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Electronic origins of the magnetic phase transitions in zinc-blende Mn chalcogenides

Su-Huai Wei and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

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Precise first-principles spin-polarized total-energy and band-structure calculations have been performed for the zinc-blende Mn chalcogenides with the use of the local-spin-density (LSD) approach. We find that the LSD is capable of identifying the correct magnetic-ground-state structure, but it overestimates the ordering temperature T_N and the valence-band exchange splitting Δ_x^p. The discrepancy is attributed to the overestimation by LSD of the *p*-*d* coupling. Adjusting this coupling by an external potential and fitting its parameters to the *s*- and *p*-band exchange splitting in MnTe alone, we find that $T_N=73$, 90, and 128 K, respectively, for MnTe, MnSe, and MnS, in good agreement with experiment. This shows that the failures of the LSD in reproducing T_N and Δ_x^p share a common physical origin, namely the overestimation of *p*-*d* coupling.

I. INTRODUCTION

While bulk Mn X^{VI} chalcogenides crystallize spontaneously in either the hexagonal NiAs-type structure (MnTe) or in the NaCl structure (α-MnSe and α-MnS), they can also be stabilized artificially in the zinc-blende (β) structure by epitaxial growth, or by alloying with II-VI semiconductors.[1-3] Neutron-diffraction and optical studies revealed that below a temperature T_N, the spin lattice associated with the Mn ions in β-MnX^{VI} orders into the "type III" antiferromagnetic structure,[4-6] while α-MnX^{VI} orders into the AF-II structure.[7] In this paper we wish first to use the local spin density (LSD) formalism[8] in conjunction with the cluster expansion method[9-13] to find whether these magnetic ground-state structures can be obtained. For β-MnX^{VI} we also compare the calculated transition temperatures T_N obtained from a Monte Carlo simulation[14] with experiment. As will be seen below, we find that the LSD formalism produces the correct magnetic ground state structures, yet T_N is overestimated by a large factor. It was also noted previously[3,15,16] that the exchange splitting Δ_x^p in the *p*-like valence bands is overestimated in the LSD description relative to experiment. We analyze the electronic origins of Δ_x and T_N, finding that the systematic LSD error in the *spectroscopic* splittings Δ_x^p and in the *thermodynamic* transition temperatures (T_N) share a common physical origin: the overestimation by the LSD of the *p*-*d* coupling between the Mn *d* bands and the anion *p* bands. The quantitative interrelations between these properties are then studied by performing self-consistent electronic structure and total-energy calculations for MnTe in the presence of an artificial Mn-centered parametric external potential which reduces the *p*-*d* coupling. We find that this weakening of the *p*-*d* coupling reduces Δ_x^p and lowers T_N, all in the right direction needed to achieve agreement with experiment. Applying this same external "pseudopotential" to MnS and MnSe without any additional fit gives the correct trends in spectroscopic, structural, and thermodynamic quantities along the MnS→MnSe→MnTe series. We conclude that leading correction needed in (future) many-body theories of magnetic semiconductors should have the effect of reducing the *p*-*d* coupling in this system.

II. GROUND-STATE STRUCTURES AND THE ORDER-DISORDER TRANSITION TEMPERATURE IN Mn CHALCOGENIDES

A. Method of calculation

Since the number of possible spin configurations that can be constructed on an *N*-point lattice is enormous (2^N), to search this space for a minimum energy we first calculate directly the LSD total energy for a few antiferromagnetic (AFM) and ferromagnetic (FM) spin configurations $\{\sigma\}$, yielding the excess energy

$$\Delta E_{\mathrm{direct}}(\sigma)=E(\sigma)-E(\mathrm{FM}) \ . \tag{1}$$

We then map the calculated LSD energies of Eq. (1) onto a spin-lattice Hamiltonian, so its ground state can be systematically searched in a *linear process*.[9-11] The Mn-Mn magnetic interaction is commonly described[1,2,15] by the *quantum* spin $\frac{5}{2}$ Heisenberg Hamiltonian $H=H_0-\sum_{i\neq j}J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$, where H_0 is a constant, $\mathbf{S}_i$ is the spin magnetic moment on Mn site *i*, and J_{ij} are the isotropic pair interactions between spins on site *i* and *j*. The *classical* analogue of this Hamiltonian is

$$E(\sigma)=E_0-\sum_{i\neq j}\tilde{J}_{ij}\hat{\sigma}_i\cdot\hat{\sigma}_j \ , \tag{2}$$

