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Theory of defect complexes in insulators

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Defect complexes exhibit intricate electronic spectra, which can neither be described as a superposition of the constituent defect spectra, nor via conventional perturbative treatment applied thereupon. Instead, one must evaluate changes in the all-electron wave function in order to predict defect complex spectra. To this end, I present a theory that predicts the defect complex electronic structure from the spectra of its constituents via atomic shielding constants, derived from a local charge conservation rule. This theory should be considered an alternative to perturbation theories and can be used to describe the wave-function mechanics of any chemical system.

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Macroscopic charge conservation gives rise to "practical doping principles,"[1] which tell us, e.g., that *n*- or *p*-type doping via extrinsic donors or acceptors instigates the formation of intrinsic, compensating defects of opposite charge. The individual defects obviously interact with one another, and may form various kinds of bound complexes, and as defect concentrations increase, such complexes form statistically, even in without a driving force.[2] It turns out that, the physics of such bound complexes is different of that of the isolated defects, or a sum thereof,[3,4] and such "clustered states" have even been dubbed as "a new paradigm of condensed matter physics."[5] In particular, clustering and complex formation is of crucial importance in understanding various phase transitions in high-temperature superconductor cuprates,[4,5] manganites exhibiting colossal magnetoresistance,[4,5] and magnetic semiconductors.[6–8] The focus of this work is on defects in semiconductors, whose complex formation has been reported to shift defect levels[8–11] and to induce new defect levels.[7,12] These effects in turn may increase the solubility of donor or acceptor impurities;[10,13] passivate electrically active impurities;[14] and/or qualitatively and quantitatively alter magnetic interactions of magnetic impurities in dilute magnetic semiconductors.[6–8] I present a theory to predict the formation and shifting of electronic levels upon the aggregation of defects into complexes via atomic shielding constants,[15] derived from local charge self-regulation,[16–19] which in essence is a microscopic charge conservation rule.

Defect levels in the forbidden band gap of an insulator can be occupied or unoccupied, depending on the electron chemical potential (Fermi energy, ε_F). The different Aufbau principle ground states are labeled by the formal charge q, and the defect levels $\varepsilon(q/q')$ defined as

$$\varepsilon(q/q') = \frac{E(q') - E(q)}{q - q'} \qquad (1)$$

indicate the threshold energies, where a defect containing system transits from charge state q to q'. The total energies $E(q)$ and $E(q')$ of the respective charge states can be obtained, e.g., from first-principles calculations so one can predict such transition energies for various defects and defect complexes. Figure 1 illustrates defect levels thus calculated[20] for some defects and complexes thereof in the gallium nitride host. One immediately notices that the levels of a defect complex are not an obvious superposition of the levels of its individual constituents, and thus will obviously exhibit different electronic, optical, and magnetic properties than its constituent defects. In this work, I draw a connection between the electronic levels of a defect complex, and its individual constituent defects, and present a theory to predict defect complex levels without resorting to heavy numerical calculations.

The formation of electronic levels of a defect complex is no different to the case of an isolated impurity, as illustrated in Fig. 2. This example is given for a transition-metal (TM) impurity in a tetrahedrally coordinated compound semiconductor but easily generalizes to describe any defects/impurities in any coordination environment. Let us describe the system by a set of one-electron wave functions $\{\psi_i\}$ with the spectrum of eigenvalues $\{\varepsilon_i\}$. The first transition energies $\varepsilon(q/q\pm 1)$ follow as the highest occupied and lowest unoccupied eigenvalues ε_i.[23] The spectrum of eigenvalues can be qualitatively described in terms of crystal field orbitals,[19,24] as illustrated in Fig. 2. Replacing a tetrahedrally coordinated cation by a TM impurity, as shown in Fig. 2(a) splits the TM *d* orbital into *t* and *e* crystal field orbitals, of which only the *t* orbital bonds with the anion dangling-bond (DB) orbitals of the same representation, forming the bonding t_b and anti-

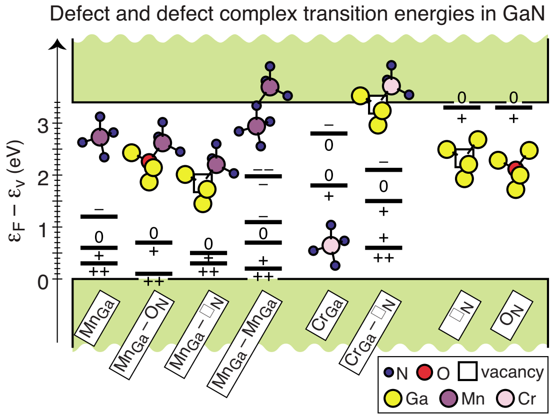

FIG. 1. (Color online) Transition energies for defect complexes involving a transition-metal impurity and intrinsic defects in GaN, given as a function of the Fermi energy ε_F.

