Spectral signatures of thermal spin disorder and excess Mn in half-metallic NiMnSb

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Effects of thermal spin disorder and excess Mn on the electronic spectrum of half-metallic NiMnSb are studied using first-principles calculations. Temperature-dependent spin disorder, introduced within the vector disordered local moment model, causes the valence band at the Γ point to broaden and shift upwards, crossing the Fermi level and thereby closing the half-metallic gap above room temperature. The spectroscopic signatures of excess Mn on the Ni, Sb, and empty sites (Mn_{Ni}, Mn_{Sb}, and Mn_{E}) are analyzed. Mn_{Ni} is spectroscopically invisible. The relatively weak coupling of Mn_{Sb} and Mn_{E} spins to the host strongly deviates from the Heisenberg model, and the spin of Mn_{E} is canted in the ground state. While the half-metallic gap is preserved in the collinear ground state of Mn_{Sb}, thermal spin disorder of the weakly coupled Mn_{Sb} spins destroys it at low temperatures. This property of Mn_{Sb} may be the source of the observed low-temperature transport anomalies.

Half-metallic ferromagnets with a band gap in one spin channel can serve as sources of highly spin-polarized currents in spintronic devices. While many materials are predicted by band structure calculations to be half-metallic, particularly among full and half-Heusler compounds, experimental observation and utilization of half-metallicity are complicated by various defects, thermal spin excitations, and surface non-stoichiometry. Correlation effects can also lead to spin depolarization already at zero temperature.

If a perfect crystal is half-metallic at T = 0, there may be a region of low temperatures and weak disorder where transport remains effectively single-channel. However, a crossover to two-channel conduction should occur if a quasiparticle band crosses the Fermi level E_{F} in the originally gapped spin channel. Thermally-induced incoherent spectral density in the gap can also lead to anomalies in transport properties.

A bulk-sensitive positron annihilation measurement found NiMnSb to be half-metallic to experimental accuracy, but other measurements paint a more complicated picture. An anomaly in the transport properties was observed near 80 K. It was suggested that it could be due to the longitudinal fluctuations of the Ni spin moments, but the effect was overestimated by improper phase space integration. Recent studies indicate that rather than being intrinsic, the 80 K anomaly is only found in samples with excess manganese, and it was suggested that thermal excitations on the interstitial Mn_{E} atoms may be involved. Here we study the influence of thermal spin fluctuations and excess Mn on the electronic spectrum of NiMnSb using first-principles calculations and identify Mn_{Sb} as the most likely source of the 80 K anomaly.

Spin disorder for the Mn atoms is described by a single-site mean-field distribution function \( p(\theta) \propto \exp(\alpha \cos \theta) \). The parameter \( \alpha = H_{W} \mu / T \), where \( H_{W} \) is the Weiss field and \( \mu \) the local spin moment, is mapped to the temperature using the experimental \( M(T) \) curve.

Both spin disorder and excess Mn defects are treated within the coherent potential approximation (CPA) applied within the Green’s function-based linear muffin-tin orbital (GF-LMTO) method. The azimuthal angle \( \phi \) in the CPA equations is integrated out analytically, while the \( \theta \) dependence is discretized using the Gauss-Legendre quadrature. This vector disordered local moment (VDLM) scheme implements the adiabatic DLM approach for partially ordered magnetic states. The potentials for all atoms (and \( \theta \) angles) are determined self-consistently by embedding the CPA self-consistency loop into the density-functional iteration. To enforce magnetic self-consistency, a transverse constraining field is introduced for each \( \theta \). The experimental lattice constant of 5.92 Å and the generalized gradient approximation are used throughout. The electronic structure in the presence of disorder is represented by the energy- and \( k \)-resolved CPA spectral functions.

First we consider the effect of thermal spin disorder on the electronic structure around the half-metallic band gap of defect-free NiMnSb. Fig. (a) shows the minority-spin band structure at \( T = 0 \), and Fig. (b) the spectral function at an elevated temperature corresponding to the reduced magnetization \( M(T)/M(0) = 0.80 \).

