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XPS ON $Mn_{0.95}Dy_{0.05}NiSb$ HEUSLER ALLOY

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ABSTRACT. XPS results on $Mn_{0.95}Dy_{0.05}NiSb$ Heusler alloy are presented. The compound is single phase with a *C*1*b* type cubic structure. All the experimental results suggest that the rare earth atoms entered in the lattice and they are not forming second phases. An exchange splitting of Mn 3s core-level spectrum of about 4.6 eV was shown, giving a direct evidence of the local magnetic moments on Mn sites. The Ni 3d states are giving the major contribution to the XPS valence band spectra. The Ni 3d satellite peak situated around 6 eV was attributed to the fact that the Ni 3d states in the valence band are not fully occupied. However, the Ni 3d band is almost full in this alloy and the Stoner criterion for the existence of a magnetic moment on Ni sites is no longer fulfilled.

Keywords: *Heusler alloys, X-ray photoelectron spectroscopy, valence band spectra.*

INTRODUCTION

Half metallicity was predicted by de Groot and his collaborators in a pioneering paper published in 1983 for the Heusler alloy MnNiSb [1]. These materials present a metallic behavior for one spin band and a semiconducting one for the opposite spin band. 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

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three interpenetrating fcc lattices of Ni, Mn, and Sb. It was shown that in order to obtain the minority spin gap it is necessary to take into account the Mn-*d*-Sb-*p* and Mn-*d*-Ni-*d* interactions. 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 [1-8]. 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 [9]. 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 [9]. 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 holmium.

In this paper we have investigated the effect of Dy substitution for Mn on the physical properties of NiMnSb compounds. X-ray diffraction and X-ray photoelectron spectroscopy (XPS) were used to characterize the samples. From the experimental data we concluded that the heavy rare-earth atoms have entered in the C1*b* structure.

EXPERIMENTAL

The $Mn_{0.95}Dy_{0.05}NiSb$ compound was prepared by arc melting of the constituent elements in a purified argon atmosphere using high purity Ni (99.8%), Mn (99.9%), Sb (99.999%) and Dy (99.95%) ingots (Alfa Aesar, Jonson & Matthey, Karlsruhe, Germany). The ingots were turned around and remelted up to 10 times. The samples were sealed in tantalum foil and heat treated in vacuum at 1000 ºC for 5 days. The crystal structure of the studied samples was checked by X-ray Diffraction using a Bruker 8 XD diffractometer at the Ioan Ursu Institute Cluj Napoca. XPS spectra were recorded at room temperature using a SPECS Multifunctional surface analysis system with monochromatized Al Kα radiation, located at Osnabrueck University.

The pressure in the ultra-high vacuum chamber was in the 10^{-10} mbar range. In order to avoid the surface contamination, the sample was crushed in situ and the surface cleanness was checked by monitoring the oxygen and carbon 1s core levels. It was found that the contamination was almost absent, so we can conclude that the XPS spectra are representative of the bulk.

In Fig.1 the survey spectra of the $Mn_{0.95}Dy_{0.05}NiSb$ is presented.

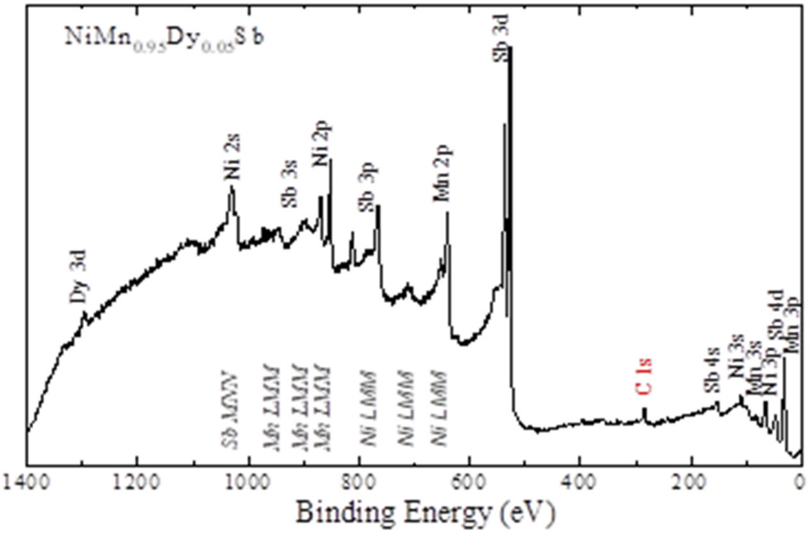

Fig. 1. XPS survey spectra of $Mn_{0.95}Dy_{0.05}NiSb$.

