Theory of exchange interactions and chemical trends in diluted magnetic semiconductors

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The electronic structure and magnetic properties of Mn-substituted II-VI diluted magnetic semiconductors are treated theoretically with emphasis on $Cd_{1-x}Mn_x$ Te. The derived electronic structure is based on a combination of *ab initio* spin-polarized band calculations, a semiempirical tightbinding model containing the relevant experimental input, and consideration of alloying effects. The magnetic properties are calculated using a multisite Anderson Hamiltonian incorporating the derived electronic structure. The derived *sp*-band-Mn-*d* and Mn-Mn exchange constants compare as well with experiment as any previous calculations of this kind. The results establish the importance of *sp*-*d* hybridization and demonstrate superexchange as the dominant Mn-Mn exchange mechanism. A phenomenological three-level model for superexchange is constructed, which gives results in excellent agreement with the detailed calculations, provides physical insight, and permits exploration of chemical trends in the magnetic behavior for the series $M_{1-x}^{II}Mn_xX^{VI}$ (M^{II} =Cd or Zn; X^{VI} =Te, Se, or S). The same model, with minor modification, is found to be applicable to MnO and α -MnS, which are insulating and have the rocksalt structure.

I. INTRODUCTION

This paper presents a comprehensive treatment of the electronic structure and magnetic properties of the Mnsubstituted II-VI class of diluted magnetic semiconductors (DMS's).¹ The discussion of the electronic structure is based on a combination of *ab initio* band calculations, a semiempirical tight-binding model (ETBM) based on these results, carefully referenced relevant experimental input, and consideration of effects associated with alloying. The resulting electronic structure model is therefore consistent with currently available experimental and theoretical evidence and represents a suitable starting point for the formulation of a model Hamiltonian useful for calculating magnetic properties.

The magnetic properties to be considered here are Mn-(sp-band) exchange and Mn-Mn exchange. The results establish the importance of *p-d* hybridization and demonstrate superexchange as the dominant Mn-Mn exchange mechanism.² Related calculations of exchange anisotropy and spin-resonance linewidths will be discussed in a subsequent publication.³ Some of the present results have been briefly reported previously.^{4,5}

The first picture of the DMS electronic structure emerged from the empirical-tight-binding-methodcoherent-potential-approximation (ETBM-CPA) calculations of Hass and Ehrenreich.⁶ These calculations emphasized the effect of chemical disorder on the s and p levels. The occupied Mn 3d states were included much in the same way as in the combined interpolation scheme⁷ for the transition metals and exhibited strong hybridization with the anion derived p states.

The results to be described here are based on selfconsistent augmented-spherical-wave (ASW) band calculations⁸ utilizing the local-spin-density approximation⁹ (LSDA) for a hypothetical zinc-blende MnTe compound. (The structure of MnTe is nickel arsenide.) The derived electronic structure represents the x = 1 limit of the $Cd_{1-x}Mn_xTe, Zn_{1-x}Mn_xTe$, and $Hg_{1-x}Mn_xTe$ alloys to be considered here. The spin-polarized band calculations for $Cd_{1-x}Mn_xTe$ will be described here in detail. In addition, we present new results for MnSe and MnS (Sec. II A). The inclusion of spin polarization in these calculations is of particular importance for the placement of occupied (spin-up) and unoccupied (spin-down) Mn *d* bands and for treating their hybridization with *sp* bands correctly. The derived band structures are fit by an appropriate parametrization of simplified ETBM results and then adjusted using optical¹⁰⁻¹³ and photoemission data¹⁴⁻¹⁶ (Sec. II B).

The magnetic interactions to be considered here are as follows.

(1) The (sp-band-edge)-Mn or sp-d exchange interaction having the Kondo form¹⁷

$$-\sum_{i}' J_{sp\cdot d}^{v,c} \mathbf{S}_{i} \cdot \boldsymbol{\sigma}^{h,e} , \qquad (1.1)$$

where S_i is the Mn moment at site *i*, $\sigma^{h,e}$ is the spin operator associated with a valence-band-edge hole (h) or a conduction-band-edge electron (e), and $J_{sp-d}^c \approx -1.0$ eV, $J_{sp-d}^c \approx 0.2$ eV are the corresponding exchange constants.¹⁸⁻³⁰ The sum extends over Mn occupied sites only.

(2) The Mn-Mn or *d-d* exchange described by the spin- $\frac{5}{2}$ Heisenberg Hamiltonian

$$-\sum_{i\neq j}' J^{dd}(\boldsymbol{R}_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j , \qquad (1.2)$$

where $J^{dd}(R_{ii}) \approx -1$ meV (Refs. 31-40) is the antiferro-

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magnetic (AF) coupling between spins separated by R_{ij} . Again, the sum extends over Mn-occupied sites only. The exchange constants are determined by a random multisite Anderson Hamiltonian (Sec. II B), which incorporates the relevant features of the DMS electronic structure⁴ (Sec. II A), using second- and fourth-order per-turbation theory^{41,42} for Eqs. (1.1) and (1.2), respectively (Secs. III and IV). $J_{sp-d}^{v,c}$ is theoretically determined from band-edge spin splittings of ferromagnetic ASW bands, or experimentally from magnetooptic experiments. The numerical relationship⁴³ between $J_{sp-d}^{v,c}$ and the hybridization parameter V_{pd} [Eq. (2.4)] determining the *sp-d* band mixing, follows directly from a Schrieffer-Wolff transformation.⁴⁴ The detailed calculation of $J^{dd}(R_{ij})$ presented here establishes superexchange, resulting from p-d hybridization, as the dominant mechanism at near-neighbor distances, and as significantly more important than the Bloembergen-Rowland interaction.⁴⁵ The latter has been previously suggested as responsible for Mn-Mn exchange.⁴⁶ Further support for the present view is provided by numerical estimates of the total ASW energy differences between ferromagnetic and antiferromagnetic configurations which are in surprisingly good agreement with the perturbation results. The excellent agreement between theory and experiment ($\sim 50\%$) results from the accuracy of the input parameters (most notably V_{pd} as determined by the experimental $J_{sp-d}^{v,c}$ and the detailed understanding of the electronic structure. The superexchange results are at least as accurate as any theoretical values previously obtained for other materials.

The detailed results for $Cd_{1-x}Mn_xTe$ are used to construct a three-level, four-parameter phenomenological model for superexchange which is able to reproduce them simply, thereby providing insight into their physical significance (Sec. V). More importantly, the model is applicable to other Mn-based DMS's and permits the exploration of chemical trends in magnetic behavior. This model expresses $J^{dd}(R_{ij})$ as a product of two factors. The first depends explicitly on the electronic level parameters; the second is a function $f(R_{ij}/a)$, where a is the lattice parameter, which is approximately the same for all members of a class of materials like the DMS's having a given chemical structure. The model is supported by the results of exchange constant estimates derived from ASW band and total-energy calculations. Applications are made to the DMS series $M_{1-x}^{II} Mn_x X^{VI} (M^{II} = Cd \text{ or } Zn;$ X^{VI} = Te, Se, or S). Experimental information is used to fix the input parameters. The calculated exchange constants are in satisfactory agreement with experiment.

Somewhat surprisingly, the model turns out to be applicable as well to at least some materials (MnO and α -MnS) which are largely ionic, insulating, and have the rocksalt rather than the zinc-blende structure. The function $f(R_{ij}/a)$, while quantitatively different from that appropriate for the zinc-blende materials, is again insensitive to the chemical composition for this crystal structure.

Discussion of theoretical matters pertaining to the accuracy of the LSDA, the ETBM model and its implementation, and the derivation and properties of the function $f(R_{ij}/a)$ are relegated to appendixes.

II. ELECTRONIC STRUCTURE AND MODEL HAMILTONIAN

A. Electronic structure

As a guide to the electronic structure of DMS's, we have performed self-consistent spin-polarized band calculations for hypothetical stochiometric antiferromagnetic MnTe, MnSe, and MnS compounds having the zincblende structure. This section discusses only results for MnTe; the results for MnSe and MnS are quite similar. The AF-I ordering, consisting of alternating (001) spin-up and spin-down planes, is chosen for simplicity, although the DMS's are believed to prefer the more complicated AF-III ordering. The zinc-blende lattice constant of 6.430 Å used here is obtained by linear extrapolation of measured values for $x < 1.^{47}$ Possible tetragonal distortions due to the antiferromagnetic ordering are neglected.

Exchange and correlation effects are treated in the local-spin-density approximation (LSDA) using an exchange-correlation functional of the von Barth-Hedin form.⁹ The LSDA is primarily a ground-state formalism and yields band gaps in semiconductors and insulators which are typically 40-60% too small. Relativistic effects are neglected.

The one-electron Schrödinger equation is solved using the augmented-spherical-wave (ASW) technique,⁸ with extra ASW spheres centered on the tetrahedral interstices.⁴⁸ This results in a bcc lattice of spheres for which the sphericalization of the Wigner-Seitz call inherent in the ASW method is a good approximation. This radii of spheres are chosen to be equal. This procedure produces results for tetrahedrally coordinated materials which agree well with state-of-the-art linear-augmented-planewave (LAPW) and pseudopotential calculations.⁴⁹ Results for zinc-blende MnTe similar to those reported here have recently been obtained using an LSDA-LAPW approach.⁵⁰

The calculated ASW bands for AFI zinc-blende MnTe are shown in Fig. 1. The energy zero is fixed at the valence-band maximum. The corresponding density of states and the densities of states projected on the Mn sphere majority (\uparrow) and minority (\downarrow) spin *d* components are plotted in Fig. 2. We define the majority (minority) spin component to be that which contains a larger (smaller) percentage of the occupied *d* states at a given site. The magnitude of the net magnetic moment inside each Mn sphere is $4.2\mu_B$. This is less than the atomic value of $5\mu_B$ because of hybridization.

The states lying between -4 and 0 eV are derived primarily from Mn majority spin d levels and Te sp levels. Those between -4 and -3 eV and between -2 and 0 eV have the largest Te sp components but display strong p-d hybridization effects. The Mn d content of the valenceband maximum E_v , for example, is roughly 50%. The bands are quite flat between -2 and -2.5 eV and consist of largely unhybridized d levels (> 80% Mn d content at Γ).

The states lying between +1.0 and +2.5 eV are derived primarily from unoccupied Mn minority spin d levels. The lower bands in this complex are only slightly hybridized with the Te levels (>80% Mn d content at Γ),

while the upper bands exhibit stronger hybridization effects (<65% Mn *d* content at Γ). The spin splitting, which is most directly associated with the splitting $\varepsilon_d^{\downarrow} - \varepsilon_d^{\uparrow}$ in Fig. 2, is roughly 3.5 eV. The bands above 3 eV correspond to the conduction band in an ordinary *sp*-bonded semiconductor. The minimum at Γ contains roughly equal contributions from the *s* orbitals in the Mn spheres, the Te spheres, and the empty spheres neighboring the Mn spheres, and none from the Mn *d* levels.

It should be noted that LSDA band energies have no rigorous significance except for the highest occupied level and the lowest unoccupied level.⁵¹ Furthermore, the approximate LSDA one-electron potential does not contain the discontinuity^{52,53} between the valence and conduction bands which must be present in the exact densityfunctional potential. Some insight is gained⁵⁴ by associating the LSDA eigenvalues with hypothetical quasiparticles which are completely screened as they would be in a uniform electron gas. Since true Landau quasiparticles in an insulator are not completely screened in the absence of other quasiparticles the LSDA underestimates quasiparticle excitation energies: conduction bands are too low, valence bands are too high, and band gaps are too small. In the present case the occupied d states may be about 1 eV too high and the unoccupied d states about 1 eV too low. Appendix A contains a more detailed discussion of the errors associated with the LSDA and with the neglect of relativistic effects.

