Excess manganese as the origin of the low-temperature anomaly in NiMnSb

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The archetype of half-metallic magnetism, NiMnSb, has been reported to show an anomaly at low temperature. The high degree of spin polarization of the conduction electrons, characteristic of a half metal, is lost above this temperature. Recently reported experiments show that this anomaly is not an intrinsic property of NiMnSb: it requires an excess of (interstitial) manganese. Electronic structure calculations reported here show that the excess manganese orders antiferromagnetically with respect to the host magnetization, reduces the half-metallic band gap, and pushes the top of the valence band up to 36 meV below the Fermi level. Thermal excitations from minority to majority spin channel induce an avalanche effect, leading to the disordering of the magnetic moments of the excess manganese. This mechanism is supported by measurements of the magnetization as a function of temperature on NiMn1.05Sb: It shows a maximum in the magnetization measured in a field of 400 Oe.

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I. INTRODUCTION

NiMnSb is the first example of a half metal,1 and its potential in what is known as a spintronic device2 was recognized from the beginning.3 The half-metallic properties in the bulk were confirmed experimentally by spin-resolved positron annihilation,4,5 but surfaces and interfaces of half metals turned out to be delicate.6–8 A complication specific for NiMnSb is the low temperature anomaly:9 a crossover of the minority to majority spin channel induce an avalanche effect, leading to the disordering of the magnetic moments of the excess manganese. This mechanism is supported by measurements of the magnetization as a function of temperature on NiMn1.05Sb: It shows a maximum in the magnetization measured in a field of 400 Oe.

II. DETAILS OF CALCULATIONS, SAMPLE SYNTHESIS, AND MAGNETIZATION MEASUREMENT

The calculations were carried out using the density functional method in both the local density approximation (LDA)19 and the generalized gradient approximation (GGA).20 Projector-augmented plane waves are employed21,22 as implemented in the Vienna ab initio simulation package (VASP).23–26 The kinetic energy cutoff is set to 368 eV and the Brillouin zone is sampled with a 6 × 6 × 4 k mesh of 400 Oe.

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TABLE I. Calculated energies of NiMn$_{106}$Sb, with the excess Mn occupying the vacant position, and interchanging with its nearest neighboring Sb, Ni, and host Mn (unit: eV, the energy of the ground state is chosen as 0).

<table>
<thead>
<tr>
<th>Coupling</th>
<th>Vacant position</th>
<th>Interchange with Sb</th>
<th>Interchange with Ni</th>
<th>Interchange with host Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antiferromagnetic</td>
<td>0</td>
<td>3.60</td>
<td>0.24</td>
<td>0.55*</td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td>0.12</td>
<td>3.10</td>
<td>not obtained</td>
<td>0.12</td>
</tr>
</tbody>
</table>

*The moment on the excess Mn is antiparallel to that of the host.

TABLE II. Energy difference (given by $E_{\text{ant}}-E_{\text{ferm}}$), and the position of Fermi level with respect to the top of the valence bands for the ground state in two codes with different exchange-correlation functionals (unit: meV).

<table>
<thead>
<tr>
<th>Functional</th>
<th>GGA (PW91) in VASP</th>
<th>GGA (PBE) in VASP</th>
<th>LDA in VASP</th>
<th>GGA (PBE) in WIEN2K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy difference</td>
<td>$-118$</td>
<td>$-118$</td>
<td>$-35$</td>
<td>$-127$</td>
</tr>
<tr>
<td>Position of Fermi level</td>
<td>36</td>
<td>29</td>
<td>37</td>
<td>40</td>
</tr>
</tbody>
</table>
to the host manganese atoms, and the red, continuous curve corresponds to the case where they couple ferromagnetically. The configuration with ferromagnetic coupling is 118 meV (shown in Table I) higher in energy compared with the antiferromagnetic case. The position of the Fermi level with respect to the edges of the band gap in the case where the excess manganese orders ferromagnetically with respect to the host manganese atoms, red curve (which is shifted by 20 states/eV/cell) stands for minority spin for NiMn$_{1.06}$Sb (Ni$_{16}$Mn$_{17}$Sb$_{16}$) with ferromagnetic ordering. The accuracy and resolution of all curves are identical. The left curve has a different scale in order to improve the visibility.

