Practical rules for orbital-controlled ferromagnetism of 3*d* impurities in semiconductors

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We distill from first-principles spin-polarized total-energy calculations some practical rules for predicting the magnetic state (ferromagnetic/antiferromagnetic/paramagnetic) of substitutional transition-metal impurity with different charge state in various host crystal groups IV, III-V, II-VI, I-III-VI_2, and II-IV-V_2 semiconductors. The basic mechanism is the stabilization of a ferromagnetic bond between two transition metals if the interacting orbitals are partially-occupied. These rules are then subjected to quantitative tests, which substantiate the mechanism of ferromagnetism in these systems. We discuss cases where current electronic structure calculations agree with these rules, and identify a few cases where conflicts exist. The effect of doping on transition-metal magnetic properties is also covered by these rules by considering the oxidation state changes due to doping. In addition, we systematically apply these rules to ideal substitutional impurities, contrasting our predictions with experiment. Discrepancies may be used to assess the role of various nonidealities such as presence of additional dopants, precipitates, clusters, or interstitial sites. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2128470]

I. INTRODUCTION

The existence of localized energy levels in the band gaps of group IV, III-V, and II-VI semiconductors doped with transition-metal (TM) impurities leads to rich optical and magnetic phenomenologies studied in great detail in the 1970s and 1980s for the then available dilute ($10^{16}-10^{17}$ cm^{-3} in III-V's) samples.[1–5] With the advent of molecular-beam epitaxy, incorporation in the early 1990s,[6] a high TM concentration ($10^{19}-10^{21}$ cm^{-3} in III-V's) into semiconductors it became possible to study TM-TM interaction and the ensuing ferromagnetism (FM) and antiferromagnetism (AFM). This has led in recent years to a flurry of experimental[6,7] and theoretical[8–12] investigations of numerous TM/host crystal combinations, covering virtually all possible 3*d* elements (each occurring in a few charge states) and most group IV, III-V, II-VI, binaries as well as chalcopyrite I-III-VI_2, and pnictide II-IV-V_2 semiconductors. This massive body of ongoing investigations naturally creates the need for understanding the basic rules deciding which particular TM-semiconductor combination and which charge state will lead to a given form of magnetism (FM, AFM, or paramagnetism). Simple model-Hamiltonian approaches[13,14] do not address the question of how *different* 3*d* elements couple to a given host crystal. Furthermore, in a model-Hamiltonian approach to this question[13,14] one selects, *a priori* a favored mechanism, and works out its physical consequences and manifestations. As an alternative to model Hamiltonians, one can use self-consistent total energy calculations for magnetic ions in a host crystal (e.g, via local spin-density approximation),[9–11,15,16] then distills *ex post facto* a mechanism. Unlike model-Hamiltonian approaches, in the direct electronic structure approach all forms of magnetic and orbital interactions are in principle present without the user having to select at the outset one mechanism over the other. However, the results are subject to specific uncertainties in the energetic position of the *d* levels due to the "self-interaction error."[17] Fortunately, such errors can be monitored and compensated by using the "LDA+U" approach.[11] Detailed first- principles calculations[8–12] do provide numerical answers, but not a simple physical model. Experimental results are currently clouded by sample-preparation issues, including the formation of magnetic precipitates,[18] TM clustering,[19,20] host crystal antisite defects[15] and TM interstitials,[21–23] so it is not always clear to what extent the results reflect the intrinsic magnetism of a given TM/host combination, as opposed to additional effects due to doping, clustering, and precipitates.

In this paper we formulate simple rules that predicts for TM impurities the type of magnetic interactions expected from given TM/host semiconductor combination and charge state. These rules has been distilled from a large set of first-principles calculations[10,11] in which we have placed two TM impurities in various relative substitutional lattice orientations $\hat{G}=[001],[110],\ldots$, in a supercell of a host semiconductor, calculating the energy difference $\Delta(\hat{G})=E_{FM}-E_{AFM}$ between the (atomically relaxed) total energies of the FM and AFM spin arrangements. However, these rules are not limited to *ideal* substitutional TM impurities. Additional doping affects the magnetic properties of transition metals by changing their oxidation states. This is covered by these rules. Future comparison of the predictions of these rules to ideal substitutional transition-metal impurities vis a vis experiment may help establish the role of extrinsic growth effects such as doping, clustering, and precipitates. The rule is based on the observations that the competition between FM and AFM is decided by the strength of the interaction between partially occupied states (either hole or electron carri-

