

Comment on “Intrinsic n -type Behavior in Transparent Conducting Oxides: A Comparative Hybrid-Functional Study of In_2O_3 , SnO_2 , and ZnO ”

The origin of n -type conductivity in nominally undoped transparent conducting oxides was addressed in a recent Letter [1]. Based on hybrid-functional calculations, Agoston *et al.* [1] predict shallow donor levels for oxygen vacancies (V_O) in In_2O_3 and SnO_2 , thereby contradicting earlier theoretical work [2]. We show here that correct interpretation of the hybrid-functional results and consideration of quasiparticle energy corrections lead to the conclusion that V_O is a deep donor, unlikely to release free electrons at room temperature.

(i) *Color-center vs shallow donor behavior of the neutral V_O .*—In Ref. [1], Agoston *et al.* claim that the hybrid-functional results predict a shallow donor state instead of the deep color-center behavior we found in Ref. [2]. A color center forms an occupied defect state inside the gap, whereas the primary defect state of shallow donors like $\text{In}_2\text{O}_3:\text{Sn}_{\text{In}}$ or $\text{SnO}_2:\text{F}_O$ is formed as a resonance *above* the conduction band minimum (CBM) [3], thereby allowing for the Moss-Burstein shift ($\Delta E = E_F - E_C$) that is typical for transparent conducting oxides. Furthermore, color centers cause a localized defect wave function, but shallow donors have delocalized (effective-mass like) states. Using the same method of calculation [4,5] as Ref. [1], we show here that in the HSE06 hybrid-functional, the defect state of V_O in In_2O_3 has a localized wave function [Fig. 1(a)] and a single-particle energy at 0.4 eV *below* the CBM [Fig. 1(b), cp. also Fig. 2 in Ref. [1]]. Thus, the HSE06 hybrid functional actually confirms the color-center behavior of V_O . This result is not affected by supercell finite-size effects [see Fig. 1(b)].

(ii) *Biased choice of different hybrid functionals for different oxides.*—In a study combining optical absorption measurements and GW theory, King *et al.* [6] recently determined for In_2O_3 a revised band gap $E_g = 2.93$ eV at room temperature (about 3.1 eV at 0 K), which, in contrast to earlier estimates, is smaller than that of ZnO . In their defect calculations, Agoston *et al.* [1] used the HSE06 functional for In_2O_3 , but the PBE0 functional for ZnO and SnO_2 . As seen in Table I, this choice was needed to reconcile the revised trend of band gap energies among the different

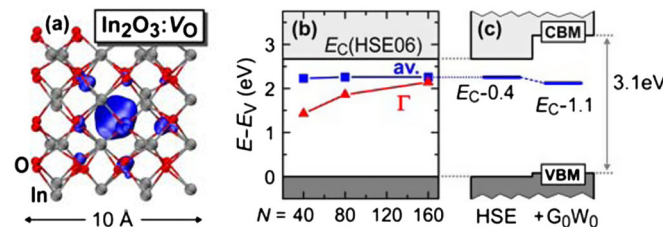


FIG. 1 (color online). Hybrid-functional (HSE06) results for the occupied V_O^0 defect state in In_2O_3 . (a) Wave function localization. (b) Single-particle energy in N -atom supercells, determined as the Brillouin-zone average (av.) and at the Γ point. (c) G_0W_0 quasiparticle energy corrections.

TABLE I. Trends of E_g (eV) in hybrid-functional theory and experiment. The oxide-functional combinations used in Ref. [1] are highlighted.

	ZnO	In_2O_3	SnO_2
HSE06	2.48	2.67	2.91
PBE0	3.14	3.35	3.60
Experiment	3.44	~ 3.1	3.63

oxides. However, this choice introduces a bias towards a shallower thermal ionization energy of V_O in In_2O_3 (being close to zero) compared to the other oxides, because the HSE06 functional predicts the (structurally relaxed) $2+/0$ donor transitions of V_O closer to the CBM than the PBE0 functional, as shown for the case of ZnO in Ref. [7].

(iii) *Quasiparticle energy corrections increase the thermal V_O ionization energies.*—Agoston *et al.* [1] claim that their hybrid-functional calculations are superior to previous works based on standard density functional theory (DFT) with empirical band gap corrections [2]. However, while hybrid functionals undoubtedly improve over *uncorrected* DFT, they may not improve over previous *corrected* DFT results. In order to test this, we calculated GW quasiparticle energy corrections for the V_O defect levels in ZnO [8], and found an increase of the thermal ionization energy of V_O by about 1 eV relative to the HSE06 functional. As shown in Fig. 1(c), we find here that in In_2O_3 , the GW quasiparticle energy of the occupied V_O defect state lies as deep as 1.1 eV below the CBM. The respective GW corrected $2+/0$ transition level (thermal ionization energy) at $E_C - 0.7$ eV is too deep to create free carriers at room temperature. Note, however, that the band gap reduction with increasing temperature reduces the ionization energy [2], leading to the release of carriers when O vacancies are generated thermally at high temperatures.

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