Electronic Correlation in Anion *p* Orbitals Impedes Ferromagnetism

vacancy introduces two holes in a non-spin-polarized t_2 symmetric state at the top of the ZnTe valence band, and conserves the tetrahedral (T_d) point group symmetry. The band-structure character of the host þ vacancy system is that of a non-spin-polarized metal [Fig. 1(a)]. However, the results obtained with the hole-state potential $V_{\cdot}$ draw an entirely different physical picture: As shown in Fig. 1(b), the previously non-spin-polarized and partially filled t_2 symmetric band at the Fermi level [see Fig. 1(a)] now becomes spin polarized where the majority spin direction is fully occupied ($a_þ^1 t_þ^3$), and the minority spin accommodates the two holes ($a_□^1 t_□^1$), leading to a high-spin (HS, $S = 1$) state. More importantly, the minority $t_□$ level splits further into one lower-energy occupied and two higher-energy unoccupied subbands (i.e., lower and upper Hubbard bands), thereby opening a gap, in direct analogy to the Mott transition [Fig. 1(b)]. A low-spin (LS, $S = 0$) state with a $a_þ^1 a_□^1 t_þ^2 t_□^2$ configuration, which is also insulating, lies only slightly higher in energy. (For ZnO, ZnS, and ZnSe, GGA finds a spin-polarized state of V^0, but the level splitting occurs only in the presence of the potential $V_{\cdot}$.)

The results of the present calculations for V are summarized in Table I.

The complex energy surface of V .—Because of a Jahn-Teller distortion, the symmetry of V^0 is reduced to C_{2v} in the insulating phase, as schematically illustrated in Fig. 2. The distances of the ligand anions from the vacancy center for the lowest energy configurations of V are given in Table I. While standard LDA or GGA calculations do find a spin-polarized vacancy state for the case of the more localized 2p orbitals of ZnO [9

So far, we discussed only the charge neutral state V^0

experiences similar difficulties as in case of the cation vacancy pair interaction.

Regarding the magnetic coupling between NN pairs of vacancies, we face here a much more complex situation than in conventional systems, like GaAs:Mn, where one needs to compare only two (FM and AF) configurations. Since, as illustrated in Fig. 4, the two vacancies on the cation sublattice share a common anion that mediates the magnetic interaction between the vacancies, one might rather view the NN vacancy pair as a single entity, where there are four holes that can be distributed over seven ligands, and the spin configurations can couple to a total spin of S