One can see that the sample is not oxidated, since the oxygen O 1s core level (around 531 eV) was almost absent. The small C 1s core line indicates the low level of sample contamination.

RESULTS AND DISCUSSIONS

The X-ray diffraction analysis show, in the limit of experimental errors, that the compound is single phase with a *C*1*b* type cubic structure (space group $F\bar{4}3m$). The lattice parameter was found to be 0.594(3) nm, somewhat higher than that of the pure compound (0.593(1) nm [10]). This small increase could be explained by the higher radius of Dy ion compared to Mn ion.

XPS core level and valence band spectra provide important information on the electronic structure of 3d transition metal alloys and compounds. Multiplet splitting and satellite emission in the core-level photoelectron spectra represent the interaction between the core hole and the valence electrons and are related to the electronic structure of the bound atoms. The localization or delocalization of the 3d valence electrons, screening, and charge transfer processes can influence the core-level photoelectron spectra. The multiplet splitting of the XPS core levels show the existence of localized magnetic moments of transition metals ions. The splitting of the Mn 3*s* core level in MnNiSb and $Mn_{0.95}Dy_{0.05}NiSb$ is presented in Fig. 2. The Mn 3s core-level spectra show an exchange splitting of about 4.6 eV, arising from the exchange interaction between the core hole and open 3d shell. A high-spin density of the 3d electrons on Mn sites is revealed by the high value of the energy separation and proof the existence of localized magnetic moments confined on Mn sites.

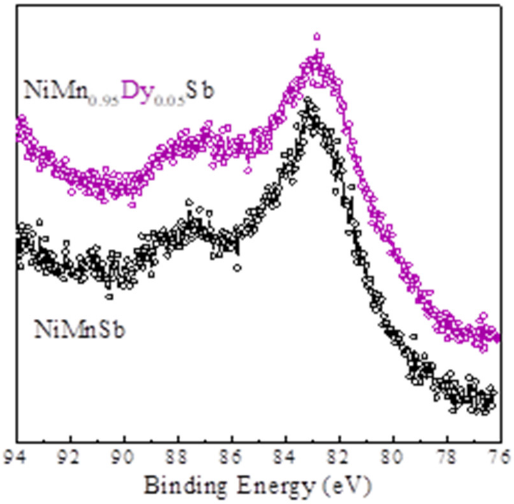

Fig. 2. XPS Mn 3s core level spectra of $Mn_{0.95}Dy_{0.05}NiSb$ and MnNiSb

The Ni 2p XPS spectra for $Mn_{0.95}Dy_{0.05}NiSb$ alloy are shown in Fig. 3.

The Ni 2p spectra in NiMnSb and in metallic Ni are also plotted. A satellite in the Ni 2p core level spectra, at about 6.5 eV higher binding energy than the main lines can be observed, suggesting the *d* character in the unoccupied bands. The intensity of this satellite in both investigated compounds is much smaller than in pure Ni. This show that, in these alloys, the Ni 3d band is almost full and the Stoner criterion for the existence of a magnetic moment on Ni sites is no longer fulfilled.

