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The effect of Gd doping on electronic properties of NiMnSb compounds

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The effects of gadolinium doping on the electronic properties of half-Heusler compound NiMnSb are presented. Band structure calculations show that the half-metallic properties are completely conserved if Gd atoms substitute the manganese ones. This effect is determined by the coupling between the Gd (*4f*) spin and the Mn (*3d*) itinerant electron spins. The antiparallel coupling of Gd and transition metal magnetic moments was found to be more favourable. The structural and XPS analysis confirm that the gadolinium atoms occupy lattice sites.

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1. Introduction

During last years theoretical and experimental investigations on the Heusler compounds have delivered new and exciting results on their physical properties. Many studies were devoted to their potential as key materials for spintronic devices [1,2]. In the field of spintronics, materials possessing 100% spin polarization of the conduction electrons are intensively studied. A new class of materials, called half-metal ferromagnets was discovered. Half metallicity was predicted by de Groot and his collaborators in a pioneering paper published in 1983 for the Heusler alloy MnNiSb [3]. Several half-metallic ferromagnetic materials have been initially predicted by theoretical ab initio calculations and afterwards synthesized experimentally [4-6]. Half metallic ferromagnets are now a subject of growing interest because of their possible applications due to their high spin polarization at the Fermi level [7]. Being metals for one spin projection and semiconductors for the opposite one they have, in magnitude, different spin contributions to electronic transport properties, which can result in a huge magnetoresistance for heterostructures containing half-metallic ferromagnets. These compounds are either ferromagnetically or ferrimagnetically ordered and were predicted to have perfect spin polarization at the Fermi level.

NiMnSb crystallizes in the cubic structure of *C*1*b* type with space group $F\bar{4}3m$. This structure can be described as three interpenetrating fcc lattices of Ni, Mn, and Sb. A detailed description of the band structure of semi-Heusler alloys was given using electronic structure calculations analysis [3,4, 8-13]. The large exchange splitting of the Mn atoms, producing the local Mn magnetic moment is crucial to induce a half-metallic structure. The spin polarized calculations reveal that the position of t_{2g} and e_g Ni states are slightly changed comparing the minority and majority spin channels, so that the exchange splitting on Ni is small. The magnetic moment calculation gives values around 3.7 μ_B for Mn and 0.3 μ_B for Ni respectively [3,4, 8-13].

Spin–orbit interaction causes the mixing of the two spin directions, the result being a reduction of the spin polarization of the conduction electrons even at zero temperature. In order to avoid the reduction of spin-polarization, special care has to be taken. Attema et.al. have shown that a properly chosen element from the lanthanide series as a substitute would increase the magnetic anisotropy and at the same time would contribute in keeping a significant spin-polarization [14]. The 4f electrons are not directly involved in chemical bonding and show a strong spin–orbit interaction and are energetically well separated from the Fermi energy. Holmium was proposed as substituent considering both the spin moment and the orbital moment. It was shown that the half-metallic properties are completely conserved if Mn is substituted with a rare earth metal [14]. According to the authors the size of the effect is not determined by the strength of the spin–orbit coupling, but limited by the interaction between the magnetic moments of manganese and gadolinium.

In this study we have checked if it is possible to prepare single phase compounds with a rare earth substitution on the manganese site. We present the results from X-ray diffraction and X-ray photoelectron spectroscopy (XPS) for $NiMn_{1-X}Gd_XSb$ compounds. Band structure calculations were also performed. From X-ray diffraction studies and XPS data, we concluded that the gadolinium atoms enter in the C1*b* structure.

