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X-ray photoelectron spectroscopy and magnetism of $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$

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X-ray photoelectron spectroscopy (XPS), magnetization and magnetic susceptibility of $Mn_{1-x}Al_xNi_3$ (x=0.5, 0.7) alloys are reported. The Ni *2p* core level and the valence band spectra of $AlMnNi_6 \equiv Al_{0.5}Mn_{0.5}Ni_3$ and $Al_7Mn_3Ni_{30} \equiv Al_{0.7}Mn_{0.3}Ni_3$ exhibit satellites at ~6.5 eV higher binding energy than the main line, indicating the presence of *d* character in the unoccupied bands. Furthermore, the density of states at the Fermi level in both alloys is smaller than in the metallic Ni, suggesting a partial filling of the Ni *3d* band. The magnetization values and its variation with magnetic field and temperature suggest that both alloys have a ferromagnetic behavior below the Curie temperatures 432 K and 361 K for $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$, respectively. The results infer the existence of local magnetic moments on Mn and Ni sites in the investigated alloys. The correlation of magnetic data in the ordered and paramagnetic states can be explained if we consider spin fluctuations on Ni sites.

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1. Introduction

The problem of local moments confined to the transition metals sites, i.e., localized behaviour in some aspects of itinerant electrons, is one of the most important issues in the physics of the magnetic alloys and intermetallic compounds. Experimentally it was demonstrated that under certain conditions the magnetic moment of a transition metal remains localized when solute in another transition metal. The condition for the existence of the local moment at the T site is $\pi\Delta / U < 1$, where Δ is the width of the *d* states (corresponds to the virtual bound states in the Friedel's model [1]) and U is the Coulomb correlation energy between d electrons [2].

The aim of this paper is to investigate the effects of the substitution of Al for Mn in the $MnNi_3$ compound on the magnetic properties and electronic structure. Previous structural and neutron diffraction studies have shown that the intermetallic compound $MnNi_3$ crystallizes in the cubic $AuCu_3$ structure type, with the lattice parameter a=3.5 Å. This compound orders ferromagnetically with the Curie temperature and a Mn magnetic moment of about 400 K and 3.2 μ_B, respectively [3]. These studies revealed also the existence of magnetic moments on the Ni sites ($\cong$ 0.3 μ_B) and the participation of these atoms in the magnetic exchange interactions in this compound.

2. Experimental

The samples were prepared from the constituent elements by argon arc melting. In order to obtain homogeneity, the samples were re-melted several times in the same atmosphere. High purity metals have been used for the compounds preparation (99.999% for Al, 99.99% for Mn and 99.99+% in case of Ni). X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance diffractometer. XRD measurements showed that both samples are single phases with the same structure type as the parent compound $MnNi_3$. In Fig. 1 are shown the XRD patterns for the two samples.

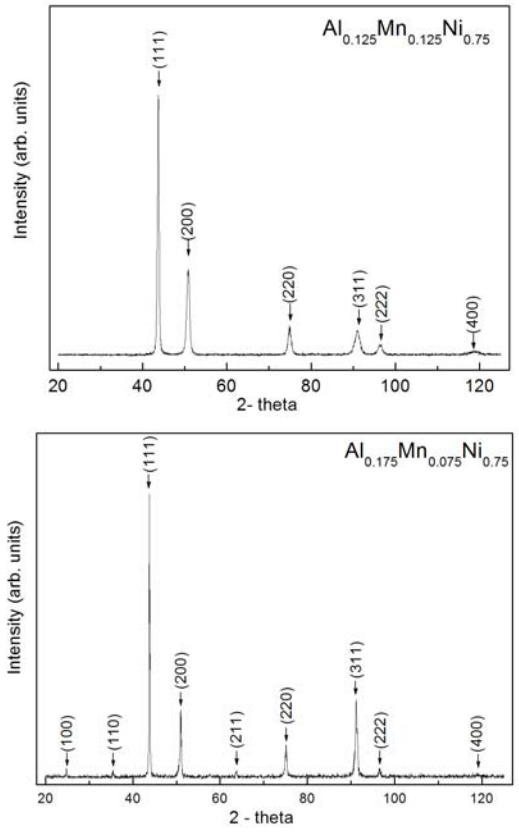

Fig. 1. X-ray diffraction pattern of $AlMnNi_6 \equiv Al_{0.125}Mn_{0.125}Ni_{0.75}$ and $Al_7Mn_3Ni_{30} \equiv Al_{0.175}Mn_{0.075}Ni_{0.75}$.

