Supplemental Material

Antidoping in Insulators and Semiconductors Having Intermediate Bands with Trapped Carriers

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Computational Methods

All DFT calculations are performed using the plane-wave projector-augmented wave method [23], as implemented in the Vienna *ab initio* simulation package [24,25]. To obtain reliable optimized structures, the maximum residual force is less than 0.01 eV/Å and energies are converged to within 10^{-5} eV. An energy cut-off of 500 eV was used in all cases. The generalized gradient approximation to exchange and correlation of Perdew, Burke and Ernzerhof (PBE) [26] is used for DFT level. We note that standard DFT exchange and correlation functionals generally fail to predict a localized polaron state because of the "delocalization error" whereby the convex nonlinear downward bowing of the total energy with respect to electron occupation number leads to energy gain by spreading the wavefunction [27]. To overcome such notorious self-interaction error, we implement a "cancellation of non-linearity" (CONL) approach by the combination of DFT+U and non-local external potentials method from Ref. [13,28]. We add electron potentials on certain *lm* decomposed orbitals on top of the DFT+U framework, in which Dudarev's approach is chosen for d states of Fe, Ir and Ni ($U - J$ = 4 eV). For hole doping, the corresponding electron state potential is given by

$$\mathrm{V}_h = \lambda_h(1 - n_{m,\sigma}/n_{host}), \quad (1)$$

where and denote the occupation of the *m* sublevel of spin , and the occupation of the host material without doping. The parameter can be tuned to fulfil the linearity of $E(N)$, i.e., the generalized Koopmans condition:

$$\Delta_{nk} = E(N\text{-}1) - E(N) + eig(N) = 0, \quad (2)$$

where $E(N\text{-}1) - E(N)$ denotes the total energy cost to remove an electron from the electron-doped system, and $eig(N)$ the single-particle energy of the highest occupied state in the electron-doped system. Based on previous experiences, here we choose = 4.5 eV for O-2p orbital, which is sufficient to predict a localized nature of wavefunction upon doping and well consistent with the generalized Koopmans condition Eq. (2) [13,27].

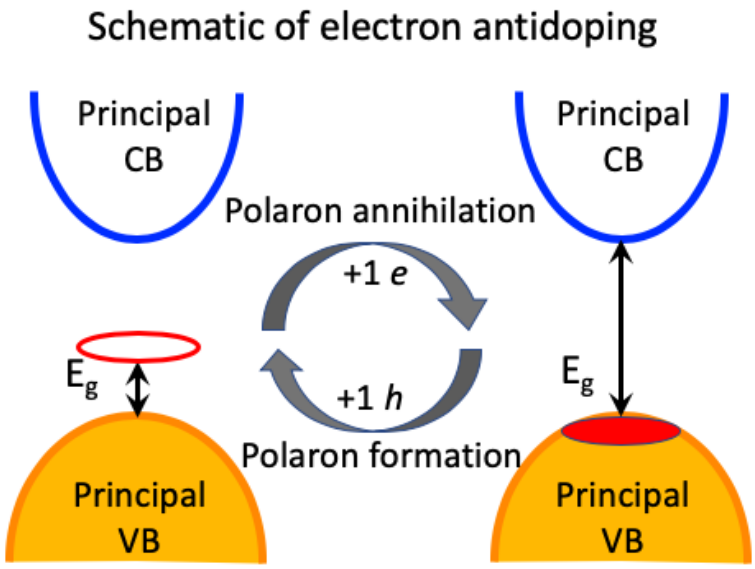

Fig. S1: Schematic illustration of electron antidoping as polaron annihilation. Doping by electron the empty hole polaron state (red ellipse) displaces this band into the valence band thus increasing the occupied-unoccupied band gap E_g.

References

[23] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[24] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[25] G. Kresse and J. Furthmuller, Comp Mater Sci **6**, 15 (1996).
[26] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[27] S. Lany, physica status solidi (b) **248**, 1052 (2011).
[28] S. Lany, H. Raebiger, and A. Zunger, Physical Review B **77**, 241201 (2008).