Mixing with majority-spin bands is apparent at 1.2-1.6 eV below \( E_{F} \), where those bands and avoided crossings show up in Fig. (b). The bands that tend to acquire a significant admixture of the opposite spin character at \( T \neq 0 \) are the flat bands with small dispersion. We do not, however, observe the traces of the dispersive majority-spin bands that cross the Fermi level. The spectral weight is, of course, transferred from those bands to the minority spin, but this transferred weight is incoherent and spreads over the entire bandwidth. Dispersive bands behave according to the Stoner picture, according to which the Bloch electrons “observe” an averaged effective field. This happens because adjusting the wavefunctions locally to the directions of individual spins costs a lot of kinetic energy for dispersive bands. This general
FIG. 1. (a-b) Minority-spin spectral functions in NiMnSb. (a) $T = 0$. (b) Spin disorder (VDLM) at $M(T)/M(0) = 0.80$. The coloring reflects the spectral weight contributions of Mn (red), Ni (blue), and Sb (green, barely seen). (c) Hybridization analysis: Red and blue coloring show, respectively, Mn $t_2g$ and Mn $e_g$ orbital character when all Sb states except 5$s$ are removed from the basis set. Green coloring shows the Sb character when the 3$d$ states of Mn and Ni are removed from the basis set. (All charges are taken from the calculation with the full basis set.) Energy in all panels is in eV measured from $E_F$.

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property is favorable for spintronic applications, because the quasiparticles near $E_F$ retain their spin polarization in the presence of spin disorder.

Of particular interest are the thermally-induced broadening and shifts of the minority-spin valence band maximum (VBM) and conduction band minimum (CBM). Fig. 1 shows that the bands near the VBM triplet at Γ are strongly broadened and shifted upward by spin disorder. The CBM at X is also broadened and shifted upward but at a smaller rate compared to the VBM. In Fig. 1b the VBM triplet at Γ is centered at $E_F$. This indicates a crossover to a conventional two-channel ferromagnetic regime. Fig. 2 displays the temperature dependence of the centers and half-widths of the VBM and CBM states. The VBM comes within its half-width of $E_F$ at about 400 K. This is where strong transport spin depolarization can be expected. Although this temperature depends on the initial position of $E_F$ at $T = 0$, it appears that spin disorder alone can not lead to low-temperature anomalies.

FIG. 2. Temperature dependence of the center and half-width of the minority-spin bands at Γ and X points at the edges of the half-metallic gap in NiMnSb.

The spin disorder-induced upward shift of the top minority-spin valence band is contrary to the expectation based on the simple exchange splitting picture. The counterintuitive band shift can be understood by examining the hybridization that forms this band in Fig. 1. As seen in Fig. 1b (and confirmed by full-potential calculations), the hybridization of the Mn $t_2g$ and Sb 5$p$ states at the VBM triplet at Γ is predominantly composed of Mn $t_2g$ states with an admixture of Sb 5$p$ and Ni $t_2g$ states. If the 3$d$ states of Mn and Ni are removed from the basis set, the remaining bands deriving primarily from Sb 5$p$ states (green in Fig. 1c) extend from $-6$ to 2 eV. The Γ point is antibonding for these bands. If, on the other hand, all Sb states except 5$s$ are removed from the basis set, we end up with the bands for which the Mn character is shown by red ($t_2g$) and blue ($e_g$) color in Fig. 1c. Comparing with Fig. 1a, we see that the hybridization of the Mn $t_2g$ and Sb 5$p$-derived states opens the gap and forms the VBM at Γ. Spin disorder reduces this hybridization by adding the spin overlap factors to the hopping matrix elements, resulting in the upward shift of the VBM triplet seen in Fig. 1b.