In applying the crystalline MnTe and well-known CdTe results to $Cd_{1-x}Mn_x$ Te, we use insight drawn from Hass and Ehrenreich's empirical tight-bindingmethod-coherent-potential-approximation (ETBM-CPA) calculations for $Hg_{1-x}Mn_x$ Te and $Cd_{1-x}Mn_x$ Te.^{6,55} The ETBM-CPA calculations indicate that the important features of the alloy electronic structure for the present purposes are understandable within the virtual-crystal approximation (VCA), which will be made in Sec. II B.

The upper valence bands in both CdTe and zinc-blende MnTe are largely Te 5p derived. Using the common anion rule, it is assumed that these lie at the same absolute energy level before p-d hybridization. The ETBM calculations indicate that the effect of such hybridization on the valence-band edge is small. The valence-band edge thus remains largely independent of x. This assertion is supported by the observed x independence of the photothreshold in $Cd_{1-x}Mn_xTe^{.14}$ It is also consistent with experimental evidence for a small valence-band offset in epitaxial $Cd_{1-x}Mn_x$ Te grown on CdTe.⁵⁶ The sp conduction-band edge, on the other hand, is predicted to increase linearly with x in the VCA due to the difference between the Cd 5s and Mn 4s atomic levels. This is consistent with the linear increase in the net sp band gap observed in optical absorption¹⁰ reflectivity¹² measurements. and

The location of the occupied and unoccupied Mn 3d





FIG. 1. Spin-polarized ASW band structure for hypothetical zinc-blende MnTe with AF-I ordering. The symmetry directions $\Gamma - M$ and $\Gamma - R$ in the tetragonal unit cell (shown) corresponding to $\Gamma - X$ and $\Gamma - L$ in the zinc-blende zone, respectively.

FIG. 2. Total and projected densities of states (per unit cell) of zinc-blende MnTe in the AF-I ordering. (a) Total density of states. (b) Mn *d* majority spin (solid line) and minority spin (dotted line) projected densities of states. Calculations employed the ASW-LSDA scheme described in the text. Majority and minority spin Mn *d* states of e_g symmetry at Γ are labeled by ε_d^{\dagger} and $\varepsilon_d^{\downarrow}$, respectively. The valence-band edge is labeled E_v .

states relative to the Te *p*-like valence-band maximum should not be very sensitive to *x*. Photoemission studies^{14,15} indeed show the growth of a Mn *d* peak approximately 3.4 eV below the valence-band edge for all concentrations. Angle-resolved measurements indicate that the occupied states contributing to this peak exhibit dispersion of about 1 eV,¹⁶ suggesting that they are actually bands resulting from *p*-*d* hybridization. Spectral changes higher in the valence band as a function of *x* are also attributable to hybridization. In addition, its presence provides a qualitative explanation¹¹ for the decrease of the E_1 optical transition energy observed in ellipsometry measurements with *x*.

The location of the unoccupied Mn d states has not yet been established definitively. Transitions from sp valence-band states to the unoccupied d states should be optically observable. Kendlewicz interprets structure at 4.5 eV in reflectivity measurements as arising from these transitions.¹² Structure at 4.5 eV has also been observed recently in ellipsometry data.¹¹ The most plausible initial-state energy for these transitions corresponds to the first maximum in the upper-valence-band density of states. This assignment would place the unoccupied dstates 3.5 eV above the valence-band edge. The optical structure at lower energies can be explained in terms of standard interband transitions in zinc-blende semiconductors and Mn²⁺ multipletlike excitations,¹³ which are essentially Frenkel excitons and do not appear in a band picture.

B. Model Hamiltonian

The model Hamiltonian to be used in the determination of the magnetic exchange constants has the form of a multisite Anderson Hamiltonian containing the essential ingredients of the band structure. Explicitly,

$$H = H_0 + H_d + H_{pd} + H_X . (2.1)$$

Here

$$H_0 = \sum_{n,k,\sigma} \varepsilon_n(k) c_{nk\sigma}^{\dagger} c_{nk\sigma}$$
(2.2)

describes the virtual-crystal sp bands, $\varepsilon_n(k)$; $c_{nk\sigma}^{\dagger}$ creates an electron in band n, with wave number k, and spin σ in the Bloch state $\psi_{nk}(r)$. The sp bands are determined by the ETBM using a basis of three anion p orbitals and one cation s orbital (Appendix B). With the proper choice of parameters this model yields band gaps in agreement with experiment as well as reasonable bandwidths and wave-function components for the highest valence bands and lowest conduction band.

The term

$$H_{d} = \sum_{i}' \sum_{m,\sigma} (\varepsilon_{d} + U_{\text{eff}} \langle n_{im-\sigma} \rangle) n_{im\sigma}$$
(2.3)

describes five degenerate Mn d levels per site i with sitelocalized linearized electron-electron interactions of the Hubbard form. Here $n_{im\sigma}$ is the number operator for d electrons of magnetic quantum number m on site i. The prime indicates that the sum extends over only Mnoccupied sites. H_d acts on a subspace (per site) consisting only of d^4 , d^5 , and d^6 configurations.⁵⁷ We assume $\langle n_{im\sigma} \rangle = 0$ or 1, and that Hund's rule remains in effect, consistent with the observed magnetic moment of $5\mu_B$.⁵⁸ The parameter ε_d is taken to have the value -3.4 eV with respect to the valence-band-edge zero of energy. The parameter U_{eff} is assigned a value of 7.0 eV in accordance with the discussion at the end of Sec. II A. This is somewhat larger than the value 5.5 eV used in our previous calculations of $J^{dd}(R_{ij})$.⁴ The results of Sec. IV are not qualitatively sensitive to variations in U_{eff} of this magnitude.

The term

$$H_{pd} = \sum_{i}' \sum_{m,\sigma} \sum_{n,k} \left[\tilde{V}_{pd}(n,k) e^{i\mathbf{k}\cdot\mathbf{R}_{i}} d^{\dagger}_{im\sigma} c_{nk\sigma} + \text{H.c.} \right]$$
(2.4)

describes Mn 3d-Te 5p hybridization. Here $d_{im\sigma}^{\dagger}$ creates a d electron at site i in orbital m with spin σ . We define V_{pd} to be the real-space hopping amplitude from a Mn d to a neighboring p orbital, neglecting any m dependence. The four-orbital ETBM model of Appendix B then yields $\tilde{V}_{pd}(n,0) = 4N^{-1/2}V_{pd}$ for the upper valence band and a general wave-vector-dependent hopping amplitude of

$$\widetilde{V}_{pd}(n,\mathbf{k}) = \widetilde{V}_{pd}(n,0) \left[\sum_{p} \langle p, 1\mathbf{k} \mid n\mathbf{k} \rangle \right] \left[\frac{1}{4} \sum_{\delta} e^{i\mathbf{k}\cdot\delta} \right] .$$
(2.5)

Here $\langle \alpha v \mathbf{k} | n \mathbf{k} \rangle$ is the coefficient in the Bloch function $|n\mathbf{k}\rangle$ of the Bloch sum $|\alpha v \mathbf{k}\rangle$ corresponding to orbital α of basis atom v [=0 (cation), 1 (anion)] in the unit cell. The δ_j are the four basis vectors to neighboring Te with respect to a Mn cation at $\mathbf{R}=0$; N is the number of unit cells in a normalization volume. The value of V_{pd} is obtained in Sec. III from experimental *sp-d* exchange constants. As discussed in Appendix B, the numerical calculations in Sec. IV involve averaging Eq. (2.5) over principal directions.

The Mn-d-sp-band potential exchange is given by

$$H_{X} = -\frac{1}{2} \sum_{i} \sum_{n} \sum_{\mathbf{k},\mathbf{k}'} J_{n}^{\text{dir}}(\mathbf{k},\mathbf{k}') e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{i}} \\ \times \mathbf{S}_{i} \cdot \left[\sum_{\mu,\nu} c_{nk\mu}^{\dagger} \sigma_{\mu\nu} c_{nk'\nu}\right].$$
(2.6)

Here

$$J_{n}^{\text{dir}}(\mathbf{k},\mathbf{k}') = \sum_{m} \int d^{3}r \int d^{3}r' \phi_{dm}^{*}(\mathbf{r})\psi_{nk}^{*}(\mathbf{r}')v_{\text{sc}}(|\mathbf{r}-\mathbf{r}'|) \times \phi_{dm}(\mathbf{r}')\psi_{nk'}(\mathbf{r})$$
(2.7)

is the ordinary exchange integral with screened Coulomb interaction $v_{sc}(|\mathbf{r}-\mathbf{r'}|)$ between a *d* wave function $\phi_{dm}(\mathbf{r})$ and *sp* Bloch states (n, \mathbf{k}) and $(n, \mathbf{k'})$; $\sigma_{\mu\nu}$ are the Pauli matrices. H_X -derived terms are unimportant for *d*-*d* exchange, and become important for *sp*-*d* exchange only when the H_{pd} contribution vanishes by symmetry. Mn-Mn direct exchange is even smaller and is neglected.

III. sp-d EXCHANGE

The commonly used sp-d exchange Hamiltonian¹⁷

$$H_{sp-d} = -\frac{1}{2} \sum_{i}' \sum_{n,\mathbf{k},\mathbf{k}'} J_{n}^{sp-d}(\mathbf{k},\mathbf{k}') e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{i}} \\ \times \mathbf{S}_{i} \cdot \left[\sum_{\mu,\nu} c_{nk\mu}^{\dagger} \sigma_{\mu\nu} c_{nk'\nu} \right]$$
(3.1)

involves $J_n^{sp-d}(\mathbf{k}, \mathbf{k}')$, the exchange between sp band states (n, \mathbf{k}) and (n, \mathbf{k}') and Mn local moments \mathbf{S}_i $(S = \frac{5}{2})$ for valence bands (n = v) and conduction band (n = c). Interband terms $n \neq n'$ in Eq. (3.1) are smaller and are neglected. The analysis below is restricted to the band-edge sp-d exchange constants $\alpha \equiv J_c^{sp-d}(0,0)$ and $\beta \equiv J_v^{sp-d}(0,0)$. The former will be seen to result exclusively from the term H_X in Eq. (2.1). The latter depends predominantly on H_{pd} and is thus more sensitive to details of the band structure.

Experimentally, α and β are determined from the enhanced Zeeman splittings of free-exciton lines in magnetooptic experiments.¹⁸ For an external magnetic field along the z direction, the spin S_i is replaced in standard mean-field theory by an average spin \overline{S}_z proportional to the magnetization. Equation (3.1) is then diagonal in k. The effect of H_{sp-d} on band-edge states,

$$-\frac{1}{2}xN\overline{S}_{z}J_{n}^{sp-d}(0,0)(c_{n0\uparrow}^{\dagger}c_{n0\uparrow}-c_{n0\downarrow}^{\dagger}c_{n0\downarrow}) \quad (n=c,v) , \quad (3.2)$$

can thus be considered independently of other k states in the same band. In all DMS's except Hg-based compounds, the splitting produced by an external magnetic field in the presence of H_{sp-d} is more than an order of magnitude larger than the intrinsic Zeeman splittings of these states.⁵⁹ The observed splittings therefore are nearly proportional to \overline{S}_z . From Eq. (3.2), the splitting of the $j = \frac{3}{2}$, $m_J = \frac{3}{2}$ (valence-band edge) to $j = \frac{1}{2}$, $m_J = \frac{1}{2}$ (conduction-band edge) exciton transition is seen to be $\Delta E_{3/2} = xN\overline{S}_z(\beta - \alpha)$. A different linear combination of α and β can be obtained from a different exciton transition. Simultaneous measurements of such transitions together with magnetization data yield the experimental values given in Table I.