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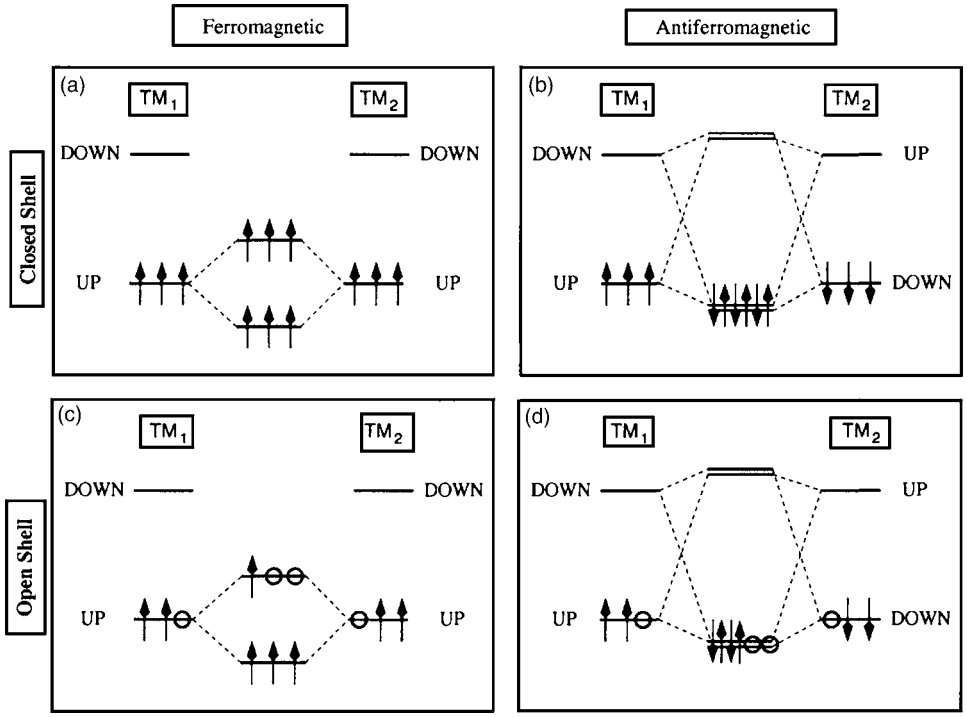

FIG. 1. Schematic energy levels for spin-up and spin-down t_2 levels of *two* identical $3d$ ions TM_1 and TM_2 with either closed or open shells. FM is generally favored in (c) while AFM is generally favored in (b).

ers) localized on neighboring TM impurities, and that the FM interaction is strongest for t_2 type (rather than e type) orbital, which shows the greatest overlap along the [110] crystallographic orientation. This surprising orientational dependence of FM revealed by our calculations[11] conflicts with the predictions of the model-Hamiltonian approaches but opens avenues for designing FM superlattices with high T_C.

II. MAGNETISM AND IMPURITY ORBITAL CHARACTER

We start by a description of the competition between FM and AFM interaction for two TM impurities (Fig. 1). Each TM is represented by an up- and down-spin orbitals, split by the exchange interaction, shown to the left and right of each panel in Fig. 1, for FM [Figs. 1(a) and 1(c)] and AFM [Figs. 1(b) and 1(d)] interactions. The up and down spins on the TM impurities interact (usually through the intervening lattice anions) via a TM-TM coupling potential V, forming a set of bonding and antibonding states for each spin channel. There are two main cases discussed in what follows.

A. Two TMs when each has fully occupied levels

In an FM spin arrangement [Fig. 1(a)] both the bonding and antibonding levels of one-spin channel are completely filled so, to first order, there is no gain in energy as a result of ferromagnetic TM-TM coupling. (The Kanamori-Goodenough mechanism of superexchange[24] may have a small FM contribution for filled shells.)

In an AFM arrangement of fully occupied orbitals [Fig. 1(b)], only the bonding states are fully occupied for both spin channels, while the antibonding levels are empty. This will lead to an energy gain for the AFM spin arrangement. Thus, for fully occupied TM orbitals the AFM spin arrangement is generally favored.

