Effect of chemical disorder on NiMnSb investigated by appearance potential spectroscopy: an experimental and theoretical study

J Minár¹, J Braun¹, S Bornemann¹, H Ebert¹ and M Donath²

¹ Department Chemie und Biochemie, Lehrbereich Physikalische Chemie, Ludwig-Maximilians-Universität München, Butenandstr 5-13, 81377 München, Germany
² Physikalisches Institut, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany

E-mail: jan.minar@cup.uni-muenchen.de

Received 29 September 2008, in final form 10 December 2008
Published 30 March 2009
Online at stacks.iop.org/JPhysD/42/084009

Abstract

The half-Heusler alloy NiMnSb is one of the local-moment ferromagnets with unique properties for future applications. Band structure calculations exclusively predict majority bands at the Fermi level, thus indicating 100% spin polarization there. For the development of functional materials, chemical disorder has to be considered quantitatively. The magnetization, spin polarization and electronic structure are expected to be sensitive to structural and stoichiometric changes. We studied the influence of chemical disorder on the unoccupied electronic density of states of NiMnSb(0 0 1) by the use of the \textit{ab initio} coherent potential approximation method and results are discussed along with corresponding measurements.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In 1903, first Heusler alloys (HAs) were singled out as a special group of magnetic materials that exhibit ferromagnetism in compounds of non-magnetic elements [1]. Currently, the Mn-based half-HAs with the generic formula \(XMnZ\) (with \(X\) being a 3d metal and \(Z\) belonging to the III or IV group) are well-known magnetic systems that crystallize in the Heusler \(\text{C}_1\text{b}\) structure, which is closely related to the zincblende structure [2]. In particular, the half-metallic ferromagnet NiMnSb [3] has motivated a variety of experimental and theoretical investigations due to the search for materials to be used as spin-injectors. These materials are defined as magnetic materials with a band gap at the Fermi level for electrons of one spin direction. Band structure calculations for bulk NiMnSb show a gap of about 0.5 eV at \(T = 0\) for the minority electrons, which means 100% spin polarization at the Fermi level \(E_F\). In fully relativistic calculations a reduced but not vanishing gap and 99% spin polarization at \(E_F\) are predicted [4]. As in the case of the group III–V semiconductors, the crystal structure is the reason for the band gap. It is, therefore, called a covalent band gap [5]. As a consequence, the crystal structure and the site occupation within the given structure are important for the appearance of the gap. Atomic disorder, especially interchange of atoms between the Ni and Mn sublattices, results in a strong reduction of the spin polarization at \(E_F\) [6]. However, this interchange costs approximately as much energy as the evaporation of the metallic constituents [5]. Therefore, half-metallic behaviour is an idealization distorted by structural inhomogeneities [7–9] and through the decrease in the spin polarization of spin carriers and vanishing of the semiconducting band gap for minority spin electrons in real crystals and interfaces caused by finite temperature effects.

A variety of experimental results for NiMnSb are available in the literature. While bulk measurements support the half-metallic behaviour (see, e.g. [10, 11]), surface-sensitive techniques have failed so far to detect the energy gap for minority electrons or the 100% spin polarization at the Fermi level \(E_F\). Most of the studies were performed on polycrystals.
or thin films, single and polycrystalline, prepared under various growth conditions on a variety of substrates. Spin-integrated photoemission (PE) spectra obtained with a photon energy of 45 eV showed clear signatures of the Ni and Mn 3d contributions [12]. Angle-integrated PE with variable photon energies identified Ni and Mn 3d emission from the valence bands emphasized the need for further careful investigations both experimentally and theoretically [13]. A spin-polarized PE study found values of the spin polarization up to 50% near the photothreshold [14]. The authors concluded that if an energy gap for minority electrons should exist, it is smaller than 0.5 eV. A further spin-resolved PE work, yet with photon energies between 38 and 76 eV, reported spin polarization values of at most 40% close to the Fermi level [15]. A reduced surface magnetization at remanence and/or a surface phase different from the bulk were proposed as possible explanations for the unexpected low polarization values. Furthermore, an angle-resolved PE study of the electronic structure single-crystalline NiMnSb sample showed that the binding energies of the PE intensities are sensitive to the particular surface condition and/or preparation [16]. Additionally, a possible surface state has been found in these k-resolved measurements. In another study, a temperature-dependent crossover from half-metallic to normal ferromagnetic behaviour at 80 K was reported and discussed as a possible reason for the detected low polarization [17]. It was suggested that, at room temperature, the spin polarization at $E_F$ may be considerably lowered due to a populated minority band, although the magnetization is not much reduced compared with the value at $T = 0$. (With a Curie temperature of about 730 K, the magnetization at room temperature amounts to $\approx 92\%$ of the saturation value [18].) However, even point contact Andreev reflection measurements at 4.2 K at the free surface of NiMnSb gave a maximal value of only 44%, independent of different surface preparations and magnetic domain structures [19]. This result is in line with former spin-polarized PE data, which did not find a higher polarization value for 20 K than for room temperature [14]. As a complement to the above reports, a room-temperature study by angle and spin-resolved inverse PE reported close to 100% spin polarization at $E_F$ and $\Gamma$ under some conditions [20]. Last but not least from a spin-resolved appearance potential spectroscopy (APS) study the measured spin asymmetry from the surface region was found to be significantly reduced compared with the theoretical prediction [21].