The exchange constants α and β can be determined within the mean-field approximation from the ASW bands for a hypothetical ferromagnetic zinc-blende MnTe compound.⁵ The ferromagnetic order is imposed only to model the effects of a magnetic field in producing finite magnetization and associated mean-field spin splittings. More-direct calculations of sp-d exchange constants for spin-disordered alloys are difficult. We believe the x = 1case to be relevant because experimentally determined exchange constants are reasonably insensitive to x, at least for $x \leq 0.30$.⁶⁰ The ASW-LSDA calculation scheme is the same as that described in Sec. II. The results for the majority and minority spin bands are shown in Fig. 3. We take \bar{S}_z to be the calculated total magnetic moment $(4.8\mu_B)$. Assuming the conduction- and valence-bandedge spin splittings $[\Delta E^{c,v} \equiv E^{c,v}(\downarrow) - E^{c,v}(\uparrow)]$ to be proportional to \overline{S}_{z} , we find

$$N\alpha = \Delta E^c / \bar{S}_z = 0.33 \text{ eV}, \quad N\beta = \Delta E^v / \bar{S}_z = -1.05 \text{ eV}.$$

(3.3)

Similar ASW calculations were performed for a ferromagnetic $Cd_{0.5}Mn_{0.5}Te$ alloy in an ordered simple tetragonal structure. These assume a basal-plane lattice constant of 6.414 Å and perfect tetrahedral coordination. The x independence of J^{sp-d} is supported by the good agreement between the calculated values $N\alpha = 0.32$ eV and $N\beta = -1.12$ eV and the results in Eq. (3.3).

The comparison of MnTe results with experiment in Table I shows satisfactory agreement. This agreement should be viewed with caution because (1) the perturbative treatment of $N\beta$ given below indicates that this exchange constant would be reduced in a calculation employing the correct *d* level locations; and (2) the experimental $N\beta$ is properly defined as the exchange constant for the Γ_8 level $(j = \frac{3}{2})$, whereas the present calculations

TABLE I. $M_{1-x}^{II} Mn_x X^{VI}$ sp -d exchange constants from experiment, and corresponding Mn- X^{VI} sp -d exchange constants from the ferromagnetic ASW band calculations.

	Experimental			ASW calculation	1
	$N\alpha$ (eV)	$N\beta$ (eV)		$N\alpha$ (eV)	$N\beta$ (eV)
$Cd_{1-x}Mn_xTe$	0.22	-0.88ª			
			MnTe	0.33	-1.05
$Zn_{1-x}Mn_xTe$	0.18	-1.05 ^b			
$Cd_{1-x}Mn_xSe$	0.26	-1.11°			
			MnSe	0.33	-1.35
$Zn_{1-x}Mn_xSe$	0.26	-1.31 ^d			
$Cd_{1-x}Mn_xS$	0.22 ^e	-1.80 ^f			
			MnS	0.36	-1.50
Zn. Mn S					

^aReferences 18 and 20.

^bReferences 19, 21, 22, and 23.

^cReferences 19, 21, 24, and 25.

^dReferences 19, 21, and 26.

^eReference 30.

^fReference 27.



FIG. 3. Spin-polarized ASW energy bands for ferromagnetic MnTe along the symmetry direction $\Gamma - X$. Left (right) panel shows majority (minority) spin bands. Shown also are the valence- and conduction-band-edge spin splittings, ΔE^{V} and ΔE^{C} .

refer to a nonrelativistic Γ_{15} band edge. The neglect of spin-orbit splitting in the present calculations may be unimportant because of experimental evidence that the exchange constants of the Γ_8 and Γ_7 $(j = \frac{1}{2})$ levels are the same.⁶¹ The uncertainty due to effects (1) and (2) should not exceed 20%.

The qualitative difference between α and β reflects the importance of p-d hybridization and the different symmetry character of the conduction- and valence-band edges. The present ASW results support the analysis of Ref. 43. The presence of hybridization introduces an appreciable Mn d admixture in the Γ_{15} valence-band maximum. This is seen in Fig. 3 to give rise to a strong repulsion from lower, occupied Mn d states in the majority spin bands and higher, unoccupied Mn d states in the minority spin bands. Large negative values of ΔE_v and hence β result. By contrast, hybridization between the Γ_1 conductionband edge and Mn d states is forbidden by symmetry. The much smaller, positive values of ΔE_c and α are thus determined exclusively by potential exchange [the H_{χ} terms in Eq. (2.1)].

An explicit theoretical expression for β in terms of the parameters defined in Sec. II B permits the calculation of the hybridization parameter V_{pd} from experimental sp-d exchange constants. By neglecting H_X , and performing a Schrieffer-Wolff canonical transformation⁴⁴ to eliminate H_{pd} to first order in Eq. (2.1), we obtain

$$N\beta = -32V_{pd}^{2} \left[(\varepsilon_{d} + U_{eff} - E_{v})^{-1} + (E_{v} - \varepsilon_{d})^{-1} \right], \quad (3.4)$$

where E_v is the valence-band-edge energy. Substituting $N\beta = -0.88$ eV, $E_v - \varepsilon_d = 3.4$ eV, and $U_{\text{eff}} = 7.0$ eV for $Cd_{1-x}Mn_xTe$ yields $V_{pd} = 0.22 \text{ eV}$. The value of V_{pd} agrees very well with that $(\sim 0.2 \text{ eV})$ obtained from an ETBM fit to the ASW bands.⁶²

IV. Mn-Mn EXCHANGE

The spin- $\frac{5}{2}$ Heisenberg Hamiltonian describing the Mn-Mn, or d-d, exchange in $Cd_{1-x}Mn_x$ Te is given by

$$H_H = -\sum_{i \neq j} J^{dd}(R_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j \quad .$$
(4.1)

 $J^{dd}(R_{ij})$ is the exchange constant for Mn local moments \mathbf{S}_i and \mathbf{S}_j , separated by $R_{ij} \equiv |\mathbf{R}_i - \mathbf{R}_j|$, and the sum extends over Mn-occupied sites. [Note that with the present convention the total interaction between two spins is $-2J^{dd}(R_{ij})\mathbf{S}_i \cdot \mathbf{S}_j$.]

The value of $J_1^{dd} \equiv J^{dd}$ (nearest neighbor R_{ii}) is estimated first from ASW-LSDA total-energy calculations. More extensive calculations of $J^{dd}(R_{ii})$ are then performed within fourth-order perturbation theory using the model Hamiltonian (2.1) and the electronic structure parameters obtained earlier.

The estimate of J_1^{dd} is based on the ASW-LSDA totalenergy difference between (hypothetical) zinc-blende MnTe in antiferromagnetic and ferromagnetic orderings. We assume only nearest-neighbor interactions in the fcc Heisenberg Hamiltonian (4.1) leading to an energy per spin of $-24J_1^{dd}S^2$ in the totally aligned (ferromagnetic) state and $8J_1^{dd}S^2$ in the AF-I state. S is taken to be onehalf the computed Mn-sphere moment: $S_F = \frac{1}{2}(4.47\mu_B)$ for ferromagnetic ordering and $S_{AF} = \frac{1}{2}(4.23\mu_B)$ for antiferromagnetic ordering. The difference in Heisenberg energies per spin, $J_1^{dd}(8S_{AF}^2 + 24S_F^2)$ is equated to ΔE^{ASW} , the difference between antiferromagnetic and ferromagnetic ASW-LSDA total energies per Mn. The computed ΔE^{ASW} of -0.23 eV yields an antiferromagnetic exchange constant of $J_1^{dd} = -17.1$ K.

This result can be directly compared to experimental $Cd_{1-x}Mn_xTe$ exchange constants since the latter are only weakly x dependent. The best evidence for the weak x dependence is the good agreement between the value of $J_{1}^{dd}/k_B \ (\approx -7 \text{ K})$ obtained from magnetization step experiments^{31,32,34} for x < 0.05 and the value (J_1^{dd}/k_B) ≈ -7.5 K) obtained from neutron scattering experiments³⁵ for $x \approx 0.65$. The ASW-LSDA calculations overestimate $|J_1^{dd}|$. Similar overestimates result from ASW-LSDA calculations of d-d exchange constants in MnO, MnS, and NiO.⁶³ This effect is probably associated with the LSDA underestimate of the energy of unoccupied Mn 3d levels discussed in Sec. II.

The perturbative calculation of $J^{dd}(R_{ij})$ begins with the unperturbed Hamiltonian $H_0 + H_d$ in Eq. (2.1). The perturbation $H_{pd} + H_X$ partially lifts the large groundstate degeneracy of $H_0 + H_d$ associated with the moment directions on each Mn site. The resulting spectrum of low-lying states is described by the Heisenberg Hamiltonian (4.1). The lowest-order contributions to $J^{dd}(R_{ii})$ arising from H_{pd} and H_X are termed kinetic and potential exchange, respectively.² As pointed out in Sec. III, H_X is important only at k points where H_{pd} vanishes (e.g., the conduction-band edge). Since $J^{dd}(\vec{R}_{ij})$ is determined by integrals over the entire zone, the contribution of H_x is significantly smaller and may be neglected. Previous estimates of $J^{dd}(R_{ij})$ in DMS's have started

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from H_0 and the sp-d exchange Hamiltonian (3.1).⁶⁴ This fundamentally different approach neglects important intermediate states in which the Mn d-shell occupations differ from five. The restriction to fixed occupancy is valid at near-neighbor distances only in materials in which potential exchange dominates kinetic exchange [e.g., EuO Since the opposite limit holds for (**Ref.** 65)]. $Cd_{1-x}Mn_xTe$ it is important to consider the effects of H_{pd} explicitly in calculating $J^{dd}(R_{ij})$ instead of starting from Eq. (3.1).

The kinetic exchange contributions are calculated by considering an initial state $|i\rangle = |, \ldots, M_i = \frac{5}{2}$, $M_j = \frac{3}{2}, \ldots$ and final state $|f\rangle = |, \ldots, M_i = \frac{3}{2}$, $M_i = \frac{5}{2}, \ldots$). The specification of $|i\rangle$ and $|f\rangle$ implicitly includes the quantum numbers associated with filled sp-valence and empty sp-conduction bands, and the magnetic quantum numbers of S_i , $-\frac{5}{2} \le M_i \le \frac{5}{2}$. H_H of Eq. (4.1) connects $|i\rangle$ and $|f\rangle$:

$$\langle f \mid H_H \mid i \rangle = -2(\frac{5}{2})J^{dd}(R_{ii}) . \qquad (4.2)$$

Since H_H is an effective Hamiltonian representing the effects of the more fundamental Hamiltonian (2.1), $J^{dd}(R_{ii})$ can be calculated by computing the matrix element on the left-hand side of (4.2) in terms of H_{nd} . The first nonvanishing terms in H_{pd} connecting $|i\rangle$ and $|f\rangle$ are of fourth order. Thus,

$$-2(\frac{5}{2})J^{dd}(R_{ij}) = \sum_{I_1, I_2, I_3} \frac{\langle f | H_{pd} | I_1 \rangle \langle I_1 | H_{pd} | I_2 \rangle \langle I_2 | H_{pd} | I_3 \rangle \langle I_3 | H_{pd} | i \rangle}{(E_0 - E_1)(E_0 - E_2)(E_0 - E_3)} .$$

$$(4.3)$$

Here I_1, I_2, I_3 label intermediate states, to be described in more detail below, specified by the occupation of sp-band states and Mn d orbitals and sites i and j with four, five, or six electrons per site. E_1, E_2, E_3 , and E_0 are the energies of the intermediate states and the ground state, respectively. This method of calculating $J^{dd}(R_{ij})$ is very similar to the approach developed for rare-earth compounds and NiO by Falicov and co-workers.^{41,42}

The assumption in Sec. II B that $\tilde{V}_{pd}(n,k)$ is independent of the Mn orbital index m allows Eq. (4.3) to be factored into two terms. The first term depends only on the Mn-ion ground state, and is exactly one for the Mn²⁺⁽⁶S_{5/2}) configuration assumed here. The second term is a perturbation expression identical to Eq. (4.3) but for $S = \frac{1}{2}$. The calculation of $J^{dd}(R_{ii})$ thus proceeds exactly as in the case of a single d orbital per Mn.

