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Published in:
Physical Review. B: Condensed Matter and Materials Physics

DOI:
[10.1103/PhysRevB.88.014418](https://doi.org/10.1103/PhysRevB.88.014418)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2013

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Zhang, B., Heuver, J. A., Wang, F., Baas, J., de Wijs, G. A., Fukuhara, T., ... de Groot, R. A. (2013). Excess manganese as the origin of the low-temperature anomaly in NiMnSb. *Physical Review. B: Condensed Matter and Materials Physics*, 88(1), 014418-1-014418-5. [014418]. DOI: 10.1103/PhysRevB.88.014418

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Excess manganese as the origin of the low-temperature anomaly in NiMnSbB. Zhang,¹ J. A. Heuver,² F. Wang,³ J. Baas,² G. A. de Wijs,¹ T. Fukuhara,³ T. T. M. Palstra,² and R. A. de Groot^{1,2,*}¹*Radboud University Nijmegen, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, The Netherlands*²*Solid State Materials for Electronics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands*³*Toyama Prefectural University, Department of Liberal Arts and Science, Imizu, Toyama 939-0398, Japan*

(Received 18 February 2013; published 18 July 2013)

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 NiMn_{1.05}Sb: It shows a maximum in the magnetization measured in a field of 400 Oe.

DOI: [10.1103/PhysRevB.88.014418](https://doi.org/10.1103/PhysRevB.88.014418)

PACS number(s): 75.50.Cc, 71.55.Ak, 85.75.—d

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 in the temperature dependence of both magnetization and resistivity (the magnetization, $M(T) \propto T^{1.5}$ below 80 K, while $M(T) \propto T^{2.0}$ above 100 K; the resistivity, $\rho(T) \propto T^\alpha$ below 50 K with $1.7 < \alpha < 2.2$, while $\rho(T) \propto T^\beta$ above 100 K with $1.3 < \beta < 1.5$). The first observation¹⁰ reports a strong increase in Mn and Ni magnetic moments upon cooling below 90 K in thin films. Thermal excitations¹¹ could be responsible for the loss of high spin polarization, possibly in the form of a noncollinear ordering of the magnetic moment on Ni with respect to the Mn,¹² but others considered thermal excitation unlikely in stoichiometric NiMnSb (the position of the Fermi level with respect to the top edge of the valence bands of the minority spin is too high).¹³ Many possible defects were considered, like antisite defects,^{14,15} but in many of the cases with reasonable formation energies the half-metallic properties were conserved. An alternative explanation is the occurrence of nonquasiparticle states,¹⁶ but the underlying many-body theory requires a Hubbard U (about 2 eV) of more than an order of magnitude in excess of the experimentally derived value (about 0 ± 0.1 eV in the isostructural and isoelectronic PtMnSb¹³). The most common method to synthesize bulk Heusler alloys is arc-melting stoichiometric amounts of high purity elements.¹⁷ The synthesis of stoichiometric NiMnSb is hindered by the large variation in vapor pressure of the constituent elements at high temperature. Recently the situation changed, when experiments using samples synthesized under controlled partial pressures, showed that the low temperature anomaly is *not* an intrinsic property of NiMnSb, but requires $\sim 5\%$ excess manganese.¹⁸ This development motivates a detailed study of the possible configurations of the excess

manganese (the vacant position in the $C1_b$ structure but also interchanges with its neighboring atoms), how the moment of the excess manganese couples with the host magnetization, and how it causes the low temperature anomaly. We report on measurements of the magnetization of NiMnSb with excess manganese at low temperature as well as calculations of electronic structure of NiMnSb with excess manganese using state-of-the-art first-principle calculations.

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 employed^{21,22} 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 of the supercell is sampled with a k mesh of $4 \times 4 \times 8$ (for density of states plots we use a k mesh of $6 \times 6 \times 12$). The lattice constant is kept fixed at the experimental value of 5.9268 Å (the GGA functional underestimates the experimental lattice parameter of the primitive cell only by 0.2%). The atomic positions are relaxed to a residual force of 0.005 eV/Å and the criterion for energy convergence is 0.01 meV. For calculations with WIEN2K,²⁷ we used the GGA (PBE)²⁸ exchange-correlation functional. An energy cutoff of $R_{\text{mt}}K_{\text{max}}$ of 8 and a k mesh of $6 \times 6 \times 12$ for Brillouin zone integration were used. 5×10^{-5} Ry for energy and 5×10^{-5} e for charge were used as convergence criteria, while 10^{-4} Ry for energy, 10^{-4} e for charge, and 10^{-4} Ry/ a_0 (a_0 is the Bohr radius) for force were used in optimization on the positional parameters. The supercell with one excess manganese (Ni₁₆Mn₁₇Sb₁₆) used in the calculation contains $2 \times 2 \times 1$ conventional cells. Both antiferromagnetic and ferromagnetic ordering between excess manganese and host magnetization were investigated. Sample NiMn_{1.05}Sb was synthesized according to the procedure described in Ref. 18. Magnetization was measured in