Since the 80 K anomaly may be due to excess Mn [13, 14], we now consider the effects of excess Mn appearing on the Ni, Sb, and empty sites. These defects will be denoted Mn$_{Ni}$, Mn$_{Sb}$, and Mn$_{E}$. Various defects in NiMnSb were studied using supercell calculations [26] and CPA [27]. While the energies of atom-pair swaps are related to the formation energies of different defects, the concentration of each individual non-stoichiometric defect depends on the chemical potentials of the relevant elements, which in turn depend on the material synthesis protocol. A polarized neutron diffraction measurement of a low-quality crystal found a large concentration of Mn$_{Sb}$ and Sb$_{Mn}$ defects. Since the Mn-Sb swap energy is rather high [26], the formation of these defects could be due to nonequilibrium growth conditions.

We assume excess Mn is randomly distributed over the given sublattice and treat each type of defect separately within CPA. First we used VASP [29] to relax the atomic structure for a 48-atom (2×2×1) host supercell [30] with one excess Mn defect and examine its magnetic coupling to the bulk. For Mn$_{Ni}$ the antiparallel spin alignment
is very stable in agreement with Ref. 31, while the self-consistent solution for the parallel alignment could not be obtained. Fig. 3 shows the total energy of a supercell as a function of the angle made by the spin of MnE or MnSB with the magnetization. In both cases there are strong deviations from the Heisenberg model predicting $E(\theta) \propto \cos \theta$. For MnE we find, in agreement with Ref. 16 that the antiparallel orientation ($\theta = \pi$) has a lower energy compared to the parallel one ($\theta = 0$). However, the energy minimum is reached for a canted spin at $\theta \approx 130^\circ$. There is a high-to-low spin crossover near $\theta = \pi/4$. In MnSB, the lowest energy is in the parallel orientation, but the range of energy variation is only 70 meV.

Since the magnetic coupling of MnE and MnSB defects to the bulk is weak, their spins should disorder at relatively low temperatures. To study the spectral properties of these defects, we again employ the CPA (separately for each defect type). The 6.25% defect concentration was the same as in the supercells; such concentrations are typical for low-quality samples 28.

To set up the CPA calculations, we first performed an LMTO calculation for each supercell, taking the atomic positions from the VASP calculation and setting the sphere radius of excess Mn to the same value as the substituted atom 22. The partial densities of states (DOS) in these LMTO calculations are similar to VASP results, and they give us the correct charge and spin moments in the atomic sphere for the excess Mn atom. In a CPA calculation with the ideal lattice, a screening correction to the Madelung potential 32 is applied with the coefficient that is adjusted to provide the correct charge on Mn. In addition, the local part of the effective GGA magnetic field for the MnE defect was scaled by a factor 1.2 to obtain good agreement with the correct local spin moment for MnE in both parallel and antiparallel alignments. This correction compensates for the absence of atomic displacements in CPA. The DOS in CPA with these corrections agree well with supercell calculations up to disorder broadening (see Fig. 4 for MnSB).

![FIG. 4. Partial DOS for MnSB in NiMnSb with a 6.25% occupation of the Sb site by Mn, parallel spin alignment. Solid (blue) lines: CPA; dashed (red) lines: VASP. Black dot-dashed line: total minority-spin DOS per formula unit ($\rho_\downarrow$), disordered spin of MnSB. Inset: $\rho_\downarrow$ at 40 K, 60 K, 80 K, 120 K, and 160 K as labeled (same units on axes).](image-url)

The spectral function is only slightly modified by MnNi defects (not shown) compared to the ideal crystal (Fig. 1a), and the broadening of the bands is very small. Since the spin of MnNi is strongly coupled to the host magnetization 31, this defect is spectroscopically invisible and can not lead to low-temperature anomalies.

The spectral functions for the MnE defect in the antiparallel orientation and in the spin-disordered (VDLM) state are shown in Fig. 5a-b. For the VDLM state the $\theta$ integration in CPA is combined with charge self-consistency. The spin moment of MnE depends strongly on $\theta$, varying from 0.84 to 3.04 $\mu_B$ between the points closest to 0 and $\pi$, in good agreement with VASP calculations. The comparison of panels (a) and (b) shows the effect of the noncollinearity of the MnE spins. The partial DOS for MnE at $\theta = 0$, $\theta = \pi$, and in the spin-disordered (VDLM) state are also shown in Fig. 6.