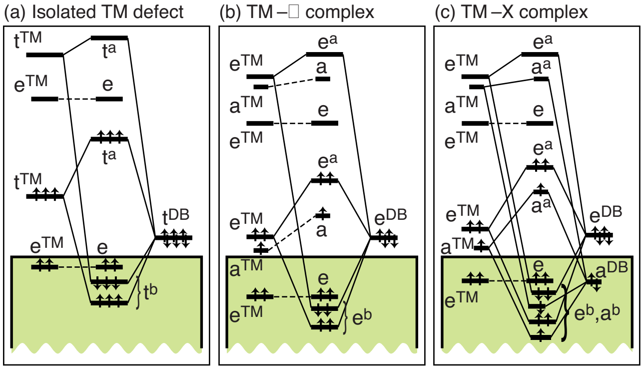

FIG. 2. (Color online) Electronic level formation for (a) an isolated TM impurity, (b) a TM-vacancy (TM-□) complex, and (c) a TM-donor (TM-*X*) complex in a tetrahedrally coordinated semiconductor. The left-hand side in each panel indicates the symmetry adapted TM valence orbitals and the right-hand side the ligand DB orbitals. The hybrid orbitals formed upon TM-DB interaction are shown in the center of each panel.

bonding t_a levels. Let us now introduce an anion vacancy □ next to the TM site by removing one of the nearest-neighbor atoms, and thus form a TM-□ complex. Focusing at first only on the TM-derived levels (the vacancy also induces its own levels, as discussed below) two significant changes occur: (i) removing an anion lowers the TM site symmetry from T_d to C_{3v}, splitting the t orbitals into e and a orbitals, of which the DB a orbital is removed altogether along with the removed anion. Thus the $t_b(t_a)$ levels are reduced to e_b (e_a and a) levels, as shown in Fig. 2(b). (ii) The removal of a neighboring atom reduces the number of electrons around the TM site, which effectively reduces the screening of the Coulomb attraction due to the TM nucleus, causing all nearby electrons to shift to lower energies. The anion vacancy, on the other hand, induces t and a levels due to its neighboring cation DBs. Replacing one of these cations by a TM atom lowers the symmetry as discussed above (i), and changes in the screening of the cation DB levels (ii) depend on the TM impurity introduced, e.g., via electronegativities. If the TM electronegativity is lower than the cation electronegativity, the cation DB levels will experience an decreased screening, shifting the vacancy levels downwards—notice however that, the TM is only a next nearest neighbor to the cations surrounding the anion vacancy, and the differences in electronegativities are small, so also the shifting of the vacancy levels is likely to be small.

The above discussion of level shifting can further be extended to various other defect complexes. For example, replacing an anion next to the TM defect by a donor defect X of a species more electronegative than the anion, the shifting of defect levels is analoguous to the discussion above given for the TM-anion vacancy pair: in such a TM-X pair, instead of removing one of the bonding orbitals altogether, the bonding orbital pointing toward the donor atom becomes increasingly localized around the donor atom [cf. Fig. 2(c)], effectively reducing the screening of the electron-nucleus Coulomb attraction at the TM site, again causing all the TM-derived levels to shift to lower energies, by a smaller amount, however, than in the case of the above discussed TM-□ pair.

Having understood the phenomenology, the formalism follows readily. Let $\{\psi_i\}$ and $\{\varepsilon_i\}$ describe the system with the isolated TM impurity, and $\{\psi_i'\}$ and $\{\varepsilon_i'\}$ the system with a TM-donor complex. Assuming that close to the atomic nuclei, say within a radius r_0 around each nucleus, these ψ_i behave like atomic orbitals, and separate into angular and radial functions $Y_i(\vartheta,\varphi)$ and $R_i(r)$. As discussed above, the changes in the local chemical environment essentially change the screening of the electron-nucleus Coulomb attraction, which is contained as the shielding constant ζ_i in the radial function[15] $R_i(r)=N_i r^{n_i^*-1}\exp(-\zeta_i r)$, where n_i^* is an effective quantum number and $N_i=(2\zeta_i)^{n+1/2}/\sqrt{(2n_i)!}$ a normalization constant. In the following, I invoke a local charge conservation rule to obtain ψ_i' from ψ_i.