TABLE I. Calculated energies of NiMn_{1.06}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).

	Vacant position	Interchange with Sb	Interchange with Ni	Interchange with host Mn
Antiferromagnetic coupling	0	3.60	0.24	0.55 ^a
Ferromagnetic coupling	0.12	3.10	not obtained	0.12

^aThe moment on the excess Mn is antiparallel to that of the host.

a Quantum Design MPMS-XL 7 magnetometer. A little bar shaped sample was cut from an ingot. The sample was placed in a gelatin capsule and fixed in place with cotton. Magnetization versus temperature was measured on heating in different fields, after cooling with 2 K/min in a magnetic field of 20 kOe. During the measurement a ramp rate of 5 K/min was used.

III. RESULTS AND DISCUSSION

NiMnSb crystallizes in the $C1_b$ (half-Heusler) structure, an fcc structure with the (0, 0, 0), (1/4, 1/4, 1/4), and (3/4, 3/4, 3/4) positions occupied by Ni, Mn, and Sb, respectively. The vacant position (1/2, 1/2, 1/2) is an obvious candidate for the excess manganese. We also consider interchanges of the excess manganese with its neighboring Ni, Sb, and host Mn atoms with distance shorter than 3 Å. Both ferromagnetic and antiferromagnetic coupling of the excess Mn with respect to the host magnetization were calculated. The results are shown in Table I: The case where excess Mn occupies the vacant position and couples antiferromagnetically to the host Mn has the lowest energy, while in the case of ferromagnetic coupling the energy is higher by 0.12 eV. Other cases where the excess Mn interchanges with Ni, Sb, and the host Mn are all higher in energy. The case where the excess Mn interchanges with Ni and couples ferromagnetically to the host magnetization is not stable and this solution is not obtained in our calculation. From Table I, we conclude that the excess Mn occupies the vacant position in the supercell, and couples antiferromagnetically to the host Mn atoms. This conclusion also agrees well with calculations using different codes and exchange-correlation functionals (results are shown in Table II). The energy difference obtained using the LDA functional is smaller compared with those using the GGA

TABLE II. Energy difference (given by $E_{\text{anti}} - E_{\text{ferro}}$), 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).

	GGA (PW91) in VASP	GGA (PBE) in VASP	LDA in VASP	GGA (PBE) in WIEN2K
Energy difference	-118	-118	-35	-127
Position of Fermi level	36	29	37	40

functional; using GGA functional (both in WIEN2K and VASP), the energy differences are quite similar. In order to avoid being trapped in a local minimum, optimization on the positional parameters should start with some (tiny) distortion on the neighboring atoms of the extra manganese in the supercell, otherwise we find the case where the excess manganese ferromagnetically couples to the host magnetization only.

In a half metal, the position of the Fermi level in the band gap is determined by the metallic spin direction, unlike the situation in a semiconductor, where impurities and surface effects play an important role. The position of the Fermi level with respect to the edges of the band gap is an important quantity determining the stability of the half-metallic properties at finite temperature. Consider a half metal with a band gap for the minority spin direction. At 0 K, the Fermi level intersects the metallic bands for one spin channel, and is located somewhere in the band gap for the semiconducting spin direction. This location is of importance: It determines the robustness of the band gap at finite temperature. For example, consider a case where the Fermi level is close to the top of the valence band (minority spin). A thermal excitation to the conduction band (majority spin) at the Fermi level *increases* the magnetization, leading to an increase of the exchange splitting (which implies a lowering of the majority spin bands with respect to the minority ones). Consequently a second excitation requires less energy and an avalanche effect occurs at temperatures much below the one corresponding to the energy of the initial excitation. It is important to note that a similar situation occurs if the Fermi level were positioned near the bottom of the conduction band (minority spin): The excitation of a majority spin electron to the bottom of the conduction band *decreases* the magnetization, leading to the decrease of the exchange splitting (which implies a rising of the majority spin bands with respect to the minority ones), and renders a second excitation more likely. The stable situation is where the effects of both type of excitations cancel: the position of the Fermi level in the middle of the band gap. The behavior of half metals with a band gap for the majority spin is identical: Excitations from the top of the valence bands (majority spin) to conduction bands (minority spin) reduce the magnetization (causing a rising of the majority spin bands with respect to the minority ones), while excitations from the minority spin to the bottom of the conduction band (majority spin) increase the exchange splitting (causing a lowering of the majority spin bands with respect to the minority ones). Detailed knowledge on the DOS (density of states) for NiMn_{1.06}Sb close to the Fermi level is an essential ingredient for the understanding of the low-temperature anomaly.