where $\hat{\sigma}_i$ is a continuous unit vector describing the direction of the moment $\mathbf{S}_i$, and $\tilde{J}_{ij}=S(S+1)J_{ij}$. To calculate $\tilde{J}_{ij}$, we consider two directions $\sigma_i=-1$ and $\sigma_i=+1$ (corresponding to occupation of site *i* by $\mathrm{Mn}^{\downarrow}$ and $\mathrm{Mn}^{\uparrow}$, respectively), and calculate $\Delta E_{\mathrm{direct}}(\sigma)$ for a few spin configuration σ. This is done using the LSD formalism,[8] as implemented by the spin-polarized linear augmented plane wave (LAPW) method.[13,17] The basis set consists of about 150 basis functions per atom. The Brillouin zone integration is performed using 10 special **k**-points for the zinc-blende structure and equivalent **k**-points for all the other structures.[3,18] The muffin-tin (MT) size we used for Mn and Te are 2.59 a.u. The local magnetic moments μ are integrated inside the muffin-tin spheres. We estimate our convergence error in ΔE_{direct} and μ at 2 meV and 0.05 μ_B per Mn atom, respectively. We consider a number of $(\text{Mn}^{\uparrow}\text{Te})_p(\text{Mn}^{\downarrow}\text{Te})_p$ "spin superlatices," including the familiar antiferromagnetic configurations AFM-I, AFM-II, and AFM-III which can be described as superlattice of period p and layer orientation **G**: AFM-I is $p=1$, $\mathbf{G}=(001)$; AFM-II is $p=1$, $\mathbf{G}=(111)$; and AFM-III is $p=2$, $\mathbf{G}=(201)$. We also add the $p=2$, $\mathbf{G}=(001)$ structure (AFM-IV) and the $p=2$, $\mathbf{G}=(110)$ structure (AFM-V). Table I shows the LSD calculated excess energies $\Delta E_{\text{direct}}(\sigma)$ and the local magnetic moments $\mu(\sigma)$ for each of these spin configuration σ, all calculated at the observed[1] lattice constant $a=6.33$ Å. Note that the magnetic moments are reduced relative to the free-atom value of $5\mu_B$. Our results agree with the previous calculations of Larson *et al.*[15] and Podgorny *et al.*[16], but disagree sharply with the pseudofunction calculation of Tsai *et al.*[19,20] yielding $\mu \approx 6.3\mu_B$, in excess of the free-atom value of 5 μ_B. This discrepancy is significant given that both our calculation and that of Tsai *et al.* are based on the same LSD Hamiltonian.

The reduction that we and others[15,16] find in the local moment relative to the free-atom value $\mu_0 = 5\mu_B$ in the d^5 configuration reflects mixing in the solid of the unoccupied Mn $d^{\downarrow}$ bands into the occupied valence p bands by the p-d hybridization. Instead, Tsai *et al.*[19,20] found that in the solids Mn takes up the $S=\frac{7}{2}$ configuration $d^{5\uparrow}s^{\uparrow}p^{\uparrow}$, so $\mu > \mu_0$. This would require, however, promoting in the solid a minority spin valence p electron into a majority spin s-like conduction band, an excitation that costs a prohibitively large band-gap energy (>3 eV). Tsai *et al.* also found a much larger d band splitting ($\Delta_x^d = 6.8$ eV) than all other LSD calculations ($\Delta_x^d \sim 4.2$ eV). They argued that this one-electron energy difference agrees better with the photoemission measurements,[20] so no corrections are needed to the LSD. However, because of strong orbital relaxation and correlation effects[3,21] the one-electron energy $\epsilon_d^{\uparrow}$ does not equal the value measured in photoemission experiments ($d^5 \rightarrow d^4$), nor does $\epsilon_d^{\downarrow}$ equal the value measured in inverse photoemission ($d^5 \rightarrow d^6$). Hence, the one-electron difference $\Delta_x^d = \epsilon_d^{\downarrow} - \epsilon_d^{\uparrow}$ cannot be compared to the values deduced from these experiments (~ 8 eV), as suggested by Franciosi *et al.*[20]

B. Ground-state structures

Fitting five of the six calculated $\Delta E_{\text{direct}}(\sigma)$ values of Table I to the expansion of Eq. (2) yields the effective nth neighbor pair interactions $\tilde{J}_n$ given in Table II. The convergence of the expansion is checked in part by using Eq. (2) and the fitted interactions $\{\tilde{J}_n\}$ to predict the excess energy of AF-V, *not used in the fit.* The predicted value of $\Delta E = -184.5$ meV agrees very well with the directly calculated value of $\Delta E_{\text{direct}} = -185.1$ meV, indicating that the expansion is converged after inclusion of up to fourth neighbor interactions.