Let us define an atomic charge Q within the radius r_0 as

$$Q=\sum_i \int_0^{r_0} d\tau |\psi_i|^2, \tag{2}$$

where the summation is taken over all occupied states i. It was first postulated by Pauling,[16] and later verified numerically[17–19] that, such atomic charges remain approximately constant under changes in the local chemical environment for atoms or ions in compounds, regardless of oxidation number, formal charge, or electronic configuration. We may thus write

$$\sum_i \int_0^{r_0} d\tau |\psi_i|^2 \approx \sum_i{}' \int_0^{r_0} d\tau |\psi_i'|^2. \tag{3}$$

Notice that, the number of occupied orbitals is likely to have changed so the summation over occupied states changes $\Sigma_i \to \Sigma_i'$. If r_0 is sufficiently large, Eq. (3) holds trivially for the core electrons so in fact we only need to sum over occupied valence states (or frontier orbitals) j. Empirically, such charge integrals are well conserved radially up to rather large r_0 (Refs. 19 and 25) regardless of the angular functions so we may replace $\int d\tau |\psi_i|^2$ by $\int dr 4\pi r^2 R_i^2$. Further assuming that all orbitals j experience the same change in screening, ψ_i' can be constructed from ψ_i by adding a constant α to the shielding constant, i.e., $R_i \to R_i'$, where $\zeta_i \to \zeta_i' = \zeta_i + \alpha$. (This assumption is reasonable for the valence orbitals while the inner shells experience a change of the opposite sign.) Summing thus only over the orbitals j, the electroneutrality principle reads

$$\int_0^{r_0} dr 4\pi r^2 \left(\sum_j R_j^2 - \sum_j{}' R_j'^2 \right) \approx 0. \tag{4}$$

If the energy eigenvalues ε_i of the relevant orbitals [illustrated in Fig. 2(a)] are known, the shielding constants simply follow as $\zeta_i = \sqrt{-\varepsilon_i}$,[15] we can (analytically) solve Eq. (4) for α at some suitable r_0, and evaluate the shifted respective eigenvalues ε_i' for a defect complex [Figs. 2(b) and 2(c)].

To solve for Eq. (4) in practice entails evaluating the relevant energy eigenvalues ε_i of the isolated impurity system (e.g., from x-ray photoemission experiment or first-principles calculation), and the summation over occupied states $\Sigma_i \to \Sigma_i'$ in the defect complex system. Here, the ε_i (given for Mn and Cr in Table I) are calculated via GGA+U (Ref. 20)

TABLE I. One-electron eigenvalues $\varepsilon_i = \varepsilon(\gamma,\sigma)$ in eV for single isolated impurities TM^q in formal charge state q [γ and σ denote the crystal field level and spin, as labeled in Fig. 2(a)]. In GGA $+U$ the ε_i are obtained with respect to the valence band edge ε_v, which here is substituted by the experimental ionization potential of 7.93 eV (Ref. 26).

	Mn^0	Mn^{-1}	Cr^0
$\varepsilon(t^b,\uparrow)$	−11.66	−10.83	−11.71
$\varepsilon(t^b,\downarrow)$	−11.13	−10.78	−11.12
$\varepsilon(e,\uparrow)$	−8.94	−8.59	−7.94
$\varepsilon(t^a,\uparrow)$	−7.32	−6.75	−6.14

as a weighted average of a TM site projected density of levels. In the following, I present two example cases how to actually predict the energy levels of defect complexes starting from the single impurity levels and solving Eq. (4) in practice.

In the first example case of TM-anion vacancy complexes in GaN, the sum over occupied states Σ_i' simply lacks two bonding orbitals. Here, as the nitrogen vacancy in GaN is a shallow single donor (formal charge $q_\square = +1$), we need to first occupy the lowest unoccupied (TM-induced) gap level by this donor electron, and construct the (TM-□)^q complex levels ε_i' from the levels of TM in charge state $q_{\mathrm{TM}} = q-1$. Two of the bonding orbitals are removed, and the remaining orbitals are replaced by their respective ψ_i' as discussed above. Setting the left-hand side of Eq. (4) to equal zero and solving for α at r_0 of 2.5 bohr yields $\alpha = -0.065$, -0.073, and -0.085 in atomic units for Mn^{-1}, Mn^0, and Cr^0, respectively. The corresponding defect levels, shown in Fig. 2(b), follow as $\varepsilon_i' = -(\sqrt{-\varepsilon_i} + \alpha)^2$, and in particular, the highest occupied levels (first ionization energies) of (Mn-□)^0, (Mn-□)$^{+1}$, and (Cr-□)$^{+1}$ occur at energies of 0.62 eV, 0.73 eV, and 0.78 eV lower than those of Mn^{-1}, Mn^0, and Cr^0, respectively. We may compare these energy lowerings with ones obtained from density-functional total energy minimization as 0.67, 0.32, and 1.24 eV (see Figs. 1 and 3).