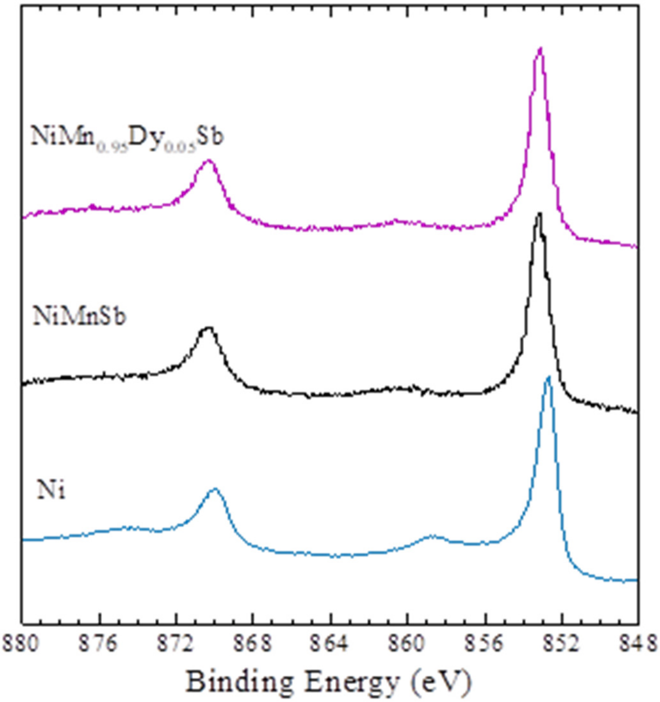

Fig. 3. Ni 2p XPS spectra of Ni, NiMnSb and $Mn_{0.95}Dy_{0.05}NiSb$ alloys

The core-level spectra in the region of Sb 4s and Dy 4d binding energies are presented in Fig. 4. Information about the atomic bonding can be subtracted from here by extracting the binding energies of the Dy atom at the 4d core shell, comparing with the values in pure metals and in oxides from Handbook of X-Ray Photoemission Spectroscopy (HXPS). The 4f binding energy was found to be 9 eV and 4d binding energy 155 eV. The experimentally determined binding energies, in the region of 4f and 4d core shells, are different from that of the pure element (8 eV and 152 eV from HXPS) or it's oxide (168 eV in Dy_2O_3 according to HXPS). These results allow us to conclude that the rare earth element occupies a lattice position in the $Mn_{0.95}Dy_{0.05}NiSb$ alloy.

The Dy concentration alloys in $Mn_{0.95}Dy_{0.05}NiSb$ alloy was calculated considering the intensity ratio of the Sb 4s and the Dy 4f peaks. The calculated values of the concentrations are presented in Table 1. One can see that the experimentally determined intensities are in a quiet good agreement with the theoretical ones, which means, that in the limit of the experimental errors, the rare earth elements entered in the composition of the $Mn_{0.95}Dy_{0.05}NiSb$ alloy.

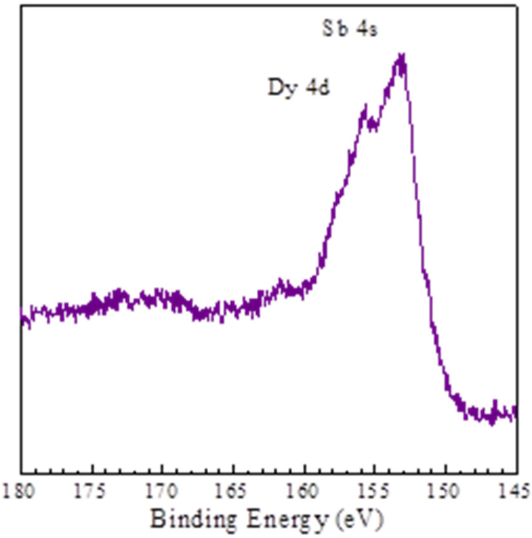

Fig. 4. Core-level spectra in the region of Sb 4s and Dy 4d binding energies

Table. 1. The calculated concentration of Sb and Dy in $Mn_{0.95}Dy_{0.05}NiSb$.

Core level	Cross section	Concentration	Theoretical int.	Exp. Int.
Sb 4s	0.011	1.00	1.00	1.00
Dy 4d	0.140	0.05	0.71	0.60

The XPS spectra of the valence band region of $Mn_{0.95}Dy_{0.05}NiSb$ compared with MnNiSb alloy is shown in Fig. 5.

