# Electronic and magnetic properties of the (111) surfaces of NiMnSb

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#### Abstract

Using an ab-initio electronic structure method, I study the (111) surfaces of the half-metallic NiMnSb alloy. In all cases there is a very pronounced surface state within the minority gap which destroys the half-metallicity This state survives for several atomic layers below the surface contrary to the (001) surfaces where surface states were located only at the surface layer. The lower dimensionality of the surface leads in general to large enhancements of the surface spin moments.

*Key words:* Electronic structure, Heusler alloy, Half-metal, NiMnSb *PACS:* 73.20.-r, 73.20.At, 71.20.-b, 71.20.Lp

## 1 Introduction

The discovery of giant magnetoresistance in 1988 [1] gave birth to a new field in condensed matter, the magneto- or spin-electronics [2]. Contrary to the conventional electronics it is the spin of the electron and not its charge which plays the central role. Key compounds to maximize the efficient of the devices based on spintronics are the so-called half-metallic materials which are ferromagnets where there is a band gap at the Fermi level  $(E_F)$  for the minority spin band while the majority spin band is metallic.

Attractive candidates for half-metallic materials are the half-Heusler alloys and it is mainly NiMnSb which has attracted most of the attention. NiMnSb was also the first material to be predicted to be a half-metal in 1983 by de Groot and his collaborators [3]. There exist several other ab-initio calculations on NiMnSb reproducing the results of de Groot [4] and Galanakis *et al.* showed

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that the gap arises from the hybridization between the d orbitals of the Ni and Mn atoms [5]. Its half-metallicity seems to be well-established in the case of single crystals; infrared absorption [6] and spin-polarized positron-annihilation [7] gave evidence supporting it.

The interest in the case of NiMnSb films has been focused mainly to films grown along the [001] direction. Several experimental groups have grown such films [8] and they were found not be half-metallic [9]; a maximum value of 58% for the spin-polarization of NiMnSb was obtained by Soulen *et al.* [10]. Also several ab-initio calculations exist on the (001) surfaces films and all the results agree that the half-metallicity is lost due to surface states [11,12]. On the other hand van Roy and collaborators have managed to grow (111) films of NiMnSb on top of GaAs(111) substrates [13,14]. These films were found to contain inclusions of MnSb and NiSb [13] and to show a large amount of defects [14] but their magnetic properties have not been studied.

In this communication I study the (111) surfaces of the half-metallic NiMnSb Heusler alloy. I take into account all possible six terminations and show that in all cases there is a minority surface states in the region of the gap. In section 2 I discuss the structure of the surface and the computational details and in section 3 I present and analyze my results. Finally in section 4 I summarize and conclude.

#### 2 Computational method and structure

In the calculations I used the the screened Korringa-Kohn-Rostoker (KKR) Green's function method [15,16] within the atomic sphere approximation (ASA) in conjunction with the local spin-density approximation [17] for the exchangecorrelation potential [18]. The ASA calculations take into account the full charge density. To simulate the surface I used a slab with 33 metal layers embedded in half-infinite vacuum from each side. This slab thickness is enough so that the layers in the middle exhibit bulk properties; they show a spin-down gap of the same width as in the bulk and the same relative position of the Fermi level and finally the magnetic moments differ less than  $0.01\mu_B$  from the bulk values. Here I should mention that this number of layers is much larger than the one needed in the case of the (001) surfaces [11] due to the very intense surface states pinned at the Fermi level (see results in next section). I have also converged the  $\mathbf{q}_{\parallel}$ -space grid, the number of energy points and the tight binding cluster so that the properties of the surfaces do not change (similar DOS and spin moments). So I have used a two-dimensional  $30 \times 30$  $\mathbf{q}_{\parallel}$ -space grid to perform the integrations in the first surface Brillouin zone. To evaluate the charge density one has to integrate the Green's function over an energy contour in the complex energy plane; for this 42 energy points were



Fig. 1. Schematic representations of the (111) surface. Each layers has a single atomic character. If I neglect the chemical character of the atoms in the  $C1_b$  structure of NiMnSb then the lattice is the bcc. Note also that there are two different terminations for each element, *e.g.* when the surface is terminated by Ni the subsurface layers can be either a Mn one or an Sb one. In the figure I show both of them together with the corresponding sequence of atoms. "S" stands for surface and "1, 2, 3" are the positions within the surface unit cell for succesive layers.

needed. A tight-binding cluster of 51 atoms was used in the calculation of the screened KKR structure constants [19]. Finally for the wavefunctions I took angular momentum up to  $\ell_{max} = 3$  into account and for the charge density up to  $\ell_{max} = 6$ .