Figure 4 shows a schematic representation of terms contributing to $J^{dd}(R_{ii})$. Each arrow represents the formation of one on the intermediate states I_1, I_2 , or I_3 through transfer of one electron between Mn ions at R_i or R_i and the sp bands. All permutations of the arrow labels consistent with particle conservation and the exclusion principle produce intermediate states that contribute to the exchange constants. The sums of terms with two-hole [Fig. 4(a)], holeelectron [Fig. 4(b)], and electron-electron (not shown) intermediate states are denoted by $J_{hh}^{dd}(R_{ii})$, $J_{he}^{dd}(R_{ii})$, and $J_{ee}^{dd}(R_{ij})$, respectively. Thus $J^{dd}(R_{ij}) = J_{hh}^{dd}(R_{ij}) + J_{he}^{dd}(R_{ij}) + J_{ee}^{dd}(R_{ij})$. Let [A, B, C, D] be the sum of the terms in Eq. (4.3) corresponding to the intermediate-state sequence shown in Fig.

4(a) plus the same term with i and j interchanged. The total contribution to⁶⁶ $J_{hh}^{dd}(R_{ij})$ is then

$$J_{hh}^{aa}(R_{ij}) = [A,B,C,D] + [C,D,A,B] + [A,C,D,B] + [A,C,B,D] + [C,A,D,B] + [C,A,B,D]$$

$$= -2 \sum_{k,k'} \sum_{n,n'} |\tilde{V}_{pd}(n,k)|^2 |\tilde{V}_{pd}(n'k')|^2 \cos[(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}]$$

$$\times \{ U_{\text{eff}}^{-1}[\varepsilon_n(k) - \varepsilon_d - U_{\text{eff}}]^{-1}[\varepsilon_{n'}(k') - \varepsilon_d - U_{\text{eff}}]^{-1} - [\varepsilon_n(k) - \varepsilon_d - U_{\text{eff}}]^{-2}[\varepsilon_{n'}(k') - \varepsilon_d - U_{\text{eff}}]^{-1} \}.$$

Here the sum on bands is restricted to the upper valence bands, and the k,k' sums extend over the first Brillouin zone. Both terms in curly brackets are positive. The rapid decrease of $|\tilde{V}_{pd}(v,k)|^2$ away from k=0 discussed in Appendix B implies that the integrals over k and k' are positive. $J_{hh}^{dd}(R_{ij})$ is thus negative or antiferromagnetic.

 $J_{hh}^{dd}(R_{ij})$ will be seen below to be the dominant exchange mechanism in $Cd_{1-x}Mn_xTe$ at near-neighbor distances. Since $J_{hh}^{dd}(R_{ij})$ involves only the anion-derived upper-valence-band states, it is identified with superexchange. The present k-space description of superexchange is believed to be superior for $Cd_{1-x}Mn_xTe$ to more familiar realspace, path-counting schemes⁶⁷ because the upper valence bands are relatively broad. In materials with narrower valence bands (e.g., NiO), the sp hopping itself can be treated as a perturbation and only the shortest paths contribute significantly to $J^{dd}(R_{ij})$. Correlation effects within the valence band may also be important. In $Cd_{1-x}Mn_xTe$, however, the broader, uncorrelated valence bands require a relatively large number of paths to be retained. The appropriate summation over paths is taken care of automatically in Eq. (4.4) by the cosine factor and k-dependent hopping amplitudes $\tilde{V}_{pd}(n,k)$.

 $J_{he}^{hd}(\dot{R}_{ii})$ contains intermediate states involving the lowest conduction band and the upper valence bands. In analogy to Eq. (4.4), we find

$$J_{he}^{dd}(R_{ij}) = -2 \sum_{k,k'} \sum_{n,n'} |\tilde{V}_{pd}(n,k)|^2 |\tilde{V}_{pd}(n',k')|^2 \cos[(\mathbf{k}-\mathbf{k}')\cdot\mathbf{R}_{ij}] \\ \times (U_{\text{eff}}^{-1}[\varepsilon_n(k)-\varepsilon_d-U_{\text{eff}}]^{-1}[\varepsilon_d-\varepsilon_{n'}(k')]^{-1} \\ + \frac{1}{2}[\varepsilon_n(k)-\varepsilon_{n'}(k')]^{-1} \{[\varepsilon_d-\varepsilon_{n'}(k')]^{-1}+[\varepsilon_n(k)-\varepsilon_d-U_{\text{eff}}]^{-1}\}^2\},$$

$$(4.5)$$

where n = c and n' = v refer to conduction and valence bands, respectively. In a metal $[\varepsilon_n(k) - \varepsilon_{n'}(k')]^{-1}$ is singular over the Fermi surface, leading to the oscillatory long-ranged Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction at large distances. In systems with an energy gap, there is no singularity and the interaction (the Bloembergen-Rowland interaction⁶⁸) is characterized by a large-distance associated exponential decay. This interaction dominates asymptotically in DMS's. The superexchange contribution $J_{hh}^{dd}(R_{ij})$ also decays exponentially but with a larger decay constant. For first and second neighbors in $Cd_{1-x}Mn_x$ Te the calculations below indicate that $J_{he}^{dd}(R_{ii})$ (which in general can be of either sign) is antiferromagnetic and much smaller ($\sim 5\%$) than $J_{hh}^{dd}(R_{ii})$. The smaller magnitude results from (1) the smaller density of states in the lowest conduction band



FIG. 4. Diagrammatic representation of fourth-order contributions to $J^{dd}(R_{ij})$. The filled valence bands, empty conduction band, and Mn *d* levels at R_i and R_j are shown. Solid (dashed) arrows at *i* and *j* represent the initial (final) Mn spin states. Terms contributing to (a) $J_{hh}^{dd}(R_{ij})$ and (b) $J_{he}^{dd}(R_{ij})$ correspond to allowable permutations of the spin-conserving transfers *A*, *B*, *C*, and *D*. The intermediate states of holes or electrons are labeled by (n,k) or (n',k').

compared to the upper valence band, and (2) the fact that $\tilde{V}_{pd}(c,k)$ vanishes at k=0 and remains small throughout the Brillouin zone. These same factors cause the twoelectron contribution $J_{ee}^{dd}(R_{ij})$, which is also antiferromagnetic, to be completely negligible.

Equation (4.3) for $J^{dd}(R_{ij})$ has been evaluated numerically for first and second neighbors in $Cd_{1-x}Mn_xTe$ $(0 \le x \le 0.70)$, using the $\varepsilon_n(k)$ and $\tilde{V}_{pd}(n,k)$ determined by the four-orbital ETBM model described in Appendix B. The sphericalization procedure which is used assumes $\varepsilon_n(k)$ and $\tilde{V}_{pd}(n,k)$ depend on $|\mathbf{k}|$ according to analytic expressions obtained along $\Gamma - X$. This approximation is reasonable because the main contribution to $J^{dd}(R_{ij})$ arises from the central region of the Brillouin zone where $\varepsilon_n(k)$ and $\tilde{V}_{pd}(n,k)$ are isotropic.

For x = 0.30, we find $J_1^{dd}/k_B \approx -8$ K and $J_2^{dd}/k_B \equiv J^{dd}$ (second neighbor R_{ij})/ $k_B \approx -0.9$ K (also antiferromagnetic). The ratio $J_2^{dd}/J_1^{dd} \approx 0.11$ is probably more accurate than the absolute values because it is independent of V_{pd} . Superexchange, or $J_{hd}^{dd}(R_{ij})$ contributes about 95% to the total J_1^{dd} and J_2^{dd} for x = 0.3. The $J_{he}^{dd}(R_{ij})$ contribution accounts for most of the remaining 5%. If V_{pd} is assumed independent of x, the calculated values of J_1^{dd} and J_2^{dd} are nearly constant throughout the physically attainable concentration range ($0 \le x \le 0.70$). In Sec. V we argue that V_{pd} should actually increase slightly with x, leading to an increase of $\sim 20\%$ in the magnitude of J_1^{dd} and J_2^{dd} between x = 0 and x = 0.7.

The nearly complete x independence of J_1^{dd}/k_B (with V_{pd} assumed constant) results in part from a competition between J_{hh}^{dd}/k_B and J_{he}^{dd}/k_B . The former increases in magnitude for nearest neighbors from -7.6 K at x = 0.1 to -8.1 K at x = 0.7. This enhancement results from the increasing Te p character of the upper valence bands which accompanies the increase in band gap. The J_{he}^{dd}/k_B contribution for nearest neighbors decreases in magnitude over the same composition range from -0.6 to -0.3 K. The much larger percentage change in J_{he}^{dd} reflects the strong band-gap dependence of the energy denominator $[\varepsilon_c(k) - \varepsilon_v(k')]^{-1}$ in Eq. (4.5).

The principal uncertainty in our numerical results lies in the parameters V_{pd} and U_{eff} . The magnitude of V_{pd} is largely constrained by Eq. (3.4) and the values of ε_d , U_{eff} , and $N\beta$ but J^{dd} is proportional to V_{pd}^4 . Sample calculations show J_1^{dd} to vary by $\sim \pm 50\%$ for changes in U_{eff} of $\sim \pm 15\%$, and by $\sim \pm 30\%$ for changes in $N\beta$ or ε_d of $\sim \pm 15\%$. The overall accuracy of the calculation of J_1^{dd} is thus $\sim \pm 50\%$.

The most accurate experimental values of J_1^{dd}/k_B in $Cd_{1-x}Mn_x$ Te range from -6.1 to -7.7 K.^{31,32,34,35} As

discussed earlier, no significant differences have been observed between experimental determinations for dilute (x < 0.05) and concentrated $(x \ge 0.6)$ samples. Much of the experimental variation, in fact, may only reflect a difference in assumptions made concerning J_2^{dd} and more distant neighbor exchange constants. Direct experimental information on interactions beyond nearest neighbors is unavailable. An upper bound of $J_2^{dd}/J_1^{dd} < 0.5$ (Ref. 69) is imposed by the observation of short-ranged AF-III ordering in neutron scattering experiments.³⁵ Detailed analysis of the neutron scattering data as well as magnetization step data place this ratio in the narrower range 0.1-0.3.^{35,31} Overall, the agreement between the present perturbative calculations of J_1^{dd} and J_2^{dd} and experiment is excellent. This agreement strongly supports the basic validity of the electronic structure model used here and confirms superexchange as the dominant source of Mn-Mn interactions at near-neighbor distances. Conversely, the success of the present calculation of superexchange may be attributed to the detailed knowledge of the relevant parts of the electronic structure.