FIG. 1. (Color online) Density of states of NiMnSb and NiMn$_{1.06}$Sb as function of the energy in the vicinity of the Fermi energy. From left to right: the dotted black curve stands for majority spin for pure NiMnSb (Ni$_{16}$Mn$_{16}$Sb$_{16}$), pink curve stands for minority spin for pure NiMnSb (Ni$_{16}$Mn$_{16}$Sb$_{16}$), black curve stands for minority spin for NiMn$_{1.06}$Sb (Ni$_{16}$Mn$_{17}$Sb$_{16}$) with excess manganese orders antiferromagnetically with respect to the host manganese atoms, red curve (which is shifted by 20 states/eV/cell) stands for minority spin for NiMn$_{1.06}$Sb (Ni$_{16}$Mn$_{17}$Sb$_{16}$) with ferromagnetic ordering. The accuracy and resolution of all curves are identical. The left curve has a different scale in order to improve the visibility.

FIG. 2. Magnetization of NiMn$_{1.05}$Sb as function of the temperature from 5 to 225 K: The curve (scaled by the left vertical axis) plotted by triangles represents magnetization measured in a field of 400 Oe, and the curve (scaled by the right vertical axis) plotted by rectangles is for magnetization measured in a field of 1200 Oe.

Next we consider the magnetization in NiMn$_{1.05}$Sb. Figure 2 shows the measured magnetization as a function of
the temperature\textsuperscript{32} for two different applied magnetic fields. In a magnetic field of 1200 Oe, it behaves like a normal ferromagnet. The behavior in a magnetic field of 400 Oe is quite different: It shows a gradual increase of the magnetization with temperature, leading to a maximum at 50 K. At higher temperatures, the magnetization decreases as is to be expected for a normal ferromagnet. The magnetic anisotropy in NiMn\textsubscript{1.05}Sb is very small (equivalent to 0.04 K per magnetic atom),\textsuperscript{9} so this local maximum cannot be related to it. This local maximum can be understood in the following way: When the magnetic field is 400 Oe, at 0 K, moment on the excess manganese couples antiferromagnetically to the host magnetization; as temperature increases, moments on the excess manganese become disordered, so the magnetization is increasing, and this results in a peak centered around 50 K in the magnetization-temperature curve. This is in perfect agreement with the conclusion in our calculations that the excess manganese couples antiferromagnetically to the host magnetization. A field of 400 Oe is not strong enough to order the excess manganese. Measurements on the magnetization are especially supported by the Netherlands Organization for Scientific Research (NWO).

\section{Conclusions}

The experimentally observed anomalous behavior of resistivity and magnetization, and loss of the high spin polarization of the conduction electrons in the low-temperature anomaly in NiMnSb, is not an intrinsic property, but due to the excess manganese. Measurements on the magnetization are in good agreement with the conclusion in our calculations that the excess manganese couples antiferromagnetically to the host magnetization. The half-metal–metal transition is the origin of both the anomaly in resistivity and the loss of high spin polarization; the disordering of moments on the excess manganese gives rise to the anomaly in the magnetization at low temperature. For future work, neutron diffraction experiments on the identification and magnetic properties of the excess Mn, some possible defects in NiMn\textsubscript{1.05}Sb, and the magnetization measurement at higher temperature (above 225 K) are desirable, and systematic experimental exploration on pure NiMnSb is expected in order to realize its potential use of half metallicity at higher temperature in spintronics.

\section{Acknowledgments}

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On the position of the Fermi level in the ground state, Table I shows four slightly different values: The smallest value is 29 meV obtained from calculation done in VASP using GGA (PBE) functional, and the largest one is 40 meV obtained from calculation done in WIEN2K using GGA (PBE) functional.

In the half-metal–metal transition, the transfer of an electron from a spin down to a spin up band violates conservation of angular momentum; consequently the real process must be more complex. A priori there is no reason to assume however that these two processes involved differ significantly in efficiency.

The sample shows a different color at the surface part compared with the bulk. We report the magnetization measurement on the bulk here; the temperature dependence of the magnetization for the surface part of the sample shows a maximum at higher temperature (around 90 K).