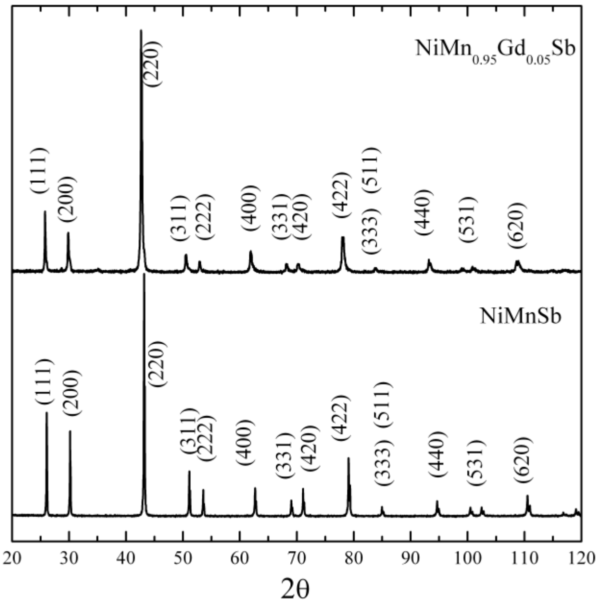

Fig. 1. Diffraction patterns of $NiMn_{0.95}Gd_{0.05}Sb$ and MnNiSb.

2. Experimetal and computational details

The $NiMn1_{-X}Gd_XSb$ compounds with x = 0, 0.01, 0.05 and 0.1 were prepared by arc melting the constituent elements in a purified argon atmosphere from high purity Ni (99.8%), Mn (99.9%), Sb (99.999%) and Gd (99.95%) ingots (Alfa Aesar, Jonson & Matthey, Karlsruhe, Germany). The ingots were remelted several times in order to ensure a good homogeneity. The samples were heat treated in vacuum at 1000 ºC for 5 days. The crystal structure was checked by X-ray Diffraction using a Bruker 8 XD diffractometer. XPS spectra were recorded at room temperature using a SPECS Multifunctional surface analysis system with monochromatized Al Kα radiation, while pressure in the ultra-high vacuum chamber was in the 10^{-10} mbar range. In order to prevent surface contamination the samples were crushed in situ and the surface cleanness was checked by monitoring the oxygen and carbon 1s core levels. Contamination was almost absent, thus the XPS spectra are representative of the bulk.

Based on experimentally determined lattice constants, we have computed the band structures of $Ni_8Mn_7GdSb_8$ and $Ni_8Mn_8Sb_8$ compounds using a supercell eight times greater than the conventional unit cell. A *d*–*f*-type model was used in the mean field approximation, in which the Mn *3d* and Gd *4f* states were described by LSDA + U method, whereas the *3d*–*4f* interaction was treated as perturbation. The mean-field Hamiltonian can be written in the form:

$$H \approx H_{LDA+U} - J\sum \sigma_i^{3d} S_{i+\delta}^{f} ,$$

where the spin of the conduction electron at site R_i is denoted by σ_i^{3d} and $S_{i+\delta}^{f}$ represents the spin of the *4f* shell at the $R_{i+\delta}$ site. LSDA+U approach is based on the local spin density approximation LSDA to the density functional theory (DFT) complemented with Hubbard-U corrections treated in a mean field approximation. The LSDA+U method is a physically motivated approach that attempts to incorporate the effects of important orbital-specific local Coulomb interactions in strongly correlated electron systems while retaining the simplicity of local density approximation (LDA) calculations for real materials [15]. Our calculations use the linearized muffin-tin orbital (LMTO) approach. This method uses an optimized basis set consisting of muffin-tin orbitals with smoothed Hankel functions as envelope functions. The partially filled and strongly correlated localized *f* orbitals were treated using the LSDA+U method. In this method the Coulomb and exchange energy in the Hartree-Fock approximation of a chosen set of localized orbitals, here the *4f* states, are added to the usual local spin density functional and their orbital independent average is substracted to avoid double counting.

3. Results and discussions

The diffraction patterns for the samples with x=0 and x=0.05 are presented in Fig. 1. The X-ray analysis shows, in the limit of experimental errors, that the compounds are single phase with a *C*1*b* type cubic structure (space group $F\bar{4}3m$). The compound with x=0.1 was not found to be single phase. The lattice parameters increase from a=0.593 nm (x=0) to 0.599 nm (x=0.05). This small increase could be explained by the higher radius of Gd ion compared to Mn ion.