Using Eq. (2) with the spin interactions up to fourth fcc neighbor (Table II) we searched explicitly for the ground-state spin structure using a linear process.[9–11] We assume all the spins are either parallel or antiparallel to each other. This search reveals that the AFM-III structure is indeed the $T=0$ ground state in MnTe, as found experimentally.[4,5] This shows that the *ratios* between the different n-neighbor interaction energies (which determine the ground state) are physically correct.

C. Order-disorder transition temperature

The *magnitude* of the interaction energy $J_n = \tilde{J}_n/[S(S+1)]$ (with $S=\frac{5}{2}$) can also be compared with experiment: we find for MnTe $J_1 = -17.4$ K. Experimental values for MnTe were mostly deduced from $A^{\text{II}}_{1-x}\text{Mn}_x\text{Te}$ alloy: the values[1,2] for J_1 range between -6 and -10 K and are hence considerably less negative than the LSD result. A related quantity is the order-disorder transition temperature T_N. To calculate it, we have used the Monte Carlo simulation of Diep and Kawamura[14] for the nearest-neighbor classical Heisenberg Hamiltonian of Eq. (2), giving $T_N = 0.894|\tilde{J}_1|$. Using our calculated $\tilde{J}_1$ value, this simulation yields $T_N = 136$ K, which is about twice as large as the experimental value[4,5] of ~ 60–70 K. This error in T_N, mostly due to the LSDA rather than due to the use of the classical Heisenberg Hamiltonian, can be verified by noting that T_N obtained by solving this Hamiltonian with the

TABLE I. Calculated magnetic interaction energies ΔE_{direct} (in meV per Mn atom) and local magnetic moments μ (in μ_B) of the FM and AFM spin configurations of MnTe at $a=6.33$ Å. Results are given using the LSD and the LSD-C with the correction potential given by Eq. (3). N denotes the number of first neighbor Mn sites having the same spin orientation as the center Mn atom in each structure.

Properties	Methods	FM	AFM-I	AFM-II	AFM-III	AFM-IV	AFM-V
N		12	4	6	4	8	6
ΔE_{direct}	LSD	0.0	−223.9	−177.0	−230.4	−132.6	−185.1
	LSD-C	0.0	−115.9	−89.8	−119.6	−65.4	−94.1
μ	LSD	4.38	4.16	4.21	4.16	4.27	4.21
	LSD-C	4.54	4.38	4.41	4.38	4.45	4.41

TABLE II. Calculated magnetic interaction parameters $\{\tilde{J}_n\}$ (in meV) and magnetic phase transition temperature T_N (in K) at $a=6.33$ Å for MnTe using the LSD and the LSD-C with the correction potential given by Eq. (3).

Methods	$\tilde{J}_1$	$\tilde{J}_2$	$\tilde{J}_3$	$\tilde{J}_4$	T_N
LSD	-13.11	-0.76	-0.44	-0.66	136
LSD-C	-7.02	-0.24	-0.12	-0.29	73

TABLE III. Calculated properties of MnS, MnSe, and MnTe, using the LSD-C with the correction potential given by Eq. (3). All the properties are calculated at their respective experimental lattice constants given in the table.

Properties a(expt.)[a] (Å)	MnS 5.606	MnSe 5.904	MnTe 6.330
B (Gpa)	63.8	46.8	36.9
$N_0\alpha$ (eV)	0.25	0.23	0.22
$N_0\beta$ (eV)	-1.23	-1.04	-0.88
$\bar{\epsilon}_d^{\uparrow}-\epsilon_{\mathrm{VBM}}$ (eV)	-2.40	-2.63	-2.91
$\epsilon_d^{\downarrow}-\epsilon_{\mathrm{VBM}}$ (eV)	2.94	2.76	2.36
$\mu(\mu_B)$	4.34	4.39	4.38
J_1(calc.) (K)	-16.3	-11.5	-9.3
J_1(expt.)[a] (K)	-11–-16	-8–-13	-6–-10
T_N(calc.) (K)	128	90	73
T_N(expt.) (K)	100–160[b]	~100[c]	60–70[d]

[a] Reference 1.

[b] Reference 6.

[c] Reference 4.

[d] References 4 and 5.

experimental J_1 is close to the observed T_N's. We concluded that whereas the LSD is capable of identifying the correct spin ground state, it gives only qualitative agreement for the *magnitude* of $\{J_n\}$, hence T_N.