B. Two TMs when each TM has partially occupied levels

In an FM spin arrangement [Fig. 1(c)] there is an energy gain as a result of TM-TM coupling since only the bonding orbitals are occupied and the up-spin antibonding levels are now only partially occupied. Here the energy separation between the interacting TM_1-up and TM_2-up levels is negligibly small, so the FM energy gain can be large. In turn, in the AFM spin arrangement [Fig. 1(d)] there is also a gain in energy, but the energy separation between the interaction levels (TM_1 up with TM_2 up) is now large, so the energy gain upon coupling would be smaller.

We see that in the presence of partially occupied orbitals (not necessary "holes"), the FM vs AFM competition is decided by the extent of TM_1-TM_2 interaction matrix element V, where the energy separation tends to prefer FM spin arrangement. This simple model suggests that the *orbital characters on each TM impurity and the relative TM-TM orientation decide the TM-TM coupling V*.

C. The states of a single TM

We thus establish next the basic electronic structure of a *single* substitutional $3d$ in III-V semiconductors. We imagine first removing a host cation, then placing a TM in its place. (Quantitative first-principles calculations are reported in Ref. 11.) The ensuing qualitative picture can be understood as arising from the interaction between the orbitals of the *unperturbed host cation vacancy* [anion dangling bonds $t_2(p)$] with the orbitals of a *free 3d ion*, $t_2(d)+e(d)$ (Fig. 2). Coupling leads to both nonbonding e-type states and to bonding and antibonding t_2-type states. The t_2 states could be either dominated by cation vacancy-dangling bonds $t_2(p)$, in which case they are called[2] "dangling bond hybrides" (DBH), or they can be dominated by $3d$ ionic orbitals $t_2(d)$ in which

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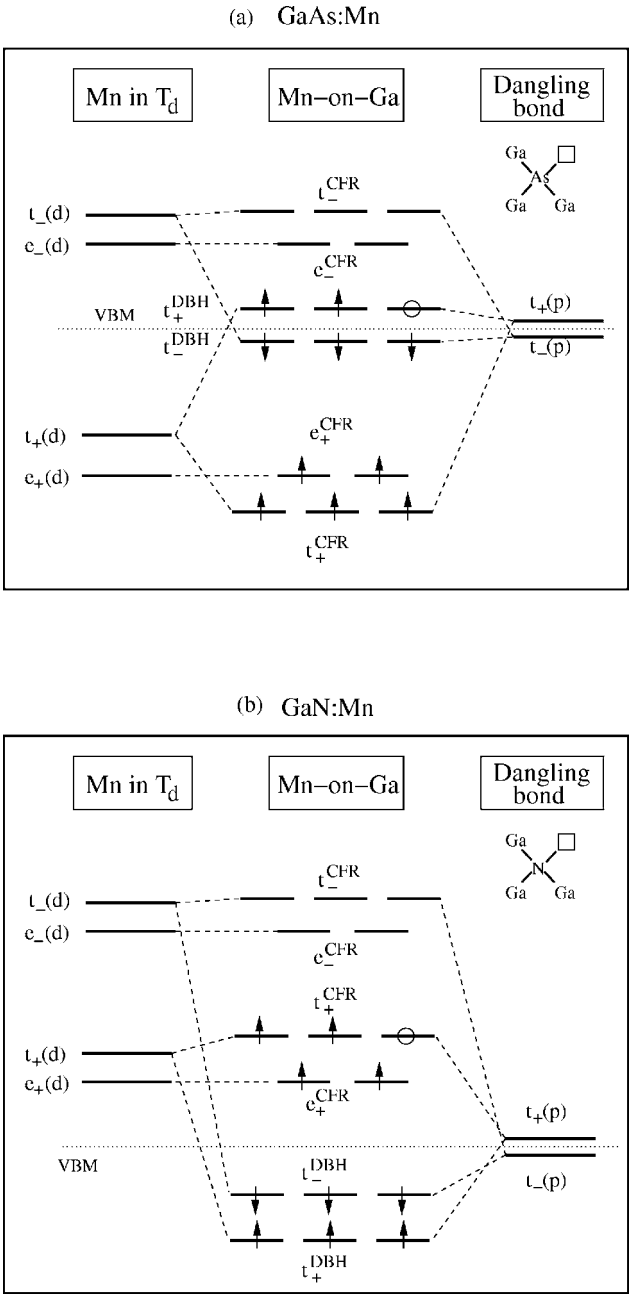