In our calculations we considered the standard representation of the $C1_b$ structure with a fcc unit cell containing three atoms, with the sites Ni(0,0,0), Mn and Gd(1/4,1/4,1/4), Sb(3/4,3/4,3/4) and a vacant site E(1/2,1/2,1/2) respectively. The experimental lattice constants were used in all of the calculations. Previously were performed calculations for different values of the average Coulomb interaction parameter U [16]. A very weak U dependence of the total DOS due to T-matrix renormalization effects was shown [17,18]. For all U values a half-metallic solution was obtained with a minority gap having similar width as in the spin polarized LDA calculation. Depending on the strength of U the Fermi level moves toward the middle of the gap, while no significant changes in the studied range between 8–12 eV were observed. In the same time a slight modification of the magnetic moment was found. Therefore, in the following calculations, we take the values U=12 eV and J=0.9 eV for the Coulomb and exchange parameters, which agree with the values reported in literature for metallic rare-earth compounds [19].

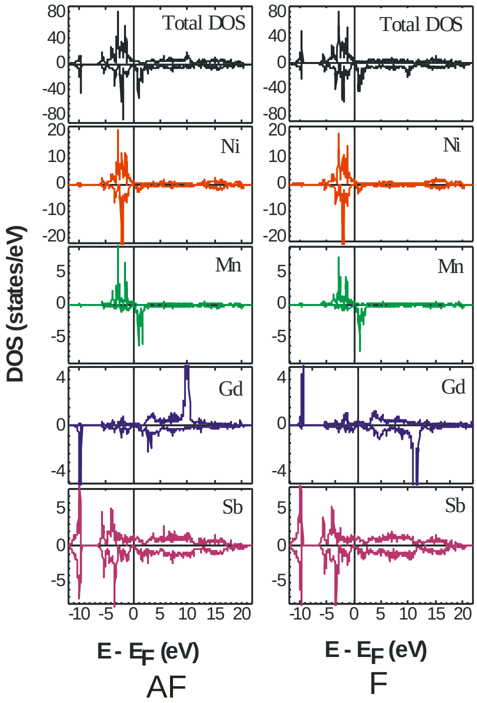

Fig. 2. Densities of states for Ni_8Mn_7GdSb in case of antiferromagnetic respectively ferromagnetic coupling.

The calculated densities of states, (DOS), for $Ni_8Mn_7GdSb_8$ are presented in Fig. 2. It was considered a ferromagnetic (F) respectively antiferromagnetic, (AF), coupling of Gd (*4f*) and Mn (*3d*) spins. The analysis of the band structures of the doped alloy shows that the half-metallic properties are completely conserved if gadolinium atoms substitute the manganese ones. This effect is determined by the coupling between the Gd (*4f*) spin and the Mn (*3d*) itinerant electron spins. The half-metallic state is stable in both cases with a band gap of 0.42 eV magnitude in case of F coupling and 0.46 eV for AF coupling, comparable with the value of 0.5 eV found in NiMnSb. The obtained values of the gap in the minority band are in good agreement with the experimental value obtained for NiMnSb by Kirillova *et. al.* who, analyzing their infrared spectra, estimated a gap of aprox. 0.4 eV [20]. The Fermi level is located at the right edge in the case of AF coupling and at the left edge in the case of F coupling of the spin-down gap. The DOS are mainly characterized by the large exchange spitting of the Mn d states, which is around 3 eV. As a result of this large exchange splitting, large localized spin moments appear on the Mn site. It was proposed that the localization comes from the fact that although *d* electrons are itinerant, the spin-down electrons are almost excluded from the Mn site [21,22].

The origin of the gap can be attributed to the covalent hybridization between the lower energy *d* state of the high valent transition metal atom (Ni) and the higher energy d states of the lower valent transition metal atom (Mn), which leads to the formation of bonding and antibonding bands with a gap in between. The minority occupied bonding d states are mainly of Ni character and the unoccupied antibonding states are mainly of Mn character. These structures are stable when the bonding states are occupied. On the other hand Sb plays an important role for the existence of these alloys with a gap at the Fermi level. The Mn and Sb atoms are second neighbors and their hybridization is weaker compared to the Mn-Ni hybridization which are first order neighbors. The Gd contribution is more important in the polarization of the itinerant 3d Mn electrons [6,8].