More-accurate calculations of J_{hh}^{dd} have been performed in connection with a recent study of anisotropic superexchange in DMS's.³ These calculations employ the Baldereschi "special k points" method, with 10 k points in the irreducible Brillouin zone (as well as more realistic e_g and t_{2g} symmetry d orbitals).^{70,71} The results are very similar to those reported here: $J_{hh}^{dd} = -5.6$ K (~25% smaller), and relative chemical and compositional trends are effectively unchanged (<10% difference). The good agreement supports the adequacy of the spherical approximation used in this section for treating J_1^{dd} . The same approximation also leads naturally to the simple three-level model for superexchange described in the following section.

V. THREE-LEVEL MODEL OF SUPEREXCHANGE IN Mn-BASED MATERIALS

A. Three-level model

A transparent expression for the superexchange contribution to $J^{dd}(R_{ij})$ that is unobscured by the elaborate

calculations of the preceding section provides physical insight for this and other Mn-based systems. The simplified expression to be developed here is based on a three-level model which contains only the most relevant characteristics of the electronic structure. The model contains four parameters: an occupied d level at energy ε_d , an unoccupied d level at energy $\varepsilon_d + U_{\text{eff}}$, a p level at the energy of the sp-valence-band edge, E_v , and the single hopping parameter V_{pd} (defined in Sec. II) which connects the p level to both d levels. The three levels ε_d , E_v , and ε_v , and $\varepsilon_d + U_{\text{eff}}$ correspond to ε_d^{\dagger} , E_v , and $\varepsilon_d^{\downarrow}$ in Fig. 2, respectively. (The numerical values of the parameters will be different from those indicated in Fig. 2.) The model neglects conduction states since these have been shown to be unimportant for superexchange (Sec. IV).

The expression for superexchange is first calculated strictly within the three-level model, where perturbation theory (in analogy to the development in Sec. IV) yields⁷²

$$J_{hh}^{dd}(R_{ij}) = -2V_{pd}^{4} [U_{\text{eff}}^{-1}(E_{v} - \varepsilon_{d} - U_{\text{eff}})^{-2} - (E_{v} - \varepsilon_{d} - U_{\text{eff}})^{-3}]f(r) .$$
(5.1)

The dimensionless function f(r) describes the dependence of $J^{dd}(R_{ij})$ on $R_{ij}/a \equiv r$, where *a* is the cubic lattice constant. This dependence is trivial for the pure three-level problem: f(r)=1 for nearest neighbors and vanishes for more distant neighbors.⁷³

The expression (5.1) is actually more widely applicable than its derivation above might suggest. It describes Mn-Mn exchange in both DMS's and the rocksalt insulators MnO and α -MnS. Within each class of materials a single—material insensitive—function f(r) may be defined. Here "material insensitive" means independent of electronic structure details within a class of materials having the same or closely related symmetries. Variations of J^{dd} within a class are therefore controlled by the simple three-level-derived prefactor in Eq. (5.1).

An expression for f(r) in DMS's which is exact within the fourth-order perturbation theory of Sec. IV may be obtained by comparing Eq. (5.1) with Eq. (4.4). We denote the result by $\tilde{f}(\mathbf{r})$:

$$\widetilde{f}(\mathbf{r}) = \sum_{n,\mathbf{k}} \sum_{n',\mathbf{k}'} \cos(a\mathbf{k}\cdot\mathbf{r}) \cos(a\mathbf{k}'\cdot\mathbf{r}) V_{pd}^{-4} | \widetilde{V}_{pd}(n,\mathbf{k}) |^{2} | \widetilde{V}_{pd}(n',\mathbf{k}') |^{2} \{ U_{\text{eff}}^{-1} [\varepsilon_{n}(\mathbf{k}) - \varepsilon_{d} - U_{\text{eff}}]^{-1} - [\varepsilon_{n}(\mathbf{k}) - \varepsilon_{d} - U_{\text{eff}}]^{-2} \} \times [\varepsilon_{n'}(\mathbf{k}') - \varepsilon_{d} - U_{\text{eff}}]^{-1} [U_{\text{eff}}^{-1} (E_{v} - \varepsilon_{d} - U_{\text{eff}})^{-2} - (E_{v} - \varepsilon_{d} - U_{\text{eff}})^{-3}]^{-1} .$$
(5.2)

In the limit of flat valence bands, $\tilde{f}(\mathbf{r})$ becomes 9 for nearest neighbors and vanishes at larger r. Thus the flat band case reproduces the results of the three-level model as generalized to include valence-band degeneracy. For finite band dispersion the sums in Eq. (5.2) are dominated by the region near $\mathbf{k}=\mathbf{0}$. The discussion in Appendix B shows that both $|\tilde{V}_{pd}(n,\mathbf{k})|^2$ and the energy denominator factors decrease away from $\mathbf{k}=\mathbf{0}$. Phase cancellation due to the $\cos(\mathbf{k}\cdot\mathbf{r})$ factors further enhance the zonecenter contribution. Because these features are common to all tetrahedrally bonded Mn-based DMS's, $\tilde{f}(\mathbf{r})$ is approximately material insensitive.

By making the following approximations to $\tilde{f}(r)$ we obtain a form for f(r) which is explicitly insensitive to variations in the DMS energy bands $\varepsilon_n(k)$ and electronic structure parameters ε_d , U_{eff} , and V_{nd} .

structure parameters ε_d , U_{eff} , and V_{pd} . (1) The energy bands and $|\tilde{V}_{pd}(n,\mathbf{k})|^2$ are assumed to depend isotropically on \mathbf{k} as discussed in Appendix B. The result for $|\tilde{V}_{pd}(n,\mathbf{k})|^2$ is [Eq. (B8)] $|\tilde{V}_{pd}(0)|^2 z^2(k) \cos^2(ak/4)$, where z(k) is the averaged projection of the periodic part of a valence-band Bloch function onto the anion p orbitals [Eq. (B7) and following; z(0)=1, $z(2\pi/a)\approx 0.8$]. The $\cos^2(ak/4)$ factor arises from the interference of hopping amplitudes to different anions.

(2) The energy denominators in Eq. (5.2) and z(k) are each averaged over the Brillouin zone, weighted by $\cos^2(ak/4)$. This averaging is performed by first interpolating the k dependence and is carried out explicitly in Appendix C. Denoting this average for a quantity A(k) by $\langle A(k) \rangle$, we define

$$a_{n} \equiv \left\langle \frac{E_{v} - \varepsilon_{d} - U_{\text{eff}}}{\varepsilon_{n}(k) - \varepsilon_{d} - U_{\text{eff}}} \right\rangle, \quad b_{n} \equiv \left\langle \left[\frac{E_{v} - \varepsilon_{d} - U_{\text{eff}}}{\varepsilon_{n}(k) - \varepsilon_{d} - U_{\text{eff}}} \right]^{2} \right\rangle,$$
(5.3)

and $z \equiv \langle z(k) \rangle$.

(3) Terms containing $a_n - b_n$ are neglected relative to those containing $a_n + b_n$. For DMS parameters this approximation is accurate to better than 10%.

With these approximations

$$f(\mathbf{r}) \approx \frac{1}{2} z^4 \left[\sum_n a_n \right] \left[\sum_m a_m + b_m \right]$$
$$\times \left[\frac{1}{2} \left[\frac{a}{\pi} \right]^3 \int d^3k \cos(a\mathbf{k} \cdot \mathbf{r}) \cos^2(\frac{1}{4}ak) \right]^2. \quad (5.4)$$

The integral on the right-hand side is expressible in terms of special functions, but for the physically interesting region r < 1.5, including out to fourth nearest neighbors, it is well approximated by $3.3e^{-2.58r^2}$ (Appendix C). Thus,

$$f(r) \approx \frac{1}{2}z^{4} \left[\sum_{n} a_{n}\right] \left[\sum_{m} a_{m} + b_{m}\right] (3.3e^{-2.58r^{2}})^{2}$$
$$\approx 30.7e^{-5.16r^{2}}.$$
(5.5)

Here $\frac{1}{2}(\sum_{n} a_{n})(\sum_{m} a_{m} + b_{m})$ is approximately 4.5 for a



FIG. 5. The dimensionless functions $\tilde{f}(r)$ (solid line), f(r) (dotted line) of Eq. (5.5), and the empirical f(r) (dashed line) of Eq. (5.6), as a function of $r \equiv R/a$. Here *a* is the cubic lattice constant. Parameters correspond to those of Cd_{0.7}Mn_{0.3}Te. Also shown is the asymptotically valid exponential form of f(r) (dot-dashed line) for the same parameters. The first four nearest neighbors on the fcc magnitude lattice are indicated by NN, NNN, 3NN, and 4NN.

wide range of DMS parameters (Appendix C), including those of Sec. IV. Finite valence-band dispersion is responsible for the 50% reduction from the flat band value of 9.

Figure 5 shows f(r) (dotted line), and the $\tilde{f}(r)$ [solid line; Eq. (5.2)] corresponding to $Cd_{0.7}Mn_{0.3}Te$ parameters. The functions f and \tilde{f} agree at small r where the averaging assumption (2) is most accurate. At larger rthe neglect of k dependence in the energy denominators causes f to fall off somewhat too quickly. The reasonableness of the functional form given by Eq. (5.5) suggests fitting f(r) empirically as

$$f(r) \approx 51.2e^{-4.89r^2} \tag{5.6}$$

(the dashed line in Fig. 5). This function reproduces $\tilde{f}(r)$ to 20% for first through fourth nearest neighbors⁷⁴ with f(NN)=4.4 and f(NNN)=0.4. (Here NN and NNN denote nearest and next-nearest neighbors, respectively.) Also shown in Fig. 5 is the exponential asymptotic form for $\tilde{f}(r)$ obtained analytically as described in Ref. 68. The exponential is apparently inapplicable for r < 1.5. Table II contains parameters and the resulting $J^{dd}(R_{ij})$ value for $Cd_{1-x}Mn_x$ Te using empirical f(r) of Eq. (5.6). [The ~5% difference between this value of J_1^{dd} and the result in Sec. IV is due to the discrepancy between f(NN) and $\tilde{f}(NN)$, and the neglect of J_{he}^{dd} terms.]

B. Chemical trends in DMS's

The usefulness of the three-level model will be illustrated first by applying it to DMS's other than $Cd_{1-x}Mn_x$ Te. Although much less experimental information is presently available for these materials, a consistent set of input data will be obtained here using what is available together with simple theoretical estimates. An additional consistency check on anion trends is provided by the results of first-principles ASW calculations.

For clarity the comparisons will be restricted to a single concentration, x = 0.1. Calculations not discussed here indicate that the chemical trends are characteristic of a wide range of concentrations. The material insensitivity of f(r) implies that the J_2^{dd}/J_1^{dd} ratio will be constant. Therefore we focus on changes in J_1^{dd} .

1. Anion substitutions

Changes in the anion species are particularly significant since both *d*-*d* and *sp*-*d* exchange in DMS's are primarily determined by the anion-derived upper valence bands. Chemical trends in the series $Cd_{0.9}Mn_{0.1}Te \rightarrow Cd_{0.9}Mn_{0.1}Se \rightarrow Cd_{0.9}Mn_{0.1}S$ are summarized in the first three columns of Table II. The input parameters $E_v - \varepsilon_d$, U_{eff} , and V_{pd} for the selenide and sulfide are obtained as follows.