Rietveld analysis suggest a cubic $AuCu_3$ crystalline structure type with the lattice parameter a = 3.579 Å for $AlMnNi_6$ and a = 3.577 Å for $Al_7Mn_3Ni_{30}$. The lattice parameters are in agreement with those reported in the literature [4, 5]. The elementary cell of the investigated alloys is shown in Fig. 2. Ni atoms have in the first vicinity eight Ni atoms and four M atoms (M=0.5Al+0.5Mn for $AlMnNi_6$ and M=0.7Al+0.3Mn for $Al_7Mn_3Ni_{30}$) situated at 2.531Å for $AlMnNi_6$ and 2.529 Å for $Al_7Mn_3Ni_{30}$. The Ni-Ni distances d=2.531 Å for $AlMnNi_6$ and d=2.529 Å for $Al_7Mn_3Ni_{30}$ are very close to the one in pure metallic Ni.

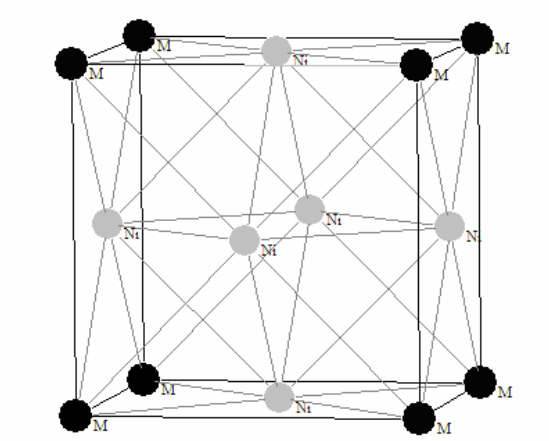

Fig. 2. Elementary cell of the investigated alloys.

The magnetization measurements were performed using a vibrating sample magnetometer in the temperature range 4.2-450 K and fields up to 9 kOe. The variation of the magnetic susceptibility with the temperature was obtained using a Weiss balance in the 300-700 K temperature range.

The XPS spectra were recorded using a PHI 5600ci ESCA spectrometer with monochromatized Al Kα radiation at room temperature. The pressure in the ultra-high vacuum chamber was in the 10^{-10} mbar range during the measurements. The samples were cleaved in situ. The surface cleanness was checked by monitoring the O *1s* and C *1s* core levels in the survey spectra.

3. Results

3.1. Magnetic measurements

The temperature dependence of the spontaneous magnetization is shown for both compounds in Fig. 3. The values and variations of magnetization of $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$ with magnetic field and temperature suggest that both alloys have a ferromagnetic behavior below the Curie temperatures 432 K and 361 K, respectively, determined from the usual Arrot plots. The spontaneous magnetizations extrapolated to 0 K have the values 3.73 μ_B/f.u. for $AlMnNi_6$ and 14.2 μ_B/f.u. for $Al_7Mn_3Ni_{30}$.