Table 1. The average calculated magnetic moments for $Ni_8Mn_{8-X}Gd_XSb_8$.

X; coupling	0	1; AF	1; F
M (Ni) (μ_B/atom)	-0.28	-0.234	-0.206
M (Mn) (μ_B/atom)	-3.748	-3.798	-3.784
M (Gd) (μ_B/atom)	-	7.214	-7.061
M (Sb) (μ_B/atom)	0.068	0.060	0.059
M (void) (μ_B/atom)	-0.04	-0.029	-0.043

In the pure NiMnSb compound the ferromagnetic Curie temperature (T_C=730 K) represents the strength of the intra Mn(3*d*-3*d*) sublattice interactions. Considering the small Gd content we expect that the strength of the intra Mn(3*d*-3*d*) sublattice interaction in $NiMn_{1-X}Gd_XSb$ is slightly changed in comparison with the pure NiMnSb compound. The substitutions introduce the competition between the intra and inter sublattice interactions. We evaluate the strength of this coupling by calculating, in an ab-initio fashion, the total energy of the $Ni_8Mn_7GdSb_8$ compound for a parallel and antiparallel *f–d* coupling. Given the geometry of the cell, the lanthanide substitution is realized in the fcc–Mn sublattice, so 12 pairs of Gd (*4f*)–Mn (*3d*) are formed. As a consequence the *f–d* coupling constant was calculated as the $E_{Ferro}–E_{Antiferro}$ energy corresponding to a pair and has the value of 54 K for U=12 eV and J=0.9 eV. One can see that the minimum energy is, in the case of an antiparallel coupling between Mn(3*d*) and Gd(4*f*) spins, as it is expected for heavy rare-earth-3*d* transition metal compounds [23]. We expect that at temperatures lower than that calculated for the exchange coupling, the gadolinium substitution could affect the magnonic excitations leaving the half metallic gap unmodified [6,14,16].

The average calculated atomic magnetic moments for the pure compound and data obtained for the Gd-doped sample are presented in Table 1. A small modification of the magnetic moments was found as a result of doping. The calculated magnetic moments are 4.00 μ_B/f.u.

(NiMnSb) and 2.62 μ_B/f.u. (AF coupling), respectively 4.38 μ_B/f.u. (F coupling) for $NiMn_{0.875}Gd_{0.125}Si$ compound.

The XPS core level spectra give information on the electrons binding energies and thus are directly correlated to the chemical environments of the ions. The Gd 4*d* and Sb 4*s* core level spectrum of $NiMn_{0.95}Gd_{0.05}Sb$, recorded between 138 eV and 165 eV binding energy, are presented in Fig. 3.

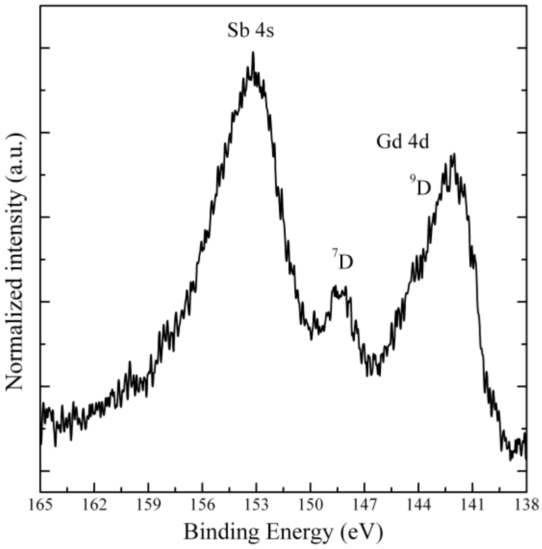

Fig. 3. XPS Gd 4d and Sb 4s core level spectra of $NiMn_{0.95}Gd_{0.05}Sb$.