(1) $E_v - \varepsilon_d$ is obtained from photoemission data.^{14,75-78} The surprising constancy of this difference in Cd-based DMS's presumably results from two competing effects. E_v shifts to lower energy (by about 1 eV between the telluride and selenide and 0.80 eV between the selenide and sulfide⁷⁹) due to the deeper anion potential seen by the outer valence p electrons. For the same sequence the ma-

tions of J_1^{dd} employed Eq. (5.1) with $f(r) = 4.4$ for nearest neighbors as given by Eq. (5.6).						
	Cd _{0.9} Mn _{0.1} Te	Cd _{0.9} Mn _{0.1} Se	Cd _{0.9} Mn _{0.1} S	Zn _{0.9} Mn _{0.1} Te	Zn _{0.9} Mn _{0.1} Se	$Zn_{0.9}Mn_{0.1}S$
Input parameters						
$E_v - \varepsilon_d$ (eV)	3.4 ^a	3.4 ^b	3.4 ^c	3.4	3.4 ^d	3.4
$U_{\rm eff}$ (eV)	7.0 ^e	7.6	7.9	7.0	7.6	7.9
V_{nd} (eV)	0.219	0.255	0.330	0.240	0.277	0.351 ^f
$d_{Mn-XVI}^{\mu u}$ (Å)	2.759	2.572	2.453	2.722	2.533	2.411
Theoretical estimates						
[Eq. (5.1)] J_1^{dd} / k_R (K)	7.6	-9.0	-21.0	-11.0	-13.0	-27.0

TABLE II. Chemical trends for $M_{1-x}^{II} Mn_x X^{VI}$, computed using the three-level model, compared with experiment. The calculations of

- 7.9^g

- 8.1^j

^aReference 14.

Experiment J_1^{dd}/k_B (K)

^bReference 76.

^cReferences 75 and 77.

^dReference 78.

^eReference 11.

^fEstimated in text.

^gReference 31.

terials become more ionic and the *d*-level energy ε_d also shifts to lower energy because of the larger Mn-to-anion charge transfer.

-6.3^g

-6.1^h

(2) The variations in $U_{\rm eff}$ are estimated using a simple electrostatic argument. Although information on this parameter is not available for DMS's other than $Cd_{1-x}Mn_xTe$, the value of U_{eff} is not expected to change appreciably as a function of anion substitution since it is largely an intra-atomic property of Mn. A slight increase is expected in the series telluride \rightarrow selenide \rightarrow sulfide due to the reduced screening associated with the increasing Mn to anion charge transfer. We estimate U_{eff} by assuming a linear dependence on the inverse dielectric constant $\tilde{\epsilon_0}^{-1}$ and fitting to $Cd_{1-x}Mn_x$ Te and MnO. ($U_{eff}=7$ and 9 eV and $\varepsilon_0 = 0.14$ and 0.25, respectively, for the two materials.^{2,80,81}) The values⁸⁰ $\varepsilon_0^{-1} = 0.17$ for CdSe and 0.19 for CdS lead immediately to the U_{eff} entries in Table II. The estimated variations from the telluride to the sulfide is less than 15%.

(3) The *p*-*d* hybridization parameter V_{pd} is determined from Eq. (3.4) using the above parameters and the experimental sp-d exchange constants $N\beta$ listed in Table I. The increase in V_{pd} from the telluride to the sulfide is qualitatively consistent with scaling arguments for V_{pd} given a decrease in the Mn-anion bond length. Different scaling theories^{82,83} predict a bond length d dependence of either d^{-4} or $d^{-7/2}$. Recent extended x-ray absorption finestructure (EXAFS) studies of a number of semiconducting alloys including $Cd_{1-x}Mn_xTe$ (Ref. 84) provide some further information. They show individual cation-anion bond lengths in the alloy to retain values close to those of the limiting crystals. A simple central-force model⁸⁵ based on those results suggests that the Mn-anion bond length in $M^{II}-X^{VI}$ DMS's should exhibit the weak x dependence

$$d_{\mathrm{Mn-}X^{\mathrm{VI}}}(x) \approx d_{\mathrm{Mn-}X^{\mathrm{VI}}} + \frac{1}{4}(1-x)(d_{M^{\mathrm{II}}-X^{\mathrm{VI}}}^{0} - d_{\mathrm{Mn-}X^{\mathrm{VI}}}^{0}).$$
(5.7)

^hReference 32.

- 8.6ⁱ

- 10.6ⁱ

-- 8.8^k

-9.3¹

-9.5^m

-9.9

12.3^m

ⁱReference 37.

^jReference 36.

^kReference 38.

¹Reference 39.

^mReference 40.

Here $d_{M^{11},X^{V1}}^0$ and $d_{M^{0},X^{V1}}^0$ are the nearest-neighbor bond lengths in the limiting x = 0 and x = 1 zinc-blende crystals. The values of $d_{Mn-X^{VI}}$ (x =0.1) listed in Table II are obtained from Eq. (5.7) and the tabulated crystalline bond lengths in Ref. 86. With the value of V_{pd} determined in Sec. III for $Cd_{0.9}Mn_{0.1}Te$ scaled by the $\dot{d}_{Mn-X^{VI}}$ (x = 0.1) of Table II, the scaling theories yield V_{pd} in $Cd_{0.9}Mn_{0.1}Se$, $Cd_{0.9}Mn_{0.1}S$ as 0.31, 0.36 eV (d^{-4}) , or 0.29, 0.34 eV $(d^{-7/2})$. Neither set of values agrees particularly well with the experimentally determined entries in Table II, probably because chemical differences between the anions are neglected.

Substitution of $E_v - \varepsilon_d$, U_{eff} , and V_{pd} determined in (1)-(3) above into Eq. (5.1) yields the theoretical prediction for J_{1}^{dd} listed in Table II. The 18% increase from the telluride to the selenide is in reasonable agreement with the 25% increase observed experimentally.^{31,34} The larger predicted increase in $|J_1^{dd}|$ from selenide to sulfide somewhat overestimates the experimental trend. The discrepancy is still within the accuracy of the model, and may be corrected when more-accurate input parameters (e.g., U_{eff}) become available. (To aid comparison, the experimental J_1^{dd} entries in Table II are all taken from experiments in which the effects of second and more-distant neighbor exchanges are approximately corrected for.)

The results of ASW-LSDA calculations listed in Table III for the limiting crystalline compounds MnTe, MnSe, and MnS are qualitatively consistent with the anion trends. The calculations assume that all three have the zinc-blende structure and an AF-I antiferromagnetic ordering. (At small Mn concentrations $Cd_{1-x}Mn_xSe$ and $Cd_{1-x}Mn_xS$ actually have the wurtzite structure.) The spin splitting $\varepsilon_d^{\downarrow} - \varepsilon_d^{\uparrow}$, or U_{eff} in the present model, increases somewhat from the telluride to the sulfide although the magnitude of this splitting is known to be seriously underestimated in the LSDA (Sec. II and Appendix A). The difference $E_v - \varepsilon_d$ is roughly constant

- 16.1^m

TABLE III. ASW-LSDA results for zinc-blende MnTe, MnSe, and MnS in the AF-I ordering. Here *a* is the cubic lattice constant, and M_{loc} is the Mn-sphere magnetic moment. The meaning of $\varepsilon_d^{\perp} - \varepsilon_d^{\perp}$ and $E_v - \varepsilon_d^{\perp}$ in all three systems is the same as indicated in Fig. 2 for MnTe.

	a (Å)	$M_{ m loc}$ (μ_B)	$ \begin{aligned} \varepsilon_d^{\downarrow} - \varepsilon_d^{\uparrow} \\ (eV) \end{aligned} $	$E_v - \varepsilon_d^{\dagger}$ (eV)	J ^{dd} ₁ /k _B (K)
MnTe	6.34	4.23	3.2	2.2	-17
MnSe	5.82	4.15	3.4	2.1	-24
MnS	5.60	4.14	3.9	2.4	-26

across the series, although the values are ~30% smaller than those listed in Table II. The increasing $|N\beta|$ values in the ASW results in Table I provide support for an increasing V_{pd} from the telluride to the sulfide. The J_1^{dd} values in Table III are obtained as before from ASW total-energy differences between AF-I and ferromagnetic orderings. The increase in magnitude is smaller than that given in Table II. As was found for the larger discrepancy in J_1^{dd} magnitudes, the discrepancy in the telluride-toselenide J_1^{dd} trend is probably associated with the LSDA underestimate of the energy of unoccupied Mn 3d levels (Sec. II and Appendix A).

2. Cation substitutions

Changes in the cation species play a far less important role in determining the magnetic properties. Here we consider only the replacement of Cd with Zn. Hg-based DMS's are omitted because of larger experimental uncertainties in *sp-d* exchange constants. Furthermore, J_{he}^{dd} associated with the Bloembergen-Rowland interaction, neglected in this section, plays a more important role in the zero-gap case. Nevertheless, superexchange is believed to be dominant in Hg-based alloys.⁸⁷

The substitution of Zn for Cd has only an indirect effect on the band-structure features relevant to superexchange. We estimate the associated changes in J_1^{dd} using Eq. (5.1) and the input data listed in Table II. $E_v - \varepsilon_d$ and U_{eff} are assumed to be the same in the corresponding Cd and Zn alloys since these parameters are determined primarily by the Mn and the anion. (Experimental information is presently available only for $Zn_{1-x}Mn_x$ Se, when $E_v - \varepsilon_d$ is 3.5 ± 0.1 eV, consistent with this assumption.⁷⁸) V_{pd} values in $Zn_{0.9}Mn_{0.1}$ Te and $Zn_{0.9}Mn_{0.1}$ Se are determined from the experimental $N\beta$ values in Table I. Small but definite increases in V_{pd} are observed relative to the corresponding Cd alloys. We interpret this trend as an indirect effect of the cation on the Mn-anion bond length. The d_{Mn-x} vi values in Table II indeed decrease slightly as Cd is replaced by Zn. The variations in V_{pd} for Cd_{0.9}Mn_{0.1}Te $\rightarrow Zn_{0.9}Mn_{0.1}$ Te and Cd_{0.9}Mn_{0.1}Se

Cd is replaced by Zn. The variations in V_{pd} for $Cd_{0.9}Mn_{0.1}Te \rightarrow Zn_{0.9}Mn_{0.1}Te$ and $Cd_{0.9}Mn_{0.1}Se \rightarrow Zn_{0.9}Mn_{0.1}Se$ in fact are well described by a $d^{-7/2}$ or d^{-4} power law. (Scaling works better here than for the anion trends because the chemical nature of the anion is unchanged and the variation in d is smaller.) In the absence of an experimental $N\beta$ value, we estimate V_{pd} for $Zn_{1-x}Mn_xS$ by scaling the $Cd_{0.9}Mn_{0.1}S$ value.

The J_1^{dd} results in Table II indicate a clear trend towards a larger superexchange interaction in Znsubstituted DMS's. Quantitative agreement with experiment is achieved for $Zn_{0.9}Mn_{0.1}Te$ and $Zn_{0.9}Mn_{0.1}Se$. The value of $|J_1^{dd}|$ in $Zn_{0.9}Mn_{0.1}S$ is found to be the largest of any of the DMS's considered here. This prediction agrees with a recent neutron scattering experiment.⁴⁰ By using the experimental values of J_1^{dd} given in Table II for $Cd_{1-x}Mn_xS$ and $Zn_{1-x}Mn_xS$ together with $N\beta$ for $Cd_{1-x}Mn_xS$ in Eqs. (5.1) and (3.4), we predict $N\beta$ for $Zn_{1-x}Mn_xS$ to be -(2.2 to 2.4) eV. This prediction should be checked experimentally.