FIG. 2. The schematic energy-level diagram of single-impurity (a) *Ga*As:Mn and (b) *Ga*N:Mn. The mixed levels (central panel) are generated from the interaction between crystal-field and exchange-split levels on the Mn ion (left panel) with the anion dangling bond levels (right panel).

case they are called[2] "crystal-field resonances" (CFR) (Fig. 2). There are two limiting cases: When the 3*d* levels are well *below* the host cation dangling bonds (e.g., Mn in *Ga*As) [Fig. 2(a)], or when the 3*d* levels are well *above* the host cation dangling bonds (e.g., Mn in *Ga*N) [Fig. 2(b)]. This identity of the t_2 states, (CFR vs DBH) depends on the ionicity of the host and on the position of the TM impurity in the periodic table. To see this we plotted in Fig. 3 the wavefunction amplitude for a few TM/host systems. If the host cation vacancy level $t_2(p)$ lies *below* the TM $t_2(d)$ orbital [Fig. 2(b)] then the partially occupied t_2 state is TM-type antibonding t^{CFR} level. This is the case for electronegative host anions (e.g., Mn in *Ga*N, *Zn*O) and low *Z* TM's (*Ga*As:V). If, on the other hand, the host cation vacancy orbital $t_2(p)$ lies *above* the TM $t_2(d)$ orbital [Fig. 2(a)], then the partially occupied t_2 state is a *dangling bondlike* antibonding t^{DBH} state. This is the case for electropositive host anions (e.g., Mn in *Ga*As, *Ga*Sb) and high-*Z* TM's. We see that the partially occupied state can be either nonbonding e^{CFR} or antibonding t_2 (DBH or CFR).

The nature (e or t_2) of the partially-occupied orbital will affect the TM-TM overlap. This can be judged by the symmetry of the e and t_2 states in zinc-blende crystal (Fig. 3) suggesting that[25] (i) the e^{CFR}-type state is highly localized, having lobes that point *in between* the neighboring anion atoms, thus providing little TM-TM communication. (ii) The partially occupied states t_+^{CFR} and t_+^{DBH} are both antibonding states and provide good coupling with the nearest neighbor anions, thus providing good TM-TM communication. (iii) The orbitals in chalcopyrite $Cu\mathrm{AlS}_2$:Mn are mixed e-t_2 on account of the lower than T_d site symmetry, but the partially occupied orbital $(et)^{\mathrm{CFR}}$ is again rather extended, providing good TM-TM communication. To examine this picture quantitatively we show in Fig. 3 the calculated wave functions for Mn in *Ga*N, *Ga*As, and $Cu\mathrm{AlS}_2$. We see that as anticipated in Fig. 2(a), for *Ga*As:Mn the hole-carrying level t_+^{DBH} has some degree of host character whereas the hole-carrying level in *Ga*N:Mn [Fig. 2(b)] is more Mn-like. Conversely, the fully occupied deep valence-band level for *Ga*As:Mn ($e^{\mathrm{CFR}}+t^{\mathrm{CFR}}$) is highly localized.

D. The basic TM-TM ferromagnetic interaction

We conclude from the wave-function analysis that *ferromagnetism will be preferred in TM/semiconductor systems if the partially occupied orbitals are t_2 (or mixed e-t), but not e type.*[26] One needs to add a simple geometric factor here, since in the zinc-blende and chalcopyrite lattice anion-cation bonds exist only along the [110] "chain direction," one expects FM to be preferred if the TM impurities occupy site along this chain. This occurs if two TM impurities are either first fcc neighbors, [atoms at $(0,0,0)$ and $(1/2,1/2,0)a$] or with fourth neighbors [atoms at $(0,0,0)$ and $(1,1,0)a$]. Other lattice directions (such as [001]) have less t_2-t_2 orbital overlap, for geometric reasons, so FM is weaker along those directions, or can even be overwhelmed by the AFM interaction [e.g., Mn(IV) in Ge, see below]. The existence of strong impurity-impurity interactions along the special zinc-blende [110] direction was noted earlier for nitrogen-doped III-V's,[27] where the electronic levels are lowest for such [110]-oriented pairs.