The main spectral features arise from multiplet splitting of the Gd 4*d* hole with the $4f^7$ valence electrons to form ^{9}D and ^{7}D final ionic states [24,25]. The Gd ^{9}D multiplet is situated at about 142.1 eV, at higher binding energy than in pure Gd (~140.4 eV) and lower than in Gd_2O_3 (~143.5 eV), which indicates that the Gd atoms occupy atomic positions in the NiMnSb cell. The width of the Sb 4*s* core level, situated at higher binding energy (~153.2 eV), is close to the width of the Gd 4*d* main line and thus the concentration of Gd atoms in the sample can be estimated from the relative intensities of the two peaks. After taking into account the different cross sections of the Gd 4*d* and Sb 4*s* levels for the AlKα radiation [26], we calculated that 6 % of the Mn atoms are substituted by Gd atoms. This is in good agreement with the starting stoichiometric proportions of the constituent elements.

The Ni 2*p* XPS spectra of pure metallic Ni and investigated alloys are shown in Fig. 4. The presence of satellites in the Ni 2*p* core level spectra, at about 6.5 eV higher binding energy than the main lines, implies the presence of *d* character in the unoccupied bands. The intensity of the satellite in $NiMn_{1-X}Gd_XSb$ compounds is much smaller than in pure Ni, which indicates that the Ni 3*d* band is almost full and the Stoner criterion for the existence of a magnetic moment on Ni sites is no more fulfilled.

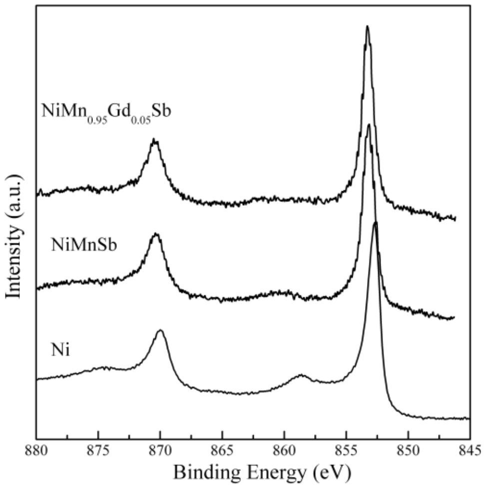

Fig. 4. Ni 2p XPS spectra of $NiMn_{0.95}Gd_{0.05}Sb$, MnNiSb and metallic Ni.

The XPS valence band spectra of $NiMn_{0.95}Gd_{0.05}Sb$ and NiMnSb are presented in Fig. 5.

At Al K_α radiation, the Ni 3*d* cross section is about four times larger than the Mn 3*d* cross section [26], thus the XPS valence-band spectra of $NiMn_{0.95}R_{0.05}Sb$ alloys are dominated by the Ni 3*d* states. The Mn 3*d* states are concentrated at the bottom of the valence band in the region around the 3 eV binding energy, as proved by band structure calculations.

The spectral feature situated at about 10–11 eV, present in both investigated alloys, is assigned to the Sb 5*s* states. The main difference between the valence band spectra of $NiMn_{0.95}Gd_{0.05}Sb$ and NiMnSb is between 7.5 eV and 10 eV due to presence of the Gd 4*f* states. The binding energy of the Gd 4*f* core level, found by subtracting the normalized XPS valence band spectra of NiMnSb from the normalized spectra of $NiMn_{0.95}Gd_{0.05}Sb$, is ~ 9 eV. This value is higher then in metallic Gd, confirming that the Gd atoms substitute Mn atoms in NiMnSb.

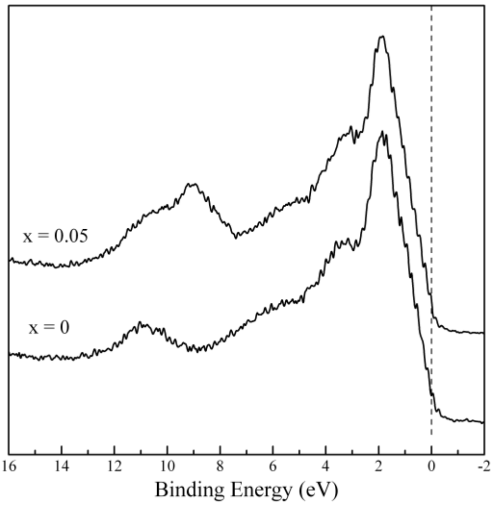

Fig. 5. XPS valence band spectra of $NiMn_{1-X}Gd_XSb$ compounds.