The Ni 3d states are giving the major contribution to the XPS valence band spectra, the typical feature being around 1 eV. One can see that this feature is not shifted. It was expected that this feature will give the main contribution, considering that the Ni 3d cross section for Al Kα radiation is about four times larger than the Mn 3d cross section situated at about ~2.8 eV. The peak at around ~6 eV is a satellite feature of the Ni 3d. These satellite features can be attributed to the fact that the Ni 3d states in the valence band are not fully occupied. The main difference between the valence band spectra of $Mn_{0.95}Dy_{0.05}NiSb$ and NiMnSb is between 8.5 eV and 10.5 eV, due to the Dy 4f states contribution. By subtracting the normalized XPS valence band spectra of NiMnSb, from the normalized spectra of $Mn_{0.95}Dy_{0.05}NiSb$, it was found that the binding energy of the Dy 4f core level is around 9.5 eV at higher binding energy than in metallic rare earth (inset of Fig. 5). We can conclude that the Dy atoms occupy atomic positions in the NiMnSb cell. The peak at around ~10-11 eV is also present in all investigated alloys and is assigned to the Sb 5s states.

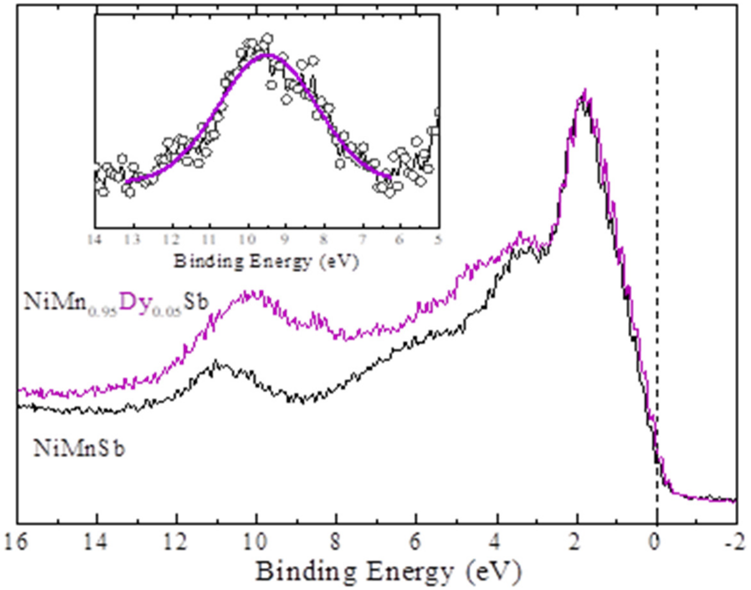

Fig. 5. XPS valence band spectra of NiMnSb and $Mn_{0.95}Dy_{0.05}NiSb$ alloys

CONCLUSIONS

XPS results on $Mn_{0.95}Dy_{0.05}NiSb$ Heusler alloy are presented. The prepared compound is single phase with a *C*1*b* type cubic structure. The survey spectra of the $Mn_{0.95}Dy_{0.05}NiSb$ confirm that the sample is not oxidated or contaminated.

An exchange splitting of Mn 3s core-level spectrum of about 4.6 eV was shown. The high value of the energy separation indicates a high-spin density of the 3d electrons on Mn sites and proof the existence of localized magnetic moments confined on Mn sites.

A satellite in the Ni 2p core level spectra, at about 6.5 eV higher binding energy than the main lines is shown, suggesting the *d* character in the unoccupied bands. The intensity of this satellite in parent and doped compounds is much smaller than in pure Ni showing that the Ni 3d band is almost full and the Stoner criterion for the existence of a magnetic moment on Ni sites is no longer fulfilled.

The experimentally determined binding energies, in the region of 4f and 4d core shells, are different from that of the pure element or it's oxides. These results allow us to conclude that the rare earth element occupies a lattice position in the $Mn_{0.95}Dy_{0.05}NiSb$ alloy.

The valence-band is dominated by the Ni 3d states. The Ni satellite is separated by approximately 6 eV from the centroids of the valence bands and can be attributed to the presence of the d character in the unoccupied bands. The main difference between the valence band spectra of $Mn_{0.95}Dy_{0.05}NiSb$ and NiMnSb is between 8.5 eV and 10.5 eV, due to the Dy 4f states contribution.

All the experimental results suggest that the rare earth ions occupy atomic positions in the lattice and they are not forming secondary phases.

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