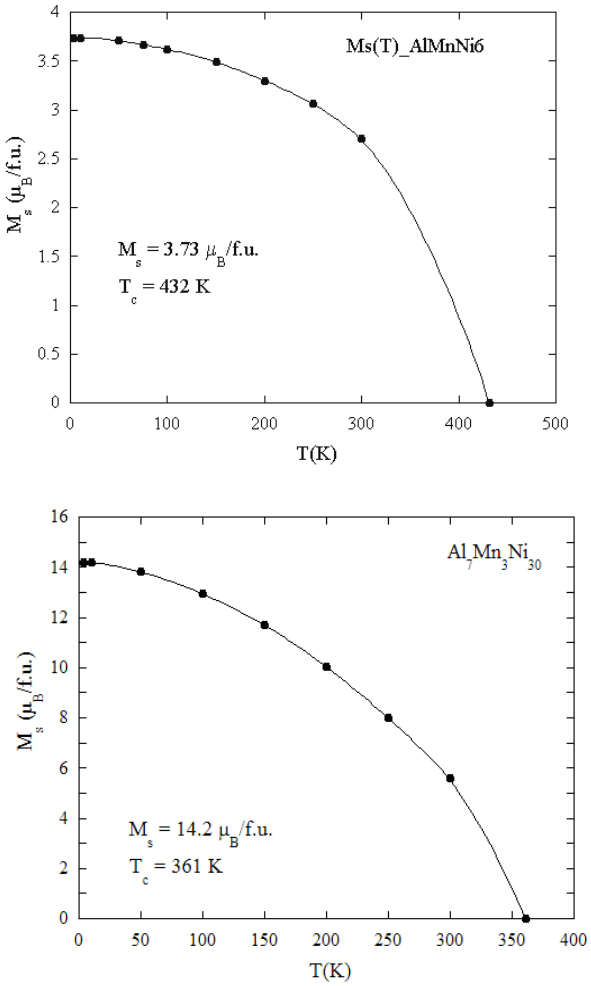

Fig. 3. Temperature dependence of spontaneous magnetization for $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$.

In the temperature range 300-700 K, the magnetic susceptibilities obey the Curie-Weiss law, $\chi = C / (T-\theta)$, with the paramagnetic Curie temperatures θ = 524K for $AlMnNi_6$ and θ = 398 K for $Al_7Mn_3Ni_{30}$. The effective magnetic moments, determined from the Curie constants, have the values 5.18 μ_B/f.u. for $AlMnNi_6$ and 8.3 μ_B/f.u. for $Al_7Mn_3Ni_{30}$.

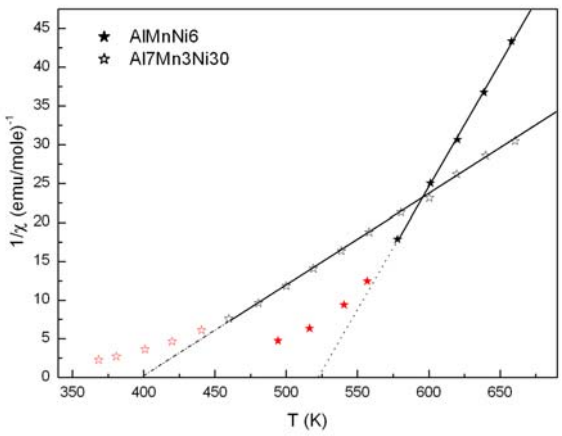

Fig. 4. Reciprocal susceptibility versus temperature for $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$.

3.2. XPS measurements

To illustrate the quality of the samples in Fig. 5 is shown the survey spectrum of $AlMnNi_6$, with the identification of the main lines.

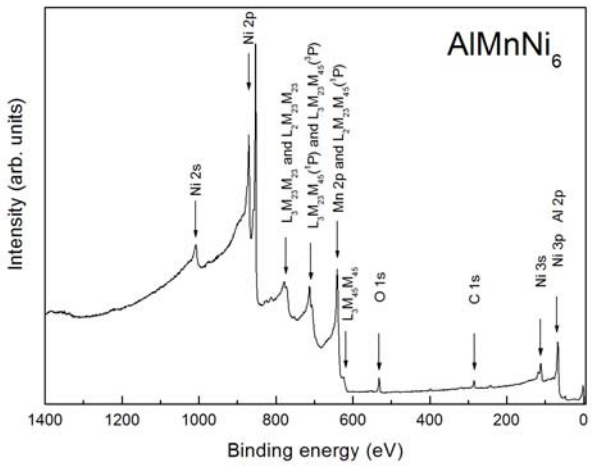

Fig. 5. Survey spectra for $AlMnNi_6$.

The Ni 2p XPS spectra for $AlMnNi_6$, $Al_7Mn_3Ni_{30}$ and pure metallic Ni are shown in Fig. 6.

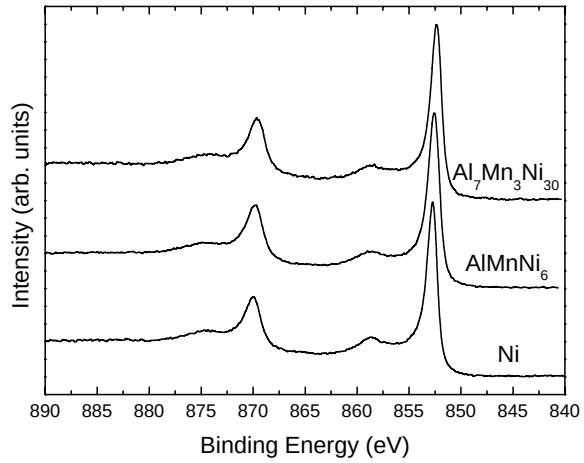

Fig. 6. Ni 2p XPS spectra of $AlMnNi_6$, $Al_7Mn_3Ni_{30}$ and metallic Ni.