III. PRACTICAL RULES

We can now combine our understanding of the symmetry of the e and t orbitals of a *single* impurity (Fig. 2) with insight on orbital maximizing the interaction between *two* TM-TM impurities (Fig. 1) to come up with predictions on the type of magnetic stabilization in different TM/host systems. We will consider a range of charge states quantified here by the "oxidation number." If a *neutral* TM impurity is substituted on a divalent cation ($Zn\mathrm{Se}:\mathrm{Mn}^0$), its nominal oxidation is II, whereas if it is substituted on a trivalent cation

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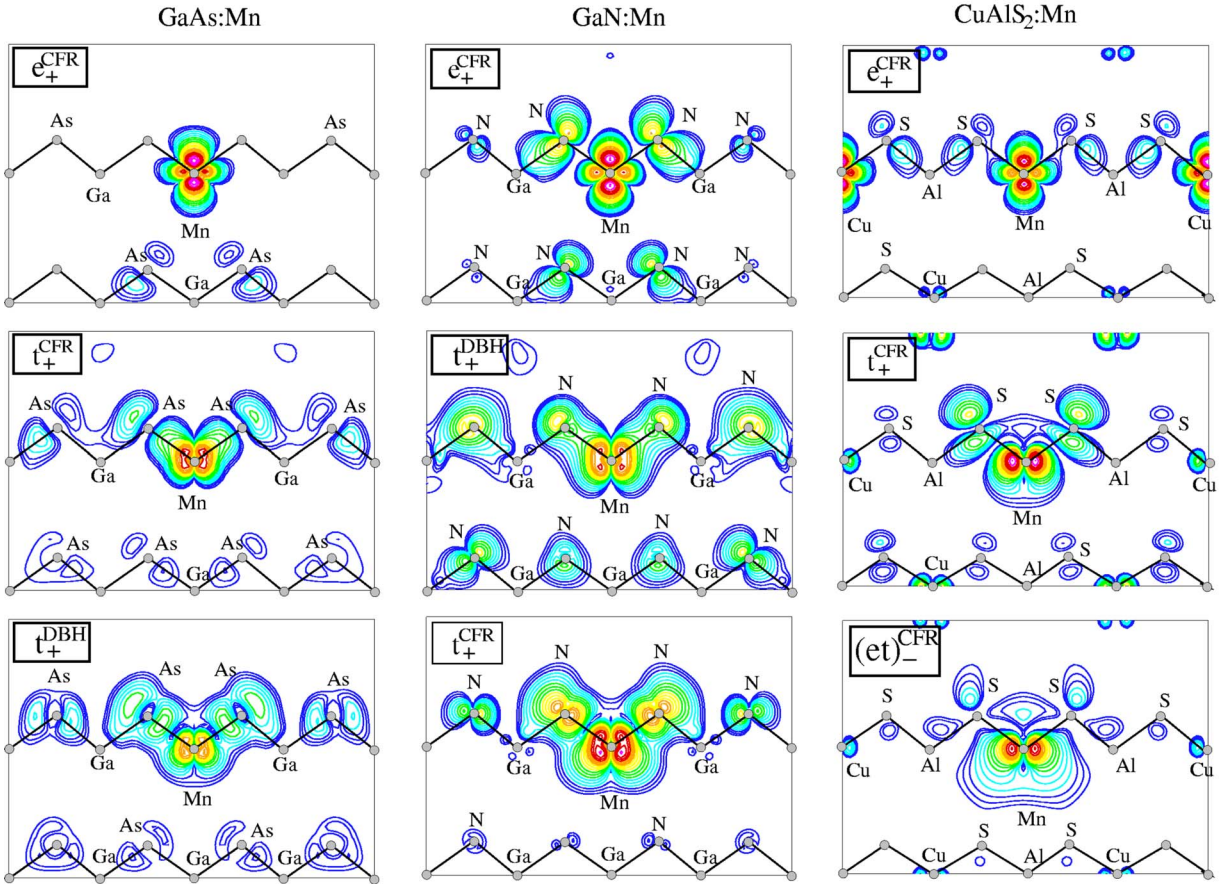

FIG. 3. (Color online) The wave-function square of Mn-induced CFR and DBH orbitals in GaAs, GaN, and $CuAlS_2$. The density contours start from 10^{-3} $e/\text{Å}^3$ and increase successively by a factor of $\sqrt{2}$. The plots of last row correspond to the orbitals with carriers.

(GaAs:Mn^0) or tetravalent cation (Ge:Mn^0), its oxidation state (OS) is III and IV, respectively. If the system is doped p type so as to transform the impurity to a *positively charged donor*, the nominal OS increases. For example, ZnSe:Mn^+ has oxidation III and GaAs:Mn^+ has oxidation IV. If, on the other hand, the system is doped n type so the impurity is a *negatively charged acceptor*, the nominal OS decreases. For example, ZnSe:Mn^- has oxidation I and GaAs:Mn^- has oxidation II.

