Polaronic hole localization and multiple hole binding of acceptors in oxide wide-gap semiconductors

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Acceptor-bound holes in oxides often localize asymmetrically at one out of several equivalent oxygen ligands. Whereas Hartree-Fock (HF) theory overly favors such symmetry-broken polaronic hole localization in oxides, standard local-density (LD) calculations suffer from spurious delocalization among several oxygen sites. These opposite biases originate from the opposite curvatures of the energy as a function of the fractional occupation number n, i.e., $d^2E/dn^2<0$ in HF and $d^2E/dn^2>0$ in LD. We recover the correct linear behavior, $d^2E/dn^2=0$, that removes the (de) localization bias by formulating a generalized Koopmans condition. The correct description of oxygen hole localization reveals that the cation-site nominal single acceptors in ZnO, In_2O_3, and SnO_2 can bind multiple holes.

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I. INTRODUCTION

Experimental evidence for cation-site acceptors in wide-gap oxides demonstrates that holes often lock into individual oxygen ligands instead of being distributed over all symmetry-equivalent oxygen sites, e.g., in case of Al_{Si} in SiO_2 or Li_{Zn} in ZnO.[1–4] Formally, the hole binding can be described by the change in the oxidation state of individual O atoms 1ForTj6.980OnO.

rameters for the band-gap corrected calculations are determined via Eq. (1) as 4.8, 4.3, and 4.1 eV for ZnO, In_2O_3, and SnO_2, respectively. Thus, the values found for λ_{hs} are comparable among the three oxides studied here. We further tested for several cases the variations between different impurities in the same oxide and found them to be even smaller, introducing uncertainties in the calculated acceptor levels of less than 0.1 eV.

We see in Table I that the acceptor level of Li at 0.9 eV above the VBM is now closer to the experimental value of 0.8 eV (Ref. 31) compared to the calculation without the band-gap correction. The latter underestimates the acceptor binding energy mainly because of overestimated *p*-*d* repulsion between the valence-band states and the Zn *d* shell, placing the VBM too high[28] relative to the Li acceptor state. In the band-gap corrected calculation, the Zn *d* energies are corrected by GGA+*U*.[25] We find that all acceptor states are localized in a single O *p* orbital (see Fig. 3) and that the ionization energies are relatively deep, $\varepsilon_A \geq 0.6$ eV (Table I), thereby strongly questioning the suitability of cation-site acceptors in ZnO, In_2O_3, and SnO_2 for the purpose to achieve *p*-type transparent conductive oxides.[11,12] In addition to the $\varepsilon(0/-)$ acceptor level, we observe also a very deep $\varepsilon(+/0)$ donor level closer to the VBM, which results from the binding of a second hole. When two holes are bound in the positive charge state, the two individual one-particle states are each localized on only a single O *p* orbital, as shown for B_{Sn}^{+} in SnO_2 (Fig. 3(d)). In case of the strongly size-mismatched impurities Be_{In} in In_2O_3 and for B_{Sn} in SnO_2, we further observe a large lattice relaxation that breaks three Be-O or B-O bonds and leads to threefold coordination (Fig. 3(d)), even in the ionized Be_{In}^{-} and B_{Sn}^{-} states. The breaking of three bonds with O neighbors facilitates the binding of yet another hole leading to a deep (double) donor transition at $\varepsilon_D(2+/+) = E_V + 0.21$ eV for Be_{In} in In_2O_3 and at $E_V + 0.62$ eV for B_{Sn} in SnO_2.

VI. GROUP Ib ACCEPTORS IN ZnO

In case of the group Ib elements Cu and Ag, the hole-wave function has mainly the *d* character of the impurity atom (see Fig. 3(b)) and not O *p* character like in case of the main group acceptors. Thus, the hole-state potential for O *p* has little effect and is not sufficient to satisfy the condition (1). Therefore, we apply GGA+*U* with $(U-J) = 5$ and 4 eV for Cu *d* and for Ag *d*, respectively. These parameters have been established before and were chosen so to reproduce photoemission spectra, e.g., for Cu_2O, i.e., to correctly place the energies of the occupied *d*-shell electrons.[28] Despite the application of GGA+*U*, the condition (3) is not fulfilled satisfactorily yet, which indicates that the energy splitting between occupied and unoccupied *d* symmetries is still underestimated.[32] Therefore, we apply an additional hole-state potential V_{hs} on Cu *d* and Ag *d* so that condition (3) is satisfied. In Table I, we give the transition energies for Cu_{Zn} and Ag_{Zn} with and without this additional correction. In either case, we find very deep acceptor states which are not conducive to *p*-type doping, in contrast to much more optimistic conclusion for Ag derived from standard LDA calculations.[11] Like all other acceptors, Cu and Ag can bind a second hole, giving rise to a deep donor transition (Table I). In contrast to the other cases, however, where both holes are bound in a O *p* orbital (Fig. 3(d)), here only one hole is located in a O *p* orbital while the other is in the Cu *d* or Ag *d* shell, e.g., forming a $Cu^{+II}(d^9) + O^{-I}$ configuration.

VII. HOLE BINDING AND MAGNETISM OF V_{Zn} IN ZnO

Previous DFT calculations of V_{Zn} predicted acceptor levels close above the VBM, which, however, could not be reconciled with magnetic-resonance data.[33] Nevertheless, as we have shown in Ref. 34, the O *p* dangling bonds lie inside the band gap in a standard GGA calculation, s

states of acceptors in oxides at their correct energies relative to the spectrum of occupied states without adversely affecting the underlying host band structure. Quantitative predic-