An alternative model of cation trends has recently been proposed by Spakek *et al.*⁸⁸ They assume that J_1^{dd} is affected principally by the change in the Mn—anion— Mn bond angle due to the structural distortions associated with different cations. This undoubtedly has some effect, but is neglected here, since, as in the case of amorphous covalent semiconductors, we regard changes in V_{pd} due to small variations in bond length to be considerably more important.

The present approach provides a consistent interpretation of the increase in both $N\beta$ and J_1^{dd} as Cd is replaced by Zn. In addition, this interpretation implies a dependence of V_{pd} on x within the Cd and Zn alloy systems, since both must extrapolate to the same value at x = 1. If $d_{Mn-X^{VI}}$ follows Eq. (5.7), a 6.2% increase in V_{pd} is predicted in Cd_{1-x}Mn_xTe between x = 0 and x = 0.75. This leads to a 13% increase in N β and a 27% increase in J_1^{dd} (if other factors are neglected).

C. MnO and *a*-MnS

It is remarkable that the three-level expression (5.1) is applicable to a quite different class of materials, illustrated by the insulators MnO and α -MnS. This is seen by calculating the Mn-Mn exchange interaction in these materials. The f(r) appropriate to the rocksalt structure, hereafter denoted $f_{RS}(r)$, is again insensitive to the specific material.

The main differences between the electronic structure of DMS's and MnX (X = 0,S) result primarily from the increased ionicity of the rocksalt compounds. They are (1) the anion *p*-derived levels lie primarily *below* the occupied Mn *d* levels and are significantly narrower than in DMS's; (2) U_{eff} is larger than in DMS's, because the screening charge on the Mn cation is decreased; (3) the higher symmetry of the rocksalt structure leads to $|\tilde{V}_{pd}(v,k)|^2 = 0$ at both Γ and X.

Although we would expect the three-level model to apply generally to Mn-based nonmetals, the corresponding f(r) for different classes of materials will generally depend on their point-group symmetry. For example, selection rules (Goodenough-Kanamori rules⁸⁹) reduce the region of the Brillouin zone where *p-d* hybridization occurs, thereby decreasing f(r). For DMS's these selection rules impose no restrictions; however, the higher symmetry of the rocksalt structure causes a reduction of nearest-neighbor superexchange by $\sim \frac{1}{2}$. The effect on f(r) will generally depend both on the functional form of $\tilde{V}_{pd}(v,k)$ and on the location of critical points in the ener-

$f_{\rm RS}(r) = 4.4$ for hearest heighbors as given by Eq. (3.6).						
	$E_v - \varepsilon_d$ (eV)	$U_{ m eff}$ (eV)	V_{pd} (eV)	d (Å)	J_1^{dd} (theory)/ k_B (K)	$\frac{J_1^{dd}(\text{expt.})/k_B}{(\text{K})}$
MnO	-2.5ª	9.0 ^b	0.46	2.225ª	-5.0	7.2ª
α-MnS	0.5 ± 1.0^{a}	8.0	0.27	2.605ª	-1.7 ± 0.4	-4.4 ^a

TABLE IV. Chemical trends for the rocksalt compounds MnO and α -MnS, computed using the three-level model, compared with experiment. The calculations of J_1^{dd} employed by Eq. (5.1) with $f_{RS}(r) = 4.4$ for nearest neighbors as given by Eq. (5.6).

^aReference 63, and references therein.

^bReference 2.

gy denominators of Eq. (5.2). For example, in DMS's the minima in energy denominators [Eq. (5.2)] and in $|\tilde{V}_{pd}(v,k)|^2$ both occur at Γ , causing f(NN) to be reduced by $\sim \frac{1}{2}$ from the flat-band result (cf. Sec. V A). By contrast, in the perovskite compound KMnF₃, the minimum in the energy denominators at Γ corresponds to a zero in $\tilde{V}_{pd}(v,k)$, leading to a larger reduction, estimated at $\sim \frac{1}{4}$.

In MnX the flat-band limit should correspond to a good approximation for $f_{\rm RS}(r)$ since $W(E_v - \varepsilon_d)$ $(-U_{\rm eff})^{-1} \ll 1$. (W is the average bandwidth of the sp valence bands.⁹⁰) In contrast to DMS's, this limit here implies $f_{RS}(r)$ is nonzero for both first and second neighbors on the fcc magnetic lattice, since superexchange to both is mediated by p orbitals of the nearest-neighbor anions. Second neighbor superexchange is reduced by the same factor $\frac{1}{2}$ as first neighbor superexchange because only one anion mediates these processes, compared to two anions for first neighbors. In DMS's, f(NN) is reduced by $\frac{1}{2}$ due to the presence of broad bands (see preceding paragraph). It therefore turns out by accident that $f_{RS}(NN) \approx f(NN)$. However, f_{RS} and f differ for second and more-distant neighbors. The function $f_{RS}(r)$ is expected to be similar in MnO and α -MnS because $W(E_v - \varepsilon_d - U_{\text{eff}})^{-1} \ll 1$ in both. As in DMS's, f_{RS} is material insensitive because the k integrations are dominated by $|\tilde{V}_{pd}(v,k)|^2$.

Table IV contains parameters and calculated values of J_1^{dd} for MnO and α -MnS using Eq. (5.1) and (5.6) with $f_{\rm RS}({\rm NN}) \approx f({\rm NN}) \approx 4.4$. $E_v - \varepsilon_d$ was taken from the ASW-LSDA calculations of Terakura *et al.*;⁹¹ $U_{\rm eff}$ for α -MnS was estimated as in Sec. V B; V_{pd} was calculated from V_{pd} for Cd_{1-x}Mn_xTe and was assumed to obey the $d^{-7/2}$ scaling law.

The good agreement of the calculated J_1^{dd} with experimental results given in Table IV in both magnitude and trend indicates that the three-level model is applicable to MnX, and that a single function $f_{\rm RS}(r)$, which needs to be calculated only once for each class of materials, can be defined. The calculations, like those for DMS's (Sec. V B), are remarkably simple, requiring only the electronic structure input parameters $(E_v - \varepsilon_d, U_{\rm eff}, \text{ and } V_{pd})$ and the function $f_{\rm RS}$. As a result it is reasonable to expect that the three-level model will also provide useful numerical estimates of exchange constants in other Mn-based nonmetals.

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APPENDIX A: CORRECTIONS TO THE LSDA

To quantify the discussion of Sec. II, corrections to the LSDA eigenvalues has been estimated, employing a simple method based on empirical dielectric constants.⁵⁴ Corrections to the MnTe conduction and valence sp band edges, and the majority and minority spin levels of e_g symmetry at Γ , were computed. The value $\varepsilon_0=7$ was derived by linear extrapolation from dielectric constants in the alloy for $x \leq 0.7$. The estimated difference between the LSDA eigenenergies, ε^{LSDA} , and the true quasiparticle energies, $^{92} \varepsilon$, is given by⁵⁴

$$\varepsilon - \varepsilon^{\text{LSDA}} = \frac{e^2}{2\varepsilon_0} \int_{\text{unit cell}} d^3r \, d^3r' \frac{\delta n(r)\delta n(r') - \delta n^{\text{LSDA}}(r)\delta n^{\text{LSDA}}(r')}{|r - r'|} \,. \tag{A1}$$

Here

$$\delta n(r) = |\psi_{\varepsilon}(r)|^2 \left[\int_{\text{unit cell}} |\psi_{\varepsilon}(r)|^2 d^3 r\right]^{-1}, \quad (A2)$$

 $\psi_{\varepsilon}(r)$ is the LSDA wave function corresponding to $\varepsilon^{\text{LSDA}}$,

and $\delta n^{\text{LSDA}}(r) = \delta n(r) + \delta n_{\text{scr}}(r)$. The LSDA screening charge $\delta n_{\text{scr}}(r)$ is given by

$$\delta n_{\rm scr}(r) = \overline{n} \int d^3 r' [g(|r-r'|;\overline{n})-1] \delta n(r'), \quad (A3)$$

<u>37</u>

where $g(|r-r'|; \overline{n})$ is the pair distribution function (taken to be spin independent) for a uniform electron gas having the weighted average density

$$\overline{n} = \left| \int \delta n(r) n^{1/3}(r) d^3 r \right|^3.$$
 (A4)

To aid comparison with experiment, scalar-relativistic corrections were also estimated. The MnTe *sp*conduction and valence-band-edge shifts were approximated using the corresponding shifts for a Te atom:

(energy shift of
$$\psi$$
)_{band} $\approx \frac{(\text{core charge of }\psi)_{\text{band}}}{(\text{core charge of }\psi)_{\text{atom}}}$

$$\times$$
 (energy shift of ψ)_{atom}.

These calculations lead to the following results.

(1) The LSDA correction is largest for the *d* levels since the associated orbitals are most localized. The occupied *d* levels are shifted to lower energies by 1.5 eV and the unoccupied levels to higher energies by 1.0 eV. Thus the energy required to create a separated *d*-electron-*d*-hole pair is underestimated by the LSDA spin splitting. Since the LSDA eigenvalues are computed using the ground-state potential, the LSDA spin splitting may actually correspond more closely to the energy of an intraatomic $S = \frac{5}{2} \rightarrow S = \frac{3}{2}$ transition.⁹³ The corrections increase U_{eff} from 3.2 to 5.7 eV. This improves agreement with the value $U_{\text{eff}} = 7$ eV, derived from experiment, which was used in the magnetic calculations.

(2) The valence-band edge is shifted to lower energy by 0.5 eV due to the LSDA corrections, and by a further 0.4 eV by scalar-relativistic corrections. These shifts, combined with (1), cause the energy required to remove an electron from the top of the valence band and place it in an unoccupied *d* level infinitely far away in the crystal to increase from 1 to 2.9 eV. Additionally, the valence-band-edge-to-occupied-*d* energy splitting increases to 0.6 eV from 2.3 to 2.9 eV. This value is closer to the 3.4 eV (for x < 0.6) value discussed in Sec. II.

APPENDIX B: ETBM MODEL AND SPHERICAL APPROXIMATION FOR H_0 AND H_{nd}

The empirical tight-binding model used to obtain the explicit forms of the H_0 and H_{pd} terms in Eq. (2.1) employs a minimal basis set consisting of one s orbital per cation and three p orbitals per anion. The resulting sp Hamiltonian H_0 provides a good semiquantitative description of the Te p-like upper valence bands in $Cd_{1-x}Mn_xTe$. The lowest conduction band is also reasonably described although this is less important for the numerical calculations of $J^{dd}(R_{ij})$ in Sec. IV. Scalar-relativistic effects are included in the model by the empirical choice of parameters. The neglect of spin-orbit splitting is not believed to lead to serious errors in $J^{dd}(R_{ij})$.

We consider interactions for first- and second-nearest neighbors. H_0 is then completely characterized by six Slater-Koster parameters⁹⁴ for which we introduce a simplified notation in Table V. The parameter values for $Cd_{1-x}Mn_x$ Te listed in the third column of the table are obtained as follows.

(1) The cation on-site energy ε_c is assumed to exhibit the linear VCA variation

$$\varepsilon_c = \Delta_c + x(\varepsilon_c(\mathbf{Mn}) - \varepsilon_c(\mathbf{Cd})) . \tag{B1}$$

Here $\varepsilon_c(Cd) = 0.12$ eV and $\varepsilon_c(Mn) = 1.72$ eV are the Cd 5s and Mn 4s on-site energy levels, respectively, and $\Delta_c = 3.16$ eV is chosen to reproduce the experimental x = 0 band gap.