In this contribution, we present spin-integrated and spin-resolved APS spectra from NiMnSb(0 0 1) and discuss by comparison with experimental data the degree of spin polarization as a function of chemical disorder. As mentioned above, NiMnSb(0 0 1) is one of the best studied Heusler material with very well-defined and fabricable (0 0 1) surface orientation. In particular, the following discussion is a follow-up of previous work of Kolev et al [21] and supports their findings. This paper can be seen as a follow-up contribution. The paper is organized as follows. Section 2 is devoted to some experimental and computational details. In section 3 we discuss the theoretical results and compare with corresponding experimental data. A summary is given in section 4.

2. Experimental and computational details

2.1. Spectroscopical scheme

In this section the relevant details of the experimental investigations are given. A more delayed report can be found in [21].

APS is a surface-sensitive tool to study the unoccupied density of states (DOS) with elemental resolution [22]. For spin-resolved APS, the sample is bombarded with a spin-polarized electron beam of variable energy while the total yield of emitted x-rays or electrons is monitored [23, 24]. At energies high enough to excite a core electron into empty states above the Fermi level, the yield of emitted particles increases due to recombination of the created core hole via x-ray or Auger electron emission. In our case, we detect the emitted x-rays [25]. Potential modulation together with lock-in techniques is used to separate the small signal from the dominating background. Since both the exciting and the excited electron are scattered into empty states, the rate of possible excitations and, thereby, of detected recombinations depends on the DOS above $E_F$. The spin-polarized electron beam used for excitation is emitted from a GaAs photocathode irradiated with circularly polarized 830 nm laser light. This arrangement provides about 30% spin polarization of the emitted electrons [26]. The spectra shown have been renormalized to 100% hypothetical beam polarization. The APS signal depends on the spin of the exciting electron in the case of ferromagnets because of the spin-dependent unoccupied DOS. The elemental resolution comes from the fact that core levels are involved, whose energies are characteristic of the various elements.