The second example of a TM-donor impurity complex (here Mn-O) is more intricate. Again, because O$_N$ is a shallow donor, I construct the (Mn-O)^q complex levels from the levels of Mn in charge state $q_{\mathrm{Mn}} = q-1$. Thus comparing the electronic configuration of (Mn-O)^q and (Mn)$^{q-1}$ one finds that the number of occupied levels is unchanged but two of the six bonding levels have shifted to lower energies because oxygen is more electronegative than nitrogen ($\chi_{\mathrm{O}} = 3.5 > \chi_{\mathrm{N}} = 3.0$). This difference in electronegativities may further be utilized in order to understand the nature of the Mn-N and Mn-O bonds,[27] namely, that these bonds can be described to be 43% and 63% ionic, respectively (see p. 98 in Ref. 27). Assuming that these percentages actually measure the amount of bonding electrons transferred to/from our atomic volume, we can include this effect into Eq. (4) by adding the weight factor (1–0.63)/(1–0.43) to two of the bonding ψ_i' in Σ_i'. Solving Eq. (4) at $r_0 = 2.5$ bohr yields $\alpha = -0.020$ and -0.023 for Mn^{-1}, Mn^0, which lower the energies of the respective highest occupied levels by 0.19 and 0.23 eV. Density-functional calculation (see Figs. 1 and 3) predicts these levels to be lowered upon Mn-O complex formation by 0.49 and 0.52 eV.

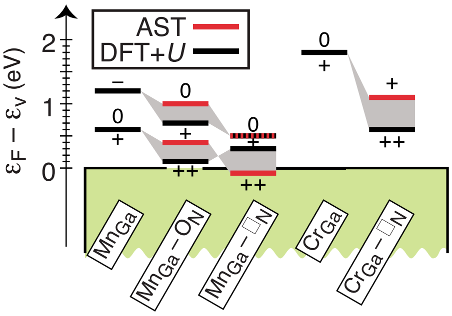

FIG. 3. (Color online) Defect complex transition energies calculated using the present atomic shielding theory (AST; red/gray lines), along with values calculated from DFT+U (black lines). The gray area connects the transitions due to the same crystal field orbital, and illustrates the difference between AST and DFT+U. The values are given as a function of the Fermi energy ε_F.

The shifting of the transition energies due to complex formation, illustrated in Fig. 3, agrees remarkably well with density-functional all-electron calculations. Obviously, the present scheme relies on good experimental or theoretical spectra for the individual constituent defects, and on the radius $r_0 = 2.5$, chosen somewhat arbitrarily. The main source of inaccuracy comes likely from the initial electronic spectra of the individual constituent defects, which within state-of-the-art density-functional methods typically have an error bar of at least a few tenths of an eV. The sensitivity on a specific choice of r_0 was tested by varying r_0 by ±0.25 bohr, which only induces an inaccuracy of a few hundredths of an electron volt to the resulting defect complex levels.

Finally, a more perplexing example is that of the Mn-Mn dimer. In the above examples, the essential changes in the electronic structure could be understood focusing on the charge conservation only for the TM atom, whereas for the Mn-Mn dimer, one needs to self-consistently conserve the local charge of the central nitrogen atom coordinated to both Mn atoms. The phenomenology, however, is the same. A charge neutral isolated Mn impurity has two occupied levels and one unoccupied level in the gap, formed as the antibonding hybrid levels from the Mn-N interaction so there is an unoccupied "holelike" state shared among the Mn and its neighboring N atoms. Thus, these N atoms are somewhat more electronegative than those coordinated only to Ga, and when another Mn is next to such a N atom, the effect doubles, and a similar lowering of the Mn levels occurs, as in the case of the above discussed Mn-O pairs, thus shifting the dimer $\varepsilon(2+/+)$ transition to a lower energy (cf. Fig. 1). At the same time, as the occupied levels get more localized on the Mn sites, the unoccupied levels get more localized on the central N site (cf. Ref. 7), causing the hole level to shift to higher energies, thus shifting the $\varepsilon(-/2-)$ transition to a higher energy (see Fig. 1). While the quantitative prediction of electronic levels becomes more intricate as the complex size increases, a qualitative understanding of the formation/shifting of electronic levels is readily obtained for any cluster size or shape.

The implications of complex formation were only discussed regarding electronic levels, but in fact, also defect solubilities are affected, since a general lowering (increase) in energy of electronic eigenvalues is accompanied by a lowering (increase) of the total energy and defect complex formation enthalpy. On top of this, the theoretical framework for constructing atomic (radial) wave functions according to changes in the local chemical environment is general, and not limited to solids. The principle of atomic electroneutrality can further be employed to easily describe the wave function mechanics of various molecular and surface reactions, including catalytic and redox processes in different environments. In summary, the present theory allows one to predict the evolution of electronic spectra along increasing complexity of the system, analogous to perturbation theory. The crucial advantage of the present theory to perturbation theories lies in the fact that changes in the wave function are immediately included (without going to higher order), in an approximately conserving manner.

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