallow defect should be resonant well above the conduction band minimum as in extrinsically doped transparent conducting oxides (TCO). In contrast to extrinsically doped TCOs like $\text{SnO}_2:\text{F}$ or $\text{In}_2\text{O}_3:\text{Sn}$, the oxygen vacancy state does in fact produce a much deeper state which, however, may still allow a thermal ionization of the defect if the subsequent structural relaxation of the defect provides a sufficient energy gain in the system.

While we find that the oxygen vacancy is a shallow donor in In_2O_3 we did not claim that the V_{O} is able to produce a pronounced Burnstein-Moss shift. This effect has mostly been observed for extrinsically doped TCOs. Moreover, the occurrence of a shift in nominally undoped In_2O_3 together with measured electron concentrations $>10^{20} \text{ cm}^{-3}$ [3] cannot be explained by the oxygen vacancies alone. We believe that such effects are likely to be produced by hydrogen defects which has recently been suggested also for In_2O_3 [4].

According to Lany and Zunger, it is the “biased” choice of the range separation parameters of our hybrid density functional calculations which results in equilibrium transitions close to the conduction band minimum. We have adopted the range separation parameters for the different materials which reproduce the experimentally observed trends for the size of the band gaps going from SnO_2 via

In_2O_3 to ZnO , which cannot be reproduced by a single hybrid functional. Moreover, in the case of In_2O_3 the actual value of the band gap is still a matter of debate and the published data span a range from 2.67 eV to maximally 3.1 eV [5–7]. The additional results which Lany and Zunger have provided in their comment and using quasi-particle corrections leads undoubtedly to the conclusion that the ionization energy of the vacancy should be increased in that case. We note, however, that the final conclusion still depends on the actual choice of the band gap.

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