In figure 1 I present the structure of the (111) surfaces in the case of NiMnSb. NiMnSb crystallizes in the  $C1_b$  structure. If one neglects the difference in the chemical character of the atoms then the underlying lattice is a simple bcc. Thus along the [111] direction the alloy is consisted from alternating layers containing only one chemical element. In the case of a Ni terminated surface, as the one shown in the figure, there are two different possibilities: either to have a Mn subsurface layer or an Sb one. I denote the first case as Ni<sup>Mn</sup> and the second as Ni<sup>Sb</sup>. Similarly Mn and Sb terminated surfaces can have either a Ni subsurface layer or one consisted from voids (denoted as Vd in the article). Of course in real systems no voids exist but its use is obligatory in the calculations to take correctly into account the charge distribution in the vacuum. The surface unit cell is a rhombus and when passing from one layer to a neighboring one, the atoms slide along the big diagonal and are positioned at 1/3 or 2/3 of its length (in the figure atoms in successive layers are denoted by 1, 2 or 3). I have used in all my calculations the experimental lattice constant of NiMnSb of 5.909 Å [20]. Finally I should mention that since my slab is made of 33 atoms I have two inequivalent surfaces. For example if the one surface is the Ni<sup>Mn</sup> then the other one should be the Ni<sup>Sb</sup> surface.

_	$\mathrm{Ni}^{\mathrm{Mn}}$		${ m Ni}^{ m Sb}$	
$\mathbf{S}$	Ni	0.537 ( 0.268)	Ni	0.207 ( 0.268)
S-1	Mn	3.934 ( $3.700$ )	$\mathbf{Sb}$	-0.060 (-0.069)
S-2	Vd	$0.058 \ ( \ 0.058)$	Vd	$0.033\ (\ 0.058)$
S-3	$\operatorname{Sb}$	-0.066 (-0.069)	Mn	3.709(3.700)
S-4	Ni	0.252 ( 0.268)	Ni	0.246 (0.268)
S-5	Mn	3.691 ( 3.700)	$\mathbf{Sb}$	-0.074 ( $-0.069$ )
S-6	Vd	$0.056 \ ( \ 0.058)$	Vd	$0.058 \ ( \ 0.058 )$
S-7	$\mathbf{Sb}$	-0.062 ( $-0.069$ )	Mn	3.682(3.700)

Table 1 Atomic spin moments given in  $\mu_B$  for the Ni terminated (111) surfaces. "S" denotes the surface layer. In parenthesis the bulk values.

#### 3 Results and discussion

Surfaces can change the bulk properties severely, since the coordination of the surface atoms is strongly reduced. Since half-metals can be considered as hybrids between the ferromagnetic metals and the semiconductors, two effects should be particularly relevant for their surfaces: (i) for ferromagnets the moments of the surface atoms are strongly enhanced due to the missing hybridization with the cut-off neighbors, and (ii) for semiconductors surface states appear in the gap, such that the surface often becomes metallic. Also this is a consequence of the reduced hybridization, leading to dangling bond states in the gap. In Heusler alloys both phenomena occur simultaneously [11] but there are cases like the Cr-terminated (001) surfaces of the half-metallic zinc-blende CrAs or CrSe compounds, where the large enhancement of the Cr spin moment kills the surface states [21].