2.2. Calculational scheme

Hence, the calculational procedure concerning APS is found in detail in [21, 27]; we restrict ourselves to a short description of some computational details. The fully relativistic DOS calculations have been performed within the SPRKKR computer program [28] running in the CPA-mode [29]. The chemical disorder introduced in the spectroscopical analysis consists of an interchange between Mn atoms on Ni sites and vice versa with concentration values $x$ of 0%, 5%, 10% and 15%. This means we have calculated $(\text{Ni}_1-x\text{Mn}_x)(\text{Mn}_{1-x}\text{Ni}_x)\text{Sb}$ in the $L_2$ crystal structure using the experimental lattice constant 5.91 Å. In figures 2 and 3 we use the compact notation $\text{Ni}_{1-x}\text{Mn}_x\text{Sb}$. Figure 1 shows the spin-resolved total DOS for NiMnSb. Clearly visible is the closing of the spin-dependent gap at the Fermi energy caused by the chemical disorder. Even at 5% interchange of Mn and Ni atoms the gap completely vanishes because the spectral weight is shifted towards the Fermi level. A significant enhancement of the spectral weight around the Fermi level is also observable in the majority DOS and therefore affects the amount of spin polarization that is measured in an APS experiment. The corresponding partial densities of states together with the spin-dependent potentials serve as input quantities for the spectroscopical calculations. In our case we probed the local DOS (LDOS) at the Mn atom in NiMnSb. The
surface sensitivity is a result of the short mean free path of the electrons in the solid for energies that correspond to the Mn $2p$ excitation ($\approx 640–650$ eV). The elemental resolution results from the fact that a core level with an element-specific binding energy is involved. Due to the excitation with spin-polarized electrons the APS method becomes a magnetically sensitive technique. The calculated spin-dependent APS intensities result from the weighted self-convolution of the corresponding LDOS. The weighting factor itself is given by the spin-dependent effective cross section consisting of an appropriate combination of relativistic Coulomb matrix elements. For a quantitative comparison between APS measurements and theoretical spectra one has to take into account various lifetime effects and experimental broadening. Electron lifetime effects have been included in our analysis in a phenomenological way introducing a parametrized complex inner potential with an imaginary part of $V_0i = 30$ eV. The core hole lifetime is set to zero. Lifetime effects in the valence-band states are accounted via a Lorentzian with an energy-dependent width. For the explicit parametrization of the Lorentzian the reader is referred again to [21].

3. Results and discussion

Figure 2 presents calculated spin-integrated AP spectra for NiMnSb(001) in comparison with APS data. The spectra are normalized to equal maximum intensity. The theoretical spectra have been calculated with respect to the Fermi level. To be comparable to the experiment the calculated spectra were shifted along the energy axis until the peak maxima of the measured and the calculated spectra coincide. As can be seen, good agreement between experiment and theory is achieved. The almost quantitative agreement suggests that the DOS as calculated resembles the Mn LDOS in NiMnSb quite well in the spin-integrated case. The spectra show a pronounced structure at 639.7 eV from the Mn $2p_{3/2}$ threshold. These features originate from the self-convoluted local density of unoccupied 3d states. The spectral feature at the high-energy side of the main line corresponds to the maximum of the sp-like DOS, whose appearance and energetic position are sensitive to the short-range crystallographic order around the atom where the local excitation occurs. As expected, the effect of chemical disorder is nearly negligible concerning the spin-integrated DOS. Only slight deviations in the APS line shapes between the spectra calculated for the ordered and for the disordered structures are observable.

By adding spin resolution (see spectra in figure 3), we are able to obtain information about the spin-dependent DOS. The experimental data for majority (↑) and minority (↓) spins are presented by red (dark) and green (grey) filled circles,
Figure 3. Spin-resolved AP spectra for NiMnSb(0 0 1) at the Mn 2p 3/2 threshold as a function of chemical disorder. The Ni_{1.00}Mn_{0.00}Sb corresponds to the ordered case and corresponding experimental data are given by filled circles and are taken from figure 5(b) of [21].

First of all, the APS lines show a clear spin asymmetry, $A$, between the spin-dependent intensities $I_\uparrow$ and $I_\downarrow$ [$A = (I_\uparrow - I_\downarrow)/(I_\uparrow + I_\downarrow)$]. The experimental spin-resolved spectra of figure 3 represent an average from many different surface regions. By taking into account the reduced remanent magnetization [21], we end up with an estimated spin asymmetry of $A = -0.230$ for 5% interchange of Ni and Mn atoms and decreases from $A = -0.215$ for 10% disorder to $A = -0.200$ for 15% interchange of Ni and Mn atoms. As a guide for the eye we compare at the bottom of figure 3 directly the spectra which belong to zero and 15% disorder to clarify the decrease in the spin asymmetry. Therefore, our analysis supports the result found by Orgassa et al that chemical disorder significantly lowers the spin polarization at $E_F$. On the other hand, introducing the effect of chemical disorder into our APS calculations, we end up with an improved agreement between experiment and theory but the predicted spin asymmetry is still too high by nearly a factor of 2. Our analysis indicates that other mechanisms besides chemical disorder must be taken into account for a quantitative explanation of the strongly reduced spin polarization in NiMnSb(0 0 1).