Table I gives the rules relating TM impurities of various oxidation states in a given semiconductor to the predicted magnetic state. We give the possible electronic configuration of TM impurities in various OS via the distribution of electrons in the e_+, e_-, t_+^{bond}, t_-^{bond}, t_+^{anti}, and t_-^{anti} states (cf. Fig. 2). We then give the predicted magnetic state and the total magnetic moment μ. We distinguish "high-spin" (HS) configuration [e.g., $(e_+^2t_+^3)(t_-^3t_+^2e_-^0)$ for Mn(III) having $\mu=4$] from "low-spin" (LS) configuration [e.g., $(e_+^2t_+^3)(t_-^3t_+^0e_-^2)$ for Mn(III) having $\mu=0$]. Actual calculations show that in covalent semiconductors with $3d$ impurities, usually *only* the HS is seen since exchange interactions are stronger than crystal-field splitting.The only exceptions we know are Co(III) in GaP, GaAs, GaSb; and Fe(IV), Co(IV), Ni(IV) in Ge or Si,[28,29] as well as a few cases in SiC and diamond.[30,31] We give in Table I also the LS configuration for all cases to show that it can alter the form of magnetism. We see from the table that in all cases that e_+ and t_+^{bond} are always fully occupied, which is referred as d_+^5 "core" in the rest of paper. Furthermore, the t_-^{anti} level is always empty in the considered ground states. We next discuss the predictions and trends in the various groups (A)–(D) of Table I.

(i) Antiferromagnetism is predicted in closed-shell configurations, e.g., group A (t^6e^2) of Fe(I), Co(II), and Ni(III); the HS group C (t^6e^0) of Cr(I), Mn(II), Fe(III), and Co(IV); the LS group D (t^3e^2) of V(I), Cr(II), Mn(III) and Fe(IV); as well as the HS group F (t^3e^0) of V(III), Cr(IV).

First-principles calculated examples confirming this include Co(II) in ZnS, ZnSe, ZnTe,[32] CdTe,[29] and $CdGeP_2$ pnictides;[33] Ni(III) in GaN;[29] Mn(II) in II-VI's;[29,32] and Fe(III) in III-V's.[11] A number of cases belonging to this category are yet unclear due to inconclusive calculated results: (a) Ni(III) in GaAs, according to the rule, is supposed to be AFM with $\mu=3.0$ μ_B/Ni but according to supercell calculations it is very weakly AFM with $\mu<1.0$ μ_B/Ni.[11] The calculated electronic configuration of Ni(III) in GaAs is not clear because of an energetic overlap of the delocalized antibonding t_+ and t_- orbitals. This is reflected in the calculated magnetic moment, $<1\mu_B$/Ni, which is much smaller than that (3 μ_B/Ni) predicted from the rule. This could also reflect the computational limitation of too small supercell. (b) Although V(III) in GaAs, according to the rule, is expected to be AFM, calculations show that this is the case only for fourth neighbors $V-V$, while the first neighbors are weakly FM.[11] Taking orientational average in the coherent potential

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TABLE I. Prediction of the type of magnetic behavior for different oxidation states (roman letters) of various $3d$ ions in different zinc-blende host semiconductors. For example, Mn(II) means Mn^0 substituted on the II site of II-VI's, Mn^- substituted on the III site of III-V's, or Mn^{2-} substituted on group IV's. We give the possible electronic configurations of substitutional $3d$ ions in host for low spin (LS) and high spin (HS). The predicted magnetic moment (in μ_B/ion) is the total moment for the systems with aligned $3d$ spins, which could deviate from an integer in actual calculations due to delocalization of the electronic states. The boxed numbers correspond to the electron numbers in the partially filled orbital. "Weak" magnetic state means weak FM or AFM.