#### 3.1 Ni terminated surfaces

The first case which I will study are the Ni-terminated surfaces. As it was already mentioned there are two different possibilities: (i) to have a Mn subsurface layer and then the sequence of the atoms is Ni - Mn - Vd - Sb - Ni - Mn - ..., (ii) an Sb subsurface layer and then the sequence is Ni - Sb - Vd - Mn - Ni - Sb - ... The first one is denoted as Ni<sup>Mn</sup> and the second one as Ni<sup>Sb</sup>. In the bulk case Ni has four Mn and four Sb atoms as first neighbors. When I open the (111) surface the Ni atom at the surface layer loses four out of its eight first neighbors. In the case of Ni<sup>Mn</sup> it loses three Sb atoms and one Mn atom while in the Ni<sup>Sb</sup> case one Sb and three Mn atoms. In table 1 I have gathered the spin moments for the first eight layers and in parenthesis the spin moments for the bulk are given. In the case of Ni<sup>Mn</sup> both Ni and Mn atoms at the surface have very large moments with respect to both the bulk calculations and the Ni<sup>Sb</sup> case. Especially Ni moments is doubled (0.54  $\mu_B$ ) with respect to the bulk value of  $0.27\mu_B$ . In the case of the bulk NiMnSb the minority gap is created by the hybridization between the *d*-orbitals of the Ni and Mn atoms, but the Sb atom plays also a crucial role since it provides states lower in energy than the d bands which accommodate electrons of the transition metal atoms [5]. When I open the (111) surface terminated at Ni<sup>Mn</sup> then each Ni surface atoms loses three out of the four Sb first neighbors and they regain most of the charge accommodated in the p bands of Sb. These extra electrons fill up mostly majority states increasing the Ni spin moment. But both majority and minority Ni-bands are already completely occupied even in the case of bulk NiMnSb. The only solution is that also Mn majority spin charge is increased to compensate for the missing Sb neighbors although Mn and Sb atoms are second neighbors. This is helped by the fact that Mn and Ni majority d states strongly hybridize forming a common majority band as it was shown in reference [5]. And thus the spin moment of Mn at the subsurface layer increases reaching the  $3.93\mu_B$  with respect to the bulk value of  $3.70\mu_B$ . If one goes further away from the surface, the atoms have a bulklike environment and their spin moments are similar to the bulk case. In the Ni<sup>Sb</sup> surface, Ni at the surface loses only one Sb first neighbor and the effect of the cut-off neighbors is much smaller. The moment is slightly smaller than the bulk one mainly due to a surface state at the minority band shown in figure 2. Already at the Sb subsurface atom one regains a bulklike behavior for the spin moment.

In figure 2 I have gathered the spin-resolved density of states (DOS) for the four layers closest to the surface for both types of Ni termination. Note that I use a different grid for the DOS in the case of Mn and Ni atoms than for the Sb atom and the vacant site. For the Ni<sup>Mn</sup> termination, there is a minority surface state pinned exactly at the Fermi level which completely destroys the half-metallicity. As mentioned above the population of the majority states increases and due to the exchange splitting the minority states are pushed higher in energy and this results to a very sharp shape of the surface state. This phenomenon is more pronounced for the Mn atom at the subsurface layer, whose occupied minority states have a small weight, and thus it presents a much larger exchange splitting energy since this one scales with the spin magnetic moment. This surface state gradually weakens and for the Ni atom at the S-4 position (not shown here) it practically vanishes.

In the case of the Ni<sup>Sb</sup> surface the Ni spin moment is much smaller and the Mn atom is deep in the substrate. Ni bands even move slightly higher in energy and thus the surface state is now much more extended in the energy axis and cannot be well separated from the rest of the DOS. This situation is similar



Fig. 2. Atom- and spin-resolved DOS for the two different surfaces terminating in Ni. I show the DOS for the four upmost layers. The zero of the energy is chosen to correspond to the Fermi level. Positive values of the DOS correspond to the majority spin and negative to the minority.

to the Ni-Void terminated (001) surface studied in reference [11]. There at the surface layer there are both Ni and void sites and the Ni surface DOS moves higher in energy with respect to the bulk killing the half-metallicity.

#### 3.2 Mn and Sb terminated surfaces

In the second part of this section I will discuss the Mn and Sb terminated surfaces. As it was the case for the Ni terminated ones, there are again two different possible terminations either having a Ni or a void as the subsurface layer. In tables 2 and 3 I have gathered the atomic spin moments in  $\mu_B$  for all the possible cases keeping the notation of table 1 to enumerate the different layers.

In the case of the Mn surfaces, Mn at the surface layer loses half of its Sb second neighbors and similarly to what happened in the case of the Ni<sup>Mn</sup> surface its spin moment is strongly enhanced reaching the 3.92  $\mu_B$  for the Mn<sup>Ni</sup> and the 4.20  $\mu_B$  for the Mn<sup>Vd</sup> case. In the later case Mn has a Vd subsurface layer and thus the hybridization between the Mn *d*-orbitals and the Sb *p*- and Ni *d*-orbitals is strongly reduced leading to an increase of its spin moment with respect to the Mn<sup>Ni</sup> case. The enhancement of the Mn spin moment at

	$\mathrm{Mn}^{\mathrm{Ni}}$		$\mathrm{Mn}^{\mathrm{Vd}}$	
S	Mn	3.918 ( 3.700)	Mn	4.202 ( 3.700)
S-1	Ni	0.167 ( 0.268)	Vd	0.052 ( 0.058)
S-2	$\mathbf{Sb}$	-0.103 (-0.069)	$\mathbf{Sb}$	-0.067 $(-0.069)$
S-3	Vd	$0.038\ (\ 0.058)$	Ni	0.260(0.268)
S-4	Mn	3.614 (3.700)	Mn	3.679(3.700)
S-5	Ni	$0.231 \ ( \ 0.268)$	Vd	$0.052 \ ( \ 0.058)$
S-6	$\operatorname{Sb}$	-0.076 (-0.069)	$\operatorname{Sb}$	-0.070 (-0.069)
S-7	Vd	$0.055\ (\ 0.058)$	Ni	$0.267\ (\ 0.268)$

Table 2Same as table 1 for the Mn terminated surfaces.