4. Summary

We have presented spin-integrated and spin-resolved APS data for the unoccupied electronic states of NiMnSb as a function of chemical disorder. The calculated series of spin-resolved and concentration dependent APS spectra demonstrates that chemical disorder influences the spin asymmetry of the unoccupied states of NiMnSb. Concerning the spin polarization at the Fermi level, one must note that APS is not particularly sensitive in that region. The nature of the APS signal does not allow one to resolve small energy gaps of the order of 0.5 eV giving rise to a positive spin asymmetry at $E_F$. The APS signal is rather dominated by the minority d states above $E_F$ leading to a negative spin asymmetry. On the other hand, the significantly reduced spin polarization observed in the experiment clearly indicates an incomplete spin polarization with a value well below 100%. Therefore, the expected 100% spin polarization at the Fermi level is not verified, as in a number of spin-polarized electron spectroscopic experiments before. Furthermore, one has to take into account other mechanisms than chemical disorder to be able to explain quantitatively the unexpected low value for the measured spin asymmetry. Therefore, we conclude that the following issues must be examined in future studies on well-defined samples. First the magnetization within the surface layers compared with the bulk should be investigated in more detail. Also surface phases with respect to composition and/or crystallographic order different from the bulk could be important and the position and width of the band gap should be analysed in more detail in the calculations. A first study on NiMnSb(1 1 0) showed the formation of microstructures upon preparation, which has consequences for the magnetic properties of the surface [30]. Another experimental study of Migoshi et al [31] supports the sensitivity of the spin polarization on chemical disorder. Even with a stoichiometric spin asymmetry decreases. This is expected because of the pronounced increase in the spectral weight in the majority spin DOS around the Fermi energy that overcompensates the shift of the spectral weight in the minority spin DOS. The concentration dependence of the spin asymmetry is demonstrated by the series of spin-dependent APS data shown in figure 3. The spin asymmetry in the main peak is calculated to be $A = -0.230$ for 5% interchange of Ni and Mn atoms and decreases from $A = -0.215$ for 10% disorder to $A = -0.200$ for 15% interchange of Ni and Mn atoms. As a guide for the eye we compare at the bottom of figure 3 directly the spectra which belong to zero and 15% disorder to clarify the decrease in the spin asymmetry. Therefore, our analysis supports the result found by Orgassa et al that chemical disorder significantly lowers the spin polarization at $E_F$. On the other hand, introducing the effect of chemical disorder into our APS calculations, we end up with an improved agreement between experiment and theory but the predicted spin asymmetry is still too high by nearly a factor of 2. Our analysis indicates that other mechanisms besides chemical disorder must be taken into account for a quantitative explanation of the strongly reduced spin polarization in NiMnSb(0 0 1).
surface, the number of nearest neighbours is changed at the surface and interface states may form and influence the gap [32, 33]. In the case that the free surface does not provide 100% spin polarization, there is still hope that specific interfaces may open the way for 100% spin-polarized charge-injection [34] in spintronic devices. Other materials with half-metallic behaviour must be considered as well in order to design functional materials for future applications [35].