Figure 1 shows the calculated DOS in the vicinity of the Fermi energy for NiMnSb and NiMn_{1.06}Sb. The left curve shows the majority spin for pristine NiMnSb. It has a fairly constant DOS deprived of any van Hove singularities, typical for a wide-band, free-electron-like material. The second curve is the corresponding minority spin, and it is typical for a III-V semiconductor. Some van Hove singularities occur in both valence and conduction bands, within the energy range of 1 eV with respect to the Fermi energy. The next two curves show the DOS for the minority spin of NiMn_{1.06}Sb. The black, continuous curve corresponds to the ground state where the excessive manganese couples antiferromagnetically

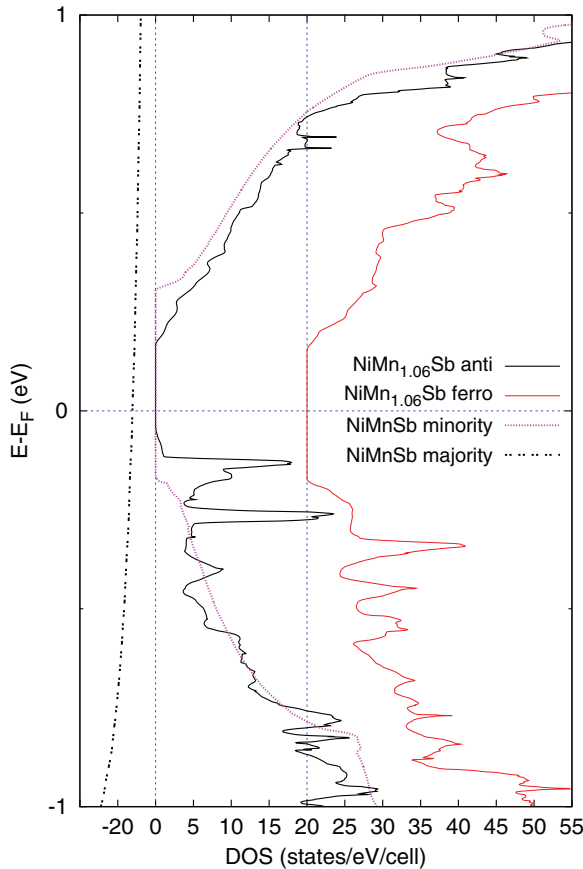


FIG. 1. (Color online) Density of states of NiMnSb and NiMn_{1.06}Sb as function of the energy in the vicinity of the Fermi energy. From left to right: the dotted black curve stands for majority spin for pure NiMnSb (Ni₁₆Mn₁₆Sb₁₆), pink curve stands for minority spin for pure NiMnSb (Ni₁₆Mn₁₆Sb₁₆), black curve stands for minority spin for NiMn_{1.06}Sb (Ni₁₆Mn₁₇Sb₁₆) 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 (Ni₁₆Mn₁₇Sb₁₆) 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.