III. IDENTIFYING THE PHYSICAL RESASON FOR THE LSD FAILURES

A. Other failures of the LSD

To search for a *physical* origin of this discrepancy, we note that J_n is dominated by superexchange interactions resulting from Mn d–anion p hybridization,[15] and that this hybridization also controls the exchange spliting at the valence band maximum (VBM).[3,15,16] Our LSD band structure[3] for F-MnTe gives an (inverted) p-band exchange splitting $\Delta_x^p=-2.60$ eV. Using a Kondo interaction model[15] this gives a valence-band hole–Mn spin interaction of $N_0\beta=\Delta_x^p/\langle S_z\rangle=-1.04$ eV. Similar LSD results were found by other groups.[15,16] The alloy-derived experimental value[1] $N_0\beta=-0.88$ eV shows that the LSD also overstimates the exchange interactions between the Mn spin moment and band electrons. This suggests to us that the systematic LSD errors in the exchange splitting Δ_x^p and in the thermodyanmic transition temperature T_N could share the same origin: an overestimated p-d hybridization by the LSD description. Simple tight-binding models[3] show that the p-d hybridization can be reduced by increasing the exchange splitting $\Delta_x^d=\epsilon_d^{\downarrow}-\epsilon_d^{\uparrow}$ between the Mn spin-up and spin-down bands. This reduces $|\Delta_x^p|$ and possibly T_N, bringing them to closer agreement with experiment. We next test this conjuncture quantitatively.

B. Reducing the p-d hybridization through an external potential

While the development of a better spin-density functional is an active area of research,[22] our aim here is only to demonstrate that spectroscopic *and* thermodynamic LSD failures indicated above share the same physical origin, hence they can be simultaneously corrected by reducing the p-d hybridization. One way to do this is to add to the self-consistent LSD band structure calculations a simple parametric external potential whose effect is to displace the d band, hence change the p-d coupling. We use

$$V_{\mathrm{ext}}(r)_{\downarrow}^{\uparrow}=\mp\bar{V}\pm V_0\frac{r_0}{r}e^{-(r/r_0)^2}\ ,\quad r\le R_{\mathrm{MT}}\ . \tag{3}$$

Here R_{MT} is the muffin-tin (MT) radius of the Mn atom and the signs apply to spin-up and spin-down band, respectively. We adopted this potential by considering the spatial distribution of s, p, and d wave functions. In Eq. (3) only the parameter $\bar{V}$ has a direct effect on the p-d hybridization. The second, δ-like potential term is adopted from Ref. 23 to adjust the s conduction band level. We used $r_0=0.02$ bohr as suggested in Ref. 23. We have adjusted the parameters $\bar{V}$ and V_0 in Eq. (3) to fit the measured[1] spin-splitting $N_0\alpha$ and $N_0\beta$ in MnTe alone. This gives $\bar{V}=0.048$ Ry and $V_0=300$ Ry. This results in a lowering of the Mn $d^{\uparrow}$ band energy by 0.63 eV, an increase of the Mn $d^{\uparrow}$ band energy by 0.54 eV, and an increase of magnetic moment by 0.2 μ_B.

Using the LSD with the correction term (LSD-C) of Eq. (3), we have repeated for MnTe the self-consistent total energy and statistical mechanics calculations. The resulting $\Delta E_{\mathrm{direct}}(\sigma)$, interaction energies J_n and magnetic moments $\mu(\sigma)$ are given in Tables I and II. We find again the correct AF-III ground state configuration, but now $T_N=73$ K and $J_1=-9.3$ K (Table III), in good agreement with experiment.[1,2,4,5] Interestingly, our calculated Mn moments $\mu_i(\sigma)$ on site i reveal a linear dependence on the local environment around i. The results (Table I) can be fit to $\mu_i(N)=4.29+0.02N$, where N is the number of nearest neighbors Mn atoms to i having the same spin orientation as that of i. A similar dependence has been noted in magnetic iron.[24]

IV. CHEMICAL TRENDS AND DISCUSSIONS

To examine the generality of this procedure, we have applied the fixed correction potential fit to MnTe alone to study other zinc-blende magnetic systems, namely MnS and MnSe. Table III shows that this reproduces, without any further adjustment, the correct chemical trends and absolute values of many physical quantities in this series. We conclude that the overestimation by the LSD of p-d hybridization in Mn chalcogenides is indeed the cause of the overestimation of the exchange splitting Δ_x^p, the exchange coupling J_n and the transition temperature T_N.