								Electronic configuration						Prediction	
Case	V	Cr	Mn	Fe	Co	Ni		e_+	t_+^{bond}	t_-^{bond}	t_+^{anti}	e_-	t_-^{anti}	Mag. State	Moment
A $d_+^5(t^6e^2)$				I	II	III	HS/LS:	2	3	3	3	2	0	AFM	3
B $d_+^5(t^6e^1)$			I	II	III	IV	HS:	2	3	3	3	$\boxed{1}$	0	Weak	4
$d_+^5(t^5e^2)$							LS:	2	3	3	$\boxed{2}$	2	0	FM	2
C $d_+^5(t^6e^0)$		I	II	III	IV		HS:	2	3	3	3	0	0	AFM	5
$d_+^5(t^4e^2)$							LS:	2	3	3	$\boxed{1}$	2	0	FM	1
D $d_+^5(t^5e^0)$	I	II	III	IV			HS:	2	3	3	$\boxed{2}$	0	0	FM	4
$d_+^5(t^3e^2)$							LS:	2	3	3	0	2	0	PM	0
$d_+^5(t^4e^0)$							HS:	2	3	3	$\boxed{1}$	0	0	FM	3
E $d_+^5(t^3e^1)$	II	III	IV				LS:	2	3	3	0	$\boxed{1}$	0	Weak	1
$d_+^5(t^2e^2)$							LS:	2	3	$\boxed{2}$	0	2	0	FM	1
F $d_+^5(t^3e^0)$	III	IV					HS:	2	3	3	0	0	0	AFM	2
$d_+^5(t^1e^2)$							LS:	2	3	$\boxed{1}$	0	2	0	FM	2

approximation calculation predicts weak FM for V(III) in III-V's. (c) While Mn(II) in ZnO is expected according to the rules to be AFM as confirmed by many calculations,[32,34] a recent calculation suggested FM coupling under 5% Mn concentration.[35] This calculation is questionable. (d) Co(II) in ZnO, according to the rule, is expected to be AFM but some calculations suggested FM coupling.[32,36] This calculation is questionable. However, a recent calculation concludes that Co(II) actually prefers the spin-glasslike state to the FM coupling although a very weakly FM coupling exists along the wurtzite c axis.[37]

(ii) Weak FM or AFM is predicted in cases having a hole in an e-type state, e.g., group B of HS (t^6e^1) Mn(I), Fe(II), Co(III), and Ni(IV). The same is true for the LS group E (t^3e^1) V(II), Cr(III), and Mn(IV).

First-principles calculated examples agreeing with this include Fe in II-VI's,[29,32] and $CdGeP_2$ pnictides,[33] and Co in GaN (Ref. 9) (Co in GaAs, GaP, and GaSb are found to be LS configuration). Note that Mn(I) resulting from substitution on the Cu site in $CuM^{III}X_2^{VI}$ is actually FM because its highest occupied orbital is not simply e type (as in case C), but rather a mixture of e-t due to its lower symmetry than zinc blende.[10]

(iii) Ferromagnetism is predicted in cases with one or two holes in the bonding t_- or antibonding t_+ levels, e.g., LS (t^5e^2) group B of Mn(I), Fe(II), Co(III), and Ni(IV); LS group C (t^4e^2) of Cr(I), Mn(II), Fe(III), and Co(VI); HS group D (t^5e^0) of V(I), Cr(II), Mn(III), and Fe(IV); HS (t^4e^0) and LS (t^2e^2) group E of V(II), Cr(III), and Mn(IV); and LS group F (t^1e^2) of V(III), Cr(IV).

First-principles calculated examples confirming this include Cr(II) in II-VI's (Refs. 32 and 36) and II-GeP_2,[33] Mn(III) in III-V's (Refs. 9, 11, and 38) and Cu-III-VI_2,[10] V(II) in II-VI's (Refs. 29 and 32) and II-GeP_2,[33] and Cr in III-V's.[9,11] There are some exceptions in the cases of this category: (a) Co(III) in GaP, GaAs, GaSb, and $AgGaS_2$, which are calculated to have LS configuration and so the rule predicts FM, but some calculations[9,33] predicted weak AFM. Our own calculation shows that *Ga*As:Co is FM, as predicted by the rule. It is weakly AFM without lattice optimization (i.e., using the experimental GaAs lattice).[29] (b) Mn(IV) in Ge, according to the rule, is expected to be FM. Calculations show that the magnetic coupling oscillates between FM and AFM as a function of the Mn-Mn distance.[39] The coupling along the special direction [110] is always FM, while it often prefers to AFM off [110] direction.