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 to the host is noteworthy: It is exactly in the middle of the gap. So, if this configuration were the ground state, no low-temperature anomaly would be present, independent of the presence of excess manganese. A substantial reduction of the band gap (0.20 eV compared to 0.46 eV for pristine NiMnSb) occurs for the antiferromagnetic case, and the position of the Fermi level is just 36 meV (corresponding to a temperature of 418 K) with respect of the top of the valence band, which renders the avalanche feedback mechanism possible. Moreover, we find that the position of the Fermi level above the top edge of the valence bands (minority spin) is little affected by different codes and exchange-correlation functionals.²⁹ Electrons are

thermally excited from the top of the valence bands (minority spin) to the metallic conduction bands (majority spin), and ultimately, the avalanche feedback ends with a half-metal-metal transition. In a normal metal, the temperature scaling of the resistivity is different from that in a half metal. This agrees with the finding in Ref. 18 that the resistivity anomaly starts around 50 K in the sample with composition NiMn_{1.05}Sb. This half-metal-metal transition gives the explanation of the anomalous behavior of the resistivity and the loss of high spin polarization in the low-temperature anomaly. In some semiconductors, a somewhat comparable situation³⁰ occurs, where thermal excitations of electrons to the conduction band leave holes behind. The electron-hole attraction effectively reduces the band gap, making subsequent excitations more likely and ultimately leads to a transition to a metallic state, the Falicov-Kimball transition.³¹ Here, an enhancement factor of 5 or 6 (418 K versus the temperature around which the low-temperature anomaly happens) is needed in order to explain the low-temperature anomaly, which is a reasonable number, compared to the enhancement factors in some semiconductor-metal transitions.³¹

Next we consider the magnetization in NiMn_{1.05}Sb. Figure 2 shows the measured magnetization as a function of

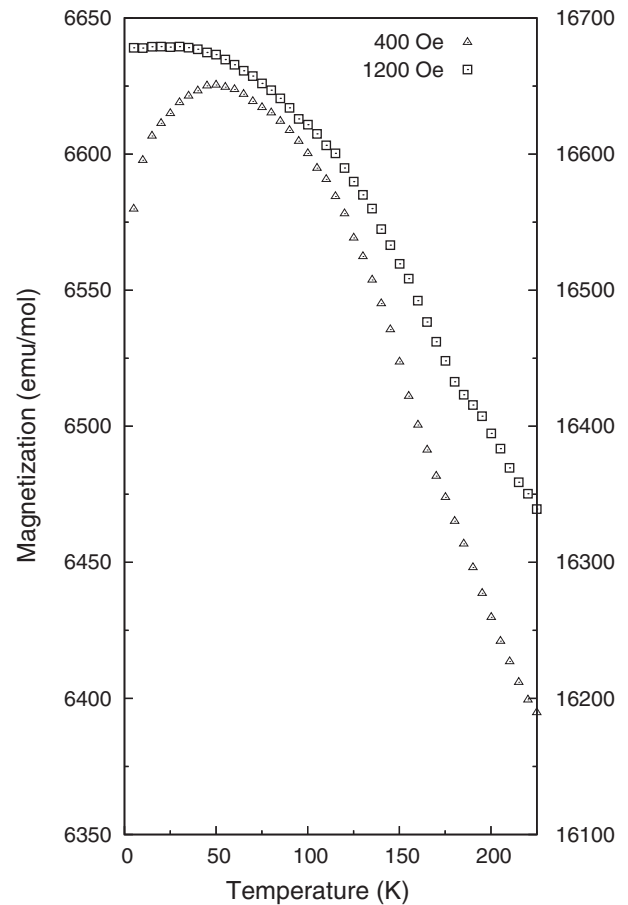


FIG. 2. Magnetization of NiMn_{1.05}Sb as function of the temperature from 5 to 225 K: The curve (scaled by the left vertical axis) plotted by triangles represents magnetization measured in a field of 400 Oe, and the curve (scaled by the right vertical axis) plotted by rectangles is for magnetization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

the temperature³² 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 NiMnSb is very small (equivalent to 0.04 K per magnetic atom),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 align the antiferromagnetic moments on the excess manganese parallel to the host magnetization, but a field of 1200 Oe can reorient them, even if this field is smaller than the saturation field for NiMn_{1.05}Sb which is about 10 kOe. We attribute the increase of the magnetization (in a field of 400 Oe) with temperature to the disordering of the magnetic moments of the interstitial manganese. The antiferromagnetic coupling between the excess manganese and the host magnetization is confirmed by the magnetization analysis. As temperature increases, moments on the excess manganese become disordered. Consequently, this has a distinct influence on the

temperature dependence of the magnetization, which gives the explanation of the anomalous behavior of magnetization in the low-temperature anomaly.

IV. 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_{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.

ACKNOWLEDGMENTS

This work is part of the research program of the Foundation for Fundamental Research on Matter (FOM) which is financially supported by the Netherlands Organization for Scientific Research (NWO).

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- ²⁹On 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.
- ³⁰In 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.
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- ³²The 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).