(2) The anion on-site energy ε_a and the single nearestneighbor hopping parameter V_{ca} are assumed to be independent of x and have the same value as in moreextensive ETBM parametrizations of CdTe.⁹⁵ The x independence of ε_a reflects a common anion assumption.

(3) The second-neighbor parameters (C, A_1, A_2) are also assumed to be x independent and are required to be no larger than ~10% of V_{ca} . The chosen values yield conduction and valence bandwidths in reasonable agreement with experiment.

The spherical approximation used in the calculation of $J^{dd}(R_{ij})$ assumes that the *sp* bands are isotropic and have the *k* dependence given by the diagonalization of H_0 along $\Gamma - X$. This direction is chosen because the resulting eigenvalues

$$\varepsilon_{2,3}(k) = \varepsilon_a + 4A_1[1 + \cos(\frac{1}{2}ak)] + 4A_2\cos(\frac{1}{2}ak)$$
(B2)

and

$$\epsilon_{4,1}(k) = \frac{1}{2} [g_1(k) + g_2(k)] \\ \pm \{ \frac{1}{4} [g_1(k) - g_2(k)]^2 + 16V_{ca}^2 \sin^2(\frac{1}{4}ak) \}^{1/2}$$
(B3)

can be obtained analytically. Here

$$g_1(k) = \varepsilon_c + 4C \left[1 + 2\cos(\frac{1}{2}ak) \right],$$

$$g_2(k) = \varepsilon_a + 4A_2 + 8A_1\cos(\frac{1}{2}ak).$$
(B4)

Bands 2 and 3 are degenerate valence bands with an xindependent bandwidth of 2.2 eV. Band 1 is the wider valence band, with a bandwidth of 5.1 eV at x = 0 and 4.8 eV at x = 1. Band 4 is the sp conduction band, with a bandwidth of 2.8 eV at x = 0 and 2.5 eV at x = 1. The band gap is given by (1.6+1.6x) eV.

TABLE V. ETBM parameters for $Cd_{1-x}Mn_xTe$. The table also establishes the correspondence between the Slater-Koster notation and the notation used in this work.

Parameter		
This work	(eV)	
ε _c ε _A	3.16 + 1.6x 0.10	
V _{CA}	1.103	
C A_1 A_2	0.015 0.13 0.15	
	eter This work ϵ_c ϵ_A V_{CA} C A_1 A_2	

We now consider H_{pd} , for which we compute $\tilde{V}_{pd}(n, \mathbf{k})$ within the ETBM. Let $|d(i)\rangle$ be a *d* function at site *i*. We assume a Löwdin orthogonalization⁹⁶ has made this function orthogonal to the other basis functions. In the VCA

$$\langle d(i) | H | n\mathbf{k} \rangle = e^{i\mathbf{k}\cdot\mathbf{R}_{i}} N^{-1/2} \sum_{i=x,y,z} a_{p_{i},a}^{(n)}(\mathbf{k}) \sum_{\delta_{j}} e^{i\mathbf{k}\cdot\delta_{j}} V_{pd}$$
$$\equiv e^{i\mathbf{k}\cdot\mathbf{R}_{j}} \widetilde{V}_{pd}(n,\mathbf{k}) .$$
(B5)

Here δ_j is one of the four \mathbf{R}_{ij} associated with nearestneighbor anions to the Mn, and $a_{\alpha\nu}^{(n)}(\mathbf{k})$ is the coefficient in the expansion of the Bloch function $|n\mathbf{k}\rangle$ of the Bloch sum $|\alpha\nu\mathbf{k}\rangle$ corresponding to the α th basis function ϕ_{α} at τ_{ν} . $(\alpha = s, p_x, p_y, p_z; \nu = a, c$ for anion and cation.) Our basic approximation is that the hopping integral V_{pd} is (1) only nonzero for nearest-neighbor anion p orbitals, and (2) independent of the type of p and d orbitals involved. We thus define

$$V_{pd} \equiv \int \phi_d^*(\mathbf{r}) H \phi_{p_i}(\mathbf{r} - \boldsymbol{\delta}_j - \boldsymbol{\tau}_a) d^3 r .$$
 (B6)

Here $\phi_{p_i}(\mathbf{r}-\delta-\tau_a)$ is a p_i orbital centered at $\delta_j + \tau_a$. The basic reason for this is a good approximation for DMS's is that V_{pd} is determined from experiments which give an orbitally averaged quantity. On the other hand, orbital indices are summed over in the calculation of $J^{dd}(R_{ij})$, so that the averaged parameter should provide a good approximation.

 $|\tilde{V}_{pd}(n,\mathbf{k})|^2$, which occurs in the calculation of $J^{dd}(R_{ij})$, contains the factor

$$\left|\sum_{\delta_{j}} e^{i\mathbf{k}\cdot\delta_{j}}\right|^{2} = 4\left[1 + \cos\left(\frac{1}{2}ak_{x}\right)\cos\left(\frac{1}{2}ak_{y}\right) + \cos\left(\frac{1}{2}ak_{y}\right)\cos\left(\frac{1}{2}ak_{z}\right) + \cos\left(\frac{1}{2}ak_{z}\right)\cos\left(\frac{1}{2}ak_{z}\right)\right] . \tag{B7}$$

This has a maximum at k=0 and decreases in all directions away from k=0, vanishing at the X point. This decrease comes from the interference of hopping amplitudes to different anion neighbors as k^{-1} becomes comparable with the Mn-anion distance. The factor $|\sum_{i=x,y,z} a_{p,1}^{(n)}(\mathbf{k})|^2 \equiv |\hat{\mathbf{z}}_n(\mathbf{k})|^2$ is the square of the projection of the periodic part of the Bloch function at k onto the anion p orbitals. For the upper valence bands, this factor is just 1 at k=0 and decreases along $\Gamma - X$. For the lowest conduction band $a_{p_i,1}^{(n)}(\mathbf{k}=\mathbf{0})=\mathbf{0}$. (This remains true for a more general basis than we consider here, because it follows from a selection rule.) The net effect of the two k dependencies is to suppress hopping through the conduction band relative to the valence bands, and to emphasize hopping through the states near the zone center.

We adopt an approximation to $\tilde{V}_{pd}(n, \mathbf{k})$ which preserves these features and is consistent with the assumed spherical energy bands (calculated along $\Gamma - X$). The $a_{\mathbf{p}_i,1}^{(n)}(\mathbf{k})$ are calculated along $\Gamma - X$, $|\tilde{V}_{pd}(n,k)|^2$ is averaged over principal directions, and the result is taken to be a function of $|\mathbf{k}|$ in a spherical Brillouin zone:

$$|\tilde{V}_{pd}(n,k)|^2 \approx 16V_{pd}^2 N^{-1} z^2(k) \cos^2(\frac{1}{4}ak)$$
 (B8)

Here $z^2(k)$ is the average of $|\hat{z}_n(\mathbf{k})|^2$ over principal directions. (For the three *sp* valence bands the result of this averaging is independent of *n*.)

APPENDIX C: DERIVATION AND PROPERTIES OF f(r)

Beginning with the definition of $\tilde{f}(r)$ given in Eq. (5.2), with the isotropic approximation made for the k dependence of energy bands and $|\tilde{V}_{pd}(n,k)|^2$ [Eq. (B7) and following], the energy denominators are averaged next over the Brillouin zone. Averaging is reasonable because the energy denominators are weakly k dependent compared to $|\tilde{V}_{pd}(n,k)|^2$. The average is weighted by the dominant $\cos^2(ak/4)$ factor in $|\tilde{V}_{pd}(n,k)|^2$ [Eq. (B8)]. This choice of weighting ensures that f(r) has the correct limit as $r \rightarrow 0$. The average of a quantity A(k), denoted by $\langle A(k) \rangle$, is given explicitly by

$$\langle A(k)\rangle \equiv \left[\int d^{3}k\cos^{2}(\frac{1}{4}ak)\right]^{-1}\int d^{3}k\cos^{2}(\frac{1}{4}ak)A(k) .$$
(C1)

In order to perform this averaging on Eq. (5.2), the k dependence of the energy denominators and of the factor z(k) [Eq. (B7) and following] are approximated by

$$[\varepsilon_n(k) - \varepsilon_d - U_{\text{eff}}]^{-1} \approx (E_v - \varepsilon_d - U_{\text{eff}})^{-1} \times [y_n + (1 - y_n)\cos^2(\frac{1}{4}ak)], \quad (C2)$$

and

$$z(k) \approx z \left(\frac{2\pi}{a}\right) + \left[1 - z \left(\frac{2\pi}{a}\right)\right] \cos^2(\frac{1}{4}ak)$$
 (C3)

The y_n are defined by

$$y_n \equiv (E_v - \varepsilon_d - U_{\text{eff}}) / (E_v - W_n - \varepsilon_d - U_{\text{eff}})$$

where W_n is the bandwidth of the valence band $\varepsilon_n(k)$ [Eqs. (B2) and (B3)]. The interpolation of Eq. (1.2) is chosen to reproduce the correct values and first derivatives of the energy denominators at Γ and X. Using

$$\langle \cos^2(\frac{1}{4}ak) \rangle \approx 0.46$$
 and $\langle \cos^4(\frac{1}{4}ak) \rangle \approx 0.28$, (C4)

we compute the quantities a_n , b_n , and z defined in Eq. (5.3):

$$a_n = y_n + 0.46(1 - y_n) , \qquad (C5)$$

$$b_n = y_n^2 + 0.92y_n(1 - y_n) + 0.28(1 - y_n)^2$$
, (C6)

and

$$z = z \left[\frac{2\pi}{a} \right] + 0.46 \left[1 - z \left[\frac{2\pi}{a} \right] \right] \approx 0.89 .$$
 (C7)

Inserting Eqs. (C5)-(C7) in Eq. (5.2) and neglecting

 $a_n - b_n$ relative to $a_n + b_n$ (accurate to ~10% for y_n corresponding to a wide range of the parameters $E_v - \varepsilon_d$, U_{eff} , and W_n), we obtain Eq. (5.4).

The integral on the right-hand side of Eq. (5.4) is

$$\frac{1}{2} \left[\frac{a}{\pi} \right]^3 \int d^3k \cos(a\mathbf{k} \cdot \mathbf{r}) \cos^2(\frac{1}{4}ak) \\ = -\frac{2}{\pi r} \frac{\partial}{\partial r} \{ [\Gamma(2+2r)\Gamma(2-2r)]^{-1} \} .$$
(C8)

By expanding

 $\ln[\Gamma(2\pm 2r)] \approx \pm 2r\psi(2) + 1/2(2r)^2\psi'(2) ,$

where $\psi(r) \equiv d(\ln \Gamma)/dr$ is the digamma function, the in-

$$\frac{16}{\pi}\psi'(2)\exp[-4\psi'(2)r^2] .$$
 (C9)

Using⁹⁷ $\psi'(2) \approx 0.645$ yields Eq. (5.5) for f(r).

The results of the averaging appear in Eq. (5.4) as the factors z^4 and $\frac{1}{2}(\sum_n a_n)(\sum_m a_m + b_m) \equiv Q$. The factor Q is insensitive to changes in valence bandwidth. To show this, we compute Q assuming all valence bands have the average bandwidth W, with $E_v - \varepsilon_d - U_{\text{eff}} = 3.6 \text{ eV}$. For W=0, one has Q=9, but for the range W=2 eV to W = 6 eV relevant to DMS's, Q changes only from 5.5 to 3.8.

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