Fig. 5a-b and 6 show that spin disorder on MnE introduces a substantial minority-spin spectral weight inside the half-metallic gap. Its magnitude at $E_F$ is about 13% of the majority-spin DOS. However, if MnE is already noncollinear at $T = 0$ as our calculations suggest (Fig. 3), it is likely not the source of the 80 K anomaly.

Fig. 5c-d shows the spectral functions for MnSB in the ground-state ferromagnetic orientation and in the VDLM state with full spin disorder. Here the local moment of MnSB depends weakly on $\theta$, varying from 3.82 to 4.18 $\mu_B$ for angles closest to 0 and $\pi$. Fig. 5c shows, in agreement with Ref. 26, that MnSB preserves the half-metallic gap in the ferromagnetic state, although the VBM moves closer to $E_F$ compared to ideal NiMnSb. Further, in Fig. 5d and 6 (dot-dashed line and inset) we see that spin disorder introduces a large spectral density inside the gap above the VBM, which is much larger compared to the
FIG. 5. Minority-spin spectral function in NiMnSb with 6.25% excess Mn occupying: (a-b) the empty site, (c-d) the Sb site. (a) The magnetic moment of Mn\textsubscript{E} is antiparallel to the magnetization. (b) VDLM state for the Mn\textsubscript{E} atom. (c) The magnetic moment of Mn\textsubscript{Sb} is parallel to the magnetization. (b) VDLM state for the Mn\textsubscript{Sb} atom. Color coding is similar to Fig. 1a; Mn\textsubscript{E} added to Mn (red), Mn\textsubscript{Sb} to Sb (green). Energy is in eV measured from \(E_F\).

FIG. 6. Total DOS for NiMnSb with a 6.25% occupation of the empty site by Mn (CPA). FM (AFM): Mn\textsubscript{E} is parallel (antiparallel) to the magnetization. VDLM: fully disordered spin on Mn\textsubscript{E}. Upper inset: magnified region near \(E_F\). Lower inset: partial DOS for Mn\textsubscript{E}. (Same units on axes in insets.)

Mn\textsubscript{E} defect (Fig. 5b). These features are due to the replacement of Mn-Sb bonds by Mn-Mn bonds; recall that the Mn-Sb hybridization pushes the Mn \(t_{2g}\) bands downward at \(\Gamma\) and forms the VBM (Fig. 1a,c).

The inset of Fig. 1 shows the minority-spin DOS near \(E_F\) for several temperatures, which were obtained using the VDLM model with the spin distribution function \(p(\theta) \propto \exp[-E(\theta)/T]\) for Mn\textsubscript{Sb} with \(E(\theta)\) from the VASP calculation (Fig. 5). We see that thermal spin disorder on Mn\textsubscript{Sb} generates a considerable minority-spin DOS at \(E_F\) at rather low temperatures; for example, \(\rho_\downarrow \approx 0.26 \rho_\uparrow\) at 80 K. These results strongly suggest that Mn\textsubscript{Sb} (found experimentally in low-quality samples) is the source of the 80 K anomaly.

In conclusion, we have studied the influence of thermal spin disorder and excess Mn on the electronic structure of NiMnSb. Thermal spin disorder broadens and shifts the minority-spin VBM at \(\Gamma\) upwards due to the unmixing of the Mn \(t_{2g}\) states from the Sb states. While Mn\textsubscript{Ni} is spectroscopically invisible, Mn\textsubscript{E} and Mn\textsubscript{Sb} have strong spectral signatures that could be observed in angular-resolved photoemission. Mn\textsubscript{Sb} is identified as a possible source of the 80 K anomaly: its spin couples weakly to the bulk, and easily excited spin disorder strongly contaminates the half-metallic gap near the \(\Gamma\) point.

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