Table 3

Same as table 1 for the Sb terminated surfaces.

	$\mathrm{Sb}^{\mathrm{Ni}}$		$\mathrm{Sb}^{\mathrm{Vd}}$	
$\mathbf{S}$	$\operatorname{Sb}$	-0.134 (-0.069)	$\mathbf{Sb}$	-0.198 (-0.069)
S-1	Ni	0.111 ( 0.268)	Vd	-0.005 (0.058)
S-2	Mn	3.493(3.700)	Mn	3.606(3.700)
S-3	Vd	$0.038 \ ( \ 0.058)$	Ni	0.194 ( $0.268$ )
S-4	$\mathbf{Sb}$	-0.067 ( $-0.069$ )	$\mathbf{Sb}$	-0.080 (-0.069)
S-5	Ni	0.237 ( 0.268)	Vd	$0.051 \ ( \ 0.058 )$
S-6	Mn	3.704 ( $3.700$ )	Mn	3.648 ( $3.700$ )
S-7	Vd	$0.056 \ ( \ 0.058)$	Ni	0.260(0.268)

the interface is also seen in the case of the (001) surfaces terminated in MnSb where the spin moment of the Mn atom at the interface reaches a value of 4.02  $\mu_B$  [11]. The atoms deeper in the surface quickly reach a bulklike behavior.

Following the same arguments as for Mn, one can understand also the behavior of the spin moments for the Sb terminated surfaces presented in table 3. The absolute value of the Sb spin moment at the surface layer increases with respect to the bulk as was also the case for the MnSb terminated (001) surfaces [11]. When the subsurface layer is the Vd one, the hybridization effects are less important and the Sb spin moment can reach a value of -0.20  $\mu_B$  almost triple the bulk value of -0.07  $\mu_B$  and double the value for the (001) surface of  $-0.10 \ \mu_B$ . The change in the Sb *p*-bands influences also through hybridization the bands of the transition metal atoms for which now the minority bands population increases leading to smaller spin moments of the Ni and Mn atoms at the subsurface layers. The phenomenon is more intense in the case of Sb<sup>Ni</sup>



Fig. 3. Same as figure 2 for the MnNi and SbNi terminated surfaces.

where the Ni layer is just below the Sb surface layer and the reduction in the spin moments of Ni and Sb is much larger than the Sb<sup>Vd</sup> case.

Finally in figure 3 I have gathered the DOS for the first four layers in the case of Ni subsurface layers. Results are similar also when I have the voids as subsurface layer. In the case of the Mn terminated surface, there is a minority surface state pinned exactly at the Fermi level which destroys the half-metallicity and which survives also at the Ni subsurface layer. But at the next Mn layer (not shown here) it vanishes. Overall the DOS's are similar to the bulk case and the increase of the Mn spin moment at the interface is taken care of high-energy lying majority antibonding d-states which in the bulk are above the Fermi level but now move below it pushing also somewhat lower in energy the majority surface state slightly below the Fermi level but which also destroys the half-metallicity at the surface. Its intensity is large also for the Ni at the subsurface layer but already for the Mn atom it starts to smear out.

## 4 Summary and conclusions

I have studied using an ab-initio technique the electronic and magnetic properties of the (111) surface of NiMnSb taking into account different terminations. In all cases there is a minority surface state which kills the half-metallicity at the surface. It is pinned at the Fermi level for the Ni and Mn terminated surfaces but it is slightly below the Fermi level for the Sb one. It is localized close to the surface region and normally vanishes within four atomic layers.

In the case of the Ni surface with Mn as subsurface layer, Ni<sup>Mn</sup>, the loss of three out of the four Sb first neighbors leads to a doubling of the Ni spin moment while in the Ni<sup>Sb</sup> case it is near the bulk value. For the Mn and Sb terminations the lowering of the coordination increases the surface spin moments and the enhancement is larger when there is a subsurface layer made by voids.

Finally I should add that from point of view of transport a single surface state does not affect the magnetoconductance since the wavefunction is orthogonal to all bulk states incident to the surface. It is the interaction of the surface state with other defect states in the bulk and/or with surface defects which makes these states conducting and leads to the low spinpolarization values for films derived by Andreev reflection measurements.

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