This suggests that future development of a better LSD should have the effect of reducing *p*-*d* hybridization in zinc-blende Mn chalcogenides. The actual development of a better general LSD potential, however, is beyond the scope of this paper.

Our calculations for zinc-blende MnS, MnSe, and MnTe (Table III) using the reduced *p*-*d* coupling also show that:

(i) All the *d*-*d* interactions J_n are antiferromagnetic. The nearest-neighbor magnetic interaction J_1 is over 20 times larger than any further neighbor interactions, in contrast with early estimates,[1,2,15] suggesting $J_1/J_2 \sim 2-10$. Further, unlike other suggestions[15] the second, third, and fourth neighbor interactions are comparable. The fall-off of J_n with the shell distance r_n is nonexponential and even nonmonotoic. Since the Mn-Mn interactions are dominated by superexchange coupling[15] which is mediated through the anions, the above observations may be understood qualitatively by considering the topology of the zinc-blende lattice. The first neighbor Mn-Mn coupling passes through a *single* anion atom (see Fig. 1 in Ref. 9), hence, J_1 is the largest. The second, third, and fourth neighbor Mn-Mn coupling all require passing through *two* anions, so they have similar magnitude, all smaller than J_1. The path connecting the fourth Mn-Mn neighbors is more direct than those between second or third neighbors, so $J_4 \geq J_2, J_3$. Further neighbor ($n > 4$) interactions are an order of magnitude smaller because they require passing through *more* than two anion atoms. Similar arguments were used by Bruno and Lascaray[25] to speculate that J_2, J_3, and J_4 may have similar magnitude. The arguments are also used to explain the trend in the chemical interactions in pseudobinary semiconductor alloys.[9]

(ii) To further test the relation between the magnitude of J_n and the atomic connectivity, we have performed calculations on α-MnS in the NaCl structure at $a = 5.21$ Å.[13,15] We find that $J_n = -1.7$, -10.3, -0.4, -1.0, and -0.5 K for $n = 1-5$, respectively. A ground-state search correctly identifies the AF-II as the ground-state spin structure.[26] The relative magnitude of J_n are consistent with our topological arguments: $J_2 > J_1$, since despite the fact that both interactions pass through a single anion, the J_2 trajectory is more direct. Similary, J_3, J_4, and J_5 have similar magnitude, but smaller than J_1 and J_2, since they pass through two anions.

(iii) While the fall-off of J_n with the shell distance is nonexponential, we find that a given interaction, e.g., J_1, changes exponentially with the unit cell volume [or alternatively the bond length $R = (\sqrt{3}/4)a$]:

$$J_1(R) = J_1(R_0)e^{-\lambda(R-R_0)}\,, \tag{4}$$

where R_0 is the ideal bond length at equilibrium and λ is found to be 5.8, 5.7, and 5.5 Å^{1}, respectively, for MnS, MnSe, and MnTe. Since the magnetic interaction lowers the energy when the volume is compressed, the calculated bulk moduli B (Table III) of MnX$^{\mathrm{VI}}$ are smaller than the corresponding values for the nonmagnetic II-VI semiconductors, in agreement with experimental observation.[2,27]

V. SUMMARY

This work establishes that the overestimation of the *p*-*d* coupling is the cause of the overestimation of Δ_x^p and T_N in the LSD description of Mn chalcogenides. We have calculated directly, for the first times, the absolute magnitudes and ratio between the various magnetic interaction energies $\{J_n\}$ in this system. The trends are interpreted in terms of atomic connectivity, and confirm that superexchange is the dominant interaction in this system.

Note added in proof. Recently, Dr. R. Kasowski informed us that he has redone the calculation of Tsai *et al.*[19] using the same pseudofunction computer program, finding for AF-MnTe a local magnetic moment $\mu = 4.23\mu_B$ ($R_{\mathrm{MT}} = 2.5$ a.u.), significantly smaller than their original value[19] $\mu = 6.3\mu_B$, but close to our LAPW value $\mu = 4.2\mu_B$. (The muffin-tin radius does not affect μ much.) We thank Dr. R. Kasowski for communicating his recent results to us. This suggests that the original calculation of Ref. 19 and the data interpretation[20] based on it are in error.

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[26] We find that a cubic structure, denoted previously $D4$ (see Fig. 11 in Ref. 10), has the same pair correlation functions as the trigonal AF-II structure. Our direct calculation shows that within the calculation precison (~ 1 meV per Mn atom) its energy is equal to the AF-II structure. This structure can be viewed as a superposition of the four equivalent AF-II structures. Its existence can shed light on the observation (Ref. 7) of a two-step phase transition in this system.

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