References

[1] Heusler F 1903 Verh. Deutsch. Phys. Ges. 5 219
[2] Webster P J and Ziebeck K R A 1999 Landolt–Börnstein New Series (Group III) vol 19c (Berlin: Springer)
[3] de Groot R A, Mueller F M, van Engen P G and Buschow K H J 1983 Phys. Rev. Lett. 50 2024
[4] Mavropoulos Ph, Sato K, Zeller R, Dederichs P H, Popescu V and Ebert H 2004 Phys. Rev. B 69 054424
[5] Fang C M, de Wijs G A and de Groot R A 2002 J. Appl. Phys. 91 8340
[6] Orgassa D, Fujiwara D, Schultheiss T C and Butler W H 1999 Phys. Rev. B 60 13237
[7] Soulen R J et al 1998 Science 282 85
[8] Raphael M P, Ravel B, Willard M A, Cheng S F, Das B N, Stroud R M, Bussmann K M, Claassen J H and Harris V G 2001 Appl. Phys. Lett. 79 4396
[9] Brown P J, Neumann K U, Webster P J and Ziebeck K R A 2000 J. Phys.: Condens. Matter 12 1827
[10] van der Heide P A M, Baelde W, de Groot R A, de Vroomen A R, van Engen P G and Buschow K H J 1985 J. Phys. F: Met. Phys. 15 L75
[11] Hanssen K E H M, Mijnarends P E, Raboui L P L M and Buschow K H J 1990 Phys. Rev. 42 1533
[12] Robey S W, Hudson L T and Kurtz R L 1992 Phys. Rev. B 46 11697
[13] Kang J S, Hong J H, Jung S W, Lee Y P, Park J G, Olson C G, Youn S J and Min B I 1993 Solid State Commun. 88 653
[14] Bona G L, Meier F, Taborelli M, Bucher E and Schmidt P H 1985 Solid State Commun. 56 391
[15] Zha W, Sinkovic B, Vescovo E, Tanaka C and Moodera J S 2001 Phys. Rev. B 64 060403
[16] Correa J S, Eibl Ch, Rangelov G, Braun J and Donath M 2006 Phys. Rev. B 73 125316
[17] Hordequin C, Ristoiu D, Ranno L and Pierre J 2000 Eur. Phys. J. B 16 287
[18] Ritchie L, Xiao G, Yi J, Chen T Y, Chien C L, Zhang M, Chen J, Liu Z, Wu G and Zhang X X 2003 Phys. Rev. B 68 104430
[19] Cloves S K, Miyoshi Y, Boguslavsky Y, Branford W R, Grigorescu C, Manea S A, Monnerau O and Cohen L F 2004 Phys. Rev. B 69 214425
[20] Ristoiu D, Nozières J P, Borca C N, Komesu T, Jeong H K and Dowben P A 2000 Europhys. Lett. 49 624
[21] Kolev H, Rangelov G, Braun J and Donath M 2005 Phys. Rev. B 72 104415
[22] Park R and Houston J E 1972 Phys. Rev. 6 1073
[23] Ertl K, Vonbank M, Dose V and Noffke J 1993 Solid State Commun. 88 557
[24] Reimnuth J, Passek F, Petrov N, Donath M, Popescu V and Ebert H 1997 Phys. Rev. B 56 12893
[25] Rangelov G, Ertl K, Passek F, Vonbank M, Bassen F, Reimnuth J, Donath M and Dose V 1998 J. Vac. Sci. Technol. A 16 2738
[26] Kolac U, Donath M, Ertl K, Liebl H and Dose V 1988 Rev. Sci. Instrum. 59 1933
[27] Donath M, Rangelov G, Braun J and Greentz W 2005 Magnetization, spin polarization and electronic structure of NiMnSb surfaces Local-Moment Ferromagnets: Unique Properties for Modern Applications (Lecture Notes in Physics vol 678) ed M Donath and W Nolting (Berlin: Springer) pp 261–72
[28] Ebert H et al The Munich SPR-KKR package, version 3.6; see http://olymp.cup.uni-muenchen.de/ak/ebert/SPRKKR
[29] Ebert H 1999 Fully relativistic band structure calculations for magnetic solids formalism and application Electronic Structure and Physical Properties of Solids. The Use of the LMTO Method (Lecture Notes in Physics vol 635) ed H Dreyssé (Berlin: Springer) pp 191–246
[30] Eickhoff Ch, Kolev H, Donath M, Rangelov G and Chi L F 2007 Phys. Rev. B 76 205440
[31] Miyoshi Y et al 2006 Comparison of free surface polarization of NiMnSb and Co2MnSi Appl. Phys. Lett. 88 142512
[32] Jenkins S J and King D A 2001 Surf. Sci. 494 L793
[33] Jenkins S J and King D A 2002 Surf. Sci. 501 L185
[34] de Wijs G A and de Groot R A 2001 Phys. Rev. B 64 020402
[35] Fonin M, Dedkov Yu S, Rüdiger U and Güntherodt G 2005 Growth and room temperature spin polarization of half-metallic epitaxial CrO2 and Fe3O4 thin films Local-Moment Ferromagnets: Unique Properties for Modern Applications (Lecture Notes in Physics vol 678) ed M Donath and W Nolting (Berlin: Springer) pp 289–306