IV. NUMERICAL TESTS OF THE RULES

To test our rules quantitatively, we have calculated[40] from first principles $\Delta = E_{FM} - E_{AFM}$ for Mn in various host crystals while shifting the Fermi level, thus changing the oxidation state. The rule of Table I states that Mn(II) will be weak FM (or even AFM, e.g., HS case C), whereas Mn(III) will be FM (e.g., HS case D), as is Mn(IV) (cases E, HS). We thus created Mn(II) by doping the divalent site of *Zn*GeP_2, *Cd*GeP_2, and *Cd*Te, finding in all cases AFM (see Fig. 4) as expected of Mn(II). We then gradually shift E_F in the calculation towards the valence band, creating *higher* OS. We find a transition towards FM as expected by the rule: in CdTe it occurs when the OS is ~ 2.5, and stays FM for +3 and +4. In $ZnGeP_2$ the transition occurs for OS > 2.5, whereas $CdGeP_2$ also tends to be less AFM as OS increases, but it is still weakly AFM for OS ≈ 3. These tests confirm the rule for Mn.

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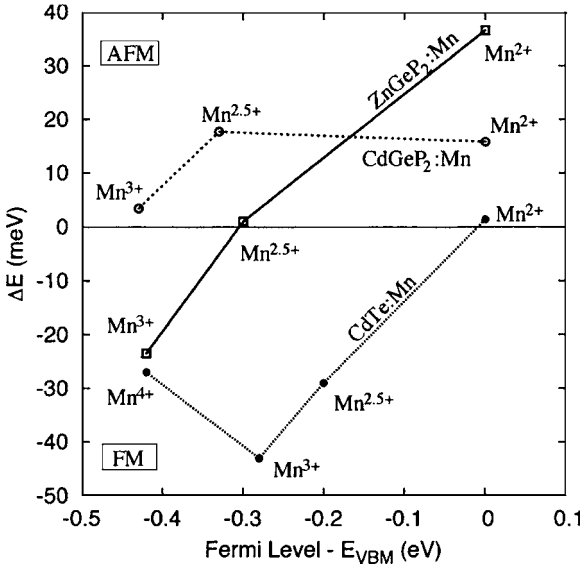

FIG. 4. The change of ferromagnetic stability energy of $ZnGeP_2$:Mn, $CdGeP_2$:Mn, and *Cd*Te:Mn by shifting E_F.

Figure 5 shows another test: it calculate Δ for $3d$ impurities in CdTe, finding Fe^0(II) and Mn^0(II) being weakly magnetic and Cr^0(II) and V^0(II) being FM, as predicted. We then use Mn in CdTe, changing its OS by shifting E_F. We see again that Mn(II) is "weak," and when its OS changes to Mn(III) [isovalent with Cr(II)] or to Mn(IV) [isovalent with V(II)] it becomes FM, just as predicted.

V. SUMMARY

In summary, we find that the orbital character e vs t_2 of TM impurity and the relative TM-TM orientation [110] vs [001] decide the magnetic coupling between the TM's in semiconductor. We established practical rules for predicting the magnetic properties of different substitutional TM's in various host semiconductors. FM coupling results from stabilizing interactions between *partially-occupied* orbitals. Doping that creates partial occupancy (e.g., *p*-type *Zn*O:Mn) promote FM, whereas doping that destroys partial occupancy (e.g., *n*-type *Ga*As:Mn) destroys FM. Thus, FM is not hole-induced, but it is induced by partial occupancy. t_2-orbitals and [110]-oriented TM pairs promote FM, whereas *e*-orbitals (in zincblende) and [001]-oriented TM pairs diminish FM.

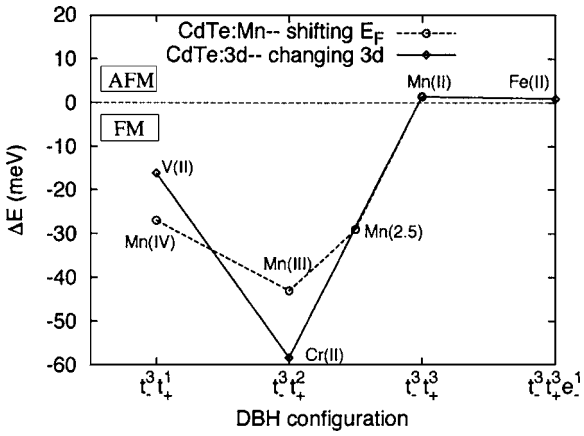

FIG. 5. The ferromagnetic stability energy of *Cd*Te:TM vs shifting E_F of CdTe:Mn with corresponding DBH configuration.

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