4 Conclusions

In this paper we have studied the structural and electronic properties of $NiMn_{1-X}Gd_XSb$ compounds. From band structure calculations it was shown that the half metallic character is not affected by alloying. XRD and XPS measurements confirm that gadolinium occupies lattice sites. The antiferromagnetic alignment of Mn and Gd magnetic moments is more favourable. Further investigations will be done in order to investigate the complex behaviour of these materials.

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References

[1] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, D. M. Treger, Science **294**, 1448 (2001).
[2] C. M. Fang, G. A. de Wijs, R. A. de Groot, J. Appl. Phys. **91**, 8340 (2002).
[3] R. A. de Groot, F. M. Mueller, P. G. van Engen, K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).
[4] V. Yu. Irkhin, M. I. Katsnelson, Phys. Usp. **37**, 659 (1994); J. Phys.: Condens. Matter **2**, 7151 (1990).
[5] W. E. Pickett, J. Moodera, Phys. Today **54**, 39 (2001).
[6] M. I. Katsnelson, V. Yu. Irkhin, L. Chioncel, A. I. Lichtestein, R. A. de Groot, Rev. Mod. Phys **80**, 315 (2008).
[7] G.A. Prinz, Science **282**, 1660 (1998).
[8] A. Yamasaki, L. Chioncel, A. I. Lichtenstein, O. K. Andersen, Phys. Rev. B **74**, 024419 (2006).
[9] S. Öğüt, K. M. Rabe, Phys. Rev. B **51**, 10443 (1995).
[10] I. Galanakis, P. H. Dederichs, N. Papanikolaou, Phys. Rev. B **66**, 134428 (2002).
[11] E. Kulatov, I. I. Mazin, J. Phys.: Condens. Matter **2**, 343 (2003).
[12] B. R. K. Nanda, I. Dasgupta, J. Phys.: Condens. Matter **15**, 7307 (2003).
[13] I. Galanakis, P. Mavropoulos, J. Phys.: Condens. Matter **19**, 315213 (2007).
[14] J. J. Attema, C. M. Fang, L. Chioncel, G. A. deWijs, A. I. Lichtenstein, R. A. de Groot, J. Phys.: Condens. Matter **16** S5517–S5524 (2004).
[15] Steven G. Louie, APS March Meeting (2006).
[16] E. Burzo, I. Balazs, L. Chioncel, E. Arrigoni, F. Beiuseanu, Phys. Rev. B **80**, 214422 (2009).
[17] M. I. Katsnelson, A. I. Lichtenstein, Eur. Phys. J. B **30**, 9 (2002).
[18] L. Chioncel, M. I. Katsnelson, R. A. de Groot, A. I. Lichtenstein, Phys. Rev. B **68**, 144425 (2003).
[19] V. I. Anisimov, P. Aryasetiawan, A. I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).
[20] M. M. Kirillova, A. A. Makhnev, E. I. Shreder, V. P. Dyakina, N. B. Gorina, Phys. Status Solidi B **187**, 231 (1995).
[21] I. Galanakis, P. H. Dederichs, N. Papanikolaou, Phys. Rev. B **66**, 134428 (2002).
[22] M. V. Yablonskikh, Yu. M. Yarmoshenko, V. I. Grebnnikov, E. Z. Kurmaev, S. M. Butorin, L. C. Duda, J. Nordgren, S. Plogmann, M. Neumann, Phys. Rev. B **63**, 235117 (2001).
[23] E. Burzo, A. Chelkovski, H. R. Kirchmayr, Landolt Bornstein Handbook, Springer, Berlin, vol III/19d2 (1990).
[24] G. van der Laan, E. Arenholz, E. Navas, A. Bauer, G. Kaindl, Phys. Rev. B **53**, R5998 (1996).
[25] W. J. Lademan, A. K. See, L. E. Klebanoff, G. van der Laan, Phys. Rev. B **54**, 17191 (1996).
[26] J. Yeh, I. Lindau, At. Data Nucl. Tables **32**, 1 (1985).

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