Like in the case of pure metallic Ni, the Ni *2p* core level spectra of $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$ exhibit satellite structures at about 6.5 eV higher binding energy than the main line. The observation of satellites implies the presence of *d* character in the unoccupied bands. By comparing the Ni *2p* core level spectra of $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$ to the one of metallic Ni, a decrease in Ni satellite intensity can be observed, which is attributed to the partial filling of the Ni *3d* band.

The XPS valence band spectra of the investigated alloys and pure Ni are shown in Fig. 7.

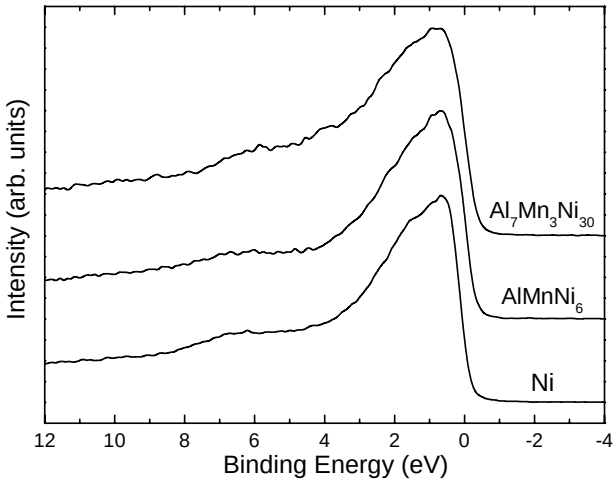

Fig. 7. XPS valence band spectra of pure Ni, $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$.

The Ni *3d* cross section for Al K_α radiation is about four times larger than the Mn *3d* cross section, i.e., the valence-bands of $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$ are dominated by the Ni *3d* states. All the valence bands spectra exhibit the Ni satellite separated by approximately 6 eV from the centroids of the valence bands. The density of states at the Fermi level in both alloys is smaller than in the pure metallic Ni.

4. Discussion

The Ni *2p* core level and valence band spectra of both alloys give clear evidence of partial filling of the Ni *3d* band, which is attributed to hybridizations between the *3d* Ni and *3sp* Al states. The correlation of XPS data and magnetic measurements for ordered and paramagnetic states suggest the existence of local magnetic moments at the Mn and Ni sites in $Mn_{1-x}Al_xNi_3$ alloys. The magnetic moment per Ni atom in Ni-Al alloys decreases linearly with the Al content in the range of solid solubility [6]. The compound $AlNi_3$, which has the same crystalline structure as $MnNi_3$, is known as a spin fluctuation system and has the 3d band almost filled with $\mu=0.075\mu_B$/Ni [7]. Taking into account that $MnNi_3$, $Al_{0.5}Mn_{0.5}Ni_3$, $Al_{0.7}Mn_{0.3}Ni_3$ and $AlNi_3$ have the same crystallographic structure, we assumed that the magnetic moment per Ni atom decreases linearly with the Al content. Starting from the known values for $MnNi_3$ and $AlNi_3$, the magnetic moment per Ni atom, in the ordered state, for our alloys, was estimated to be $\mu=0.19\mu_B$/Ni for $AlMnNi_6$ and $\mu=0.14\mu_B$/Ni for $Al_7Mn_3Ni_{30}$. The correlation of these values with the experimental data obtained from the magnetization measurements lead to the following values for the magnetic moments and the effective magnetic moments per Mn atom: μ = 2.6 μ_B/Mn and μ_{eff} = 3.46 μ_B/Mn for $AlMnNi_6$ and respectively μ = 3.3 μ_B/Mn and μ_{eff} = 4.18 μ_B/Mn for $Al_7Mn_3Ni_{30}$. The effective magnetic moment per Ni atom determined from the Curie constant is 1.57 μ_B/Ni for $AlMnNi_6$ and 0.74 μ_B/Ni for $Al_7Mn_3Ni_{30}$, considering the previous estimated values for the effective

magnetic moments per Mn atom. We may explain the contribution of Ni atoms to the measured susceptibility in both alloys in terms of the self-consistent renormalization theory of spin fluctuations [8]. This theory has revealed that only a small-q part of the wave-number-dependent susceptibility χ_q contributes to the temperature dependence of χ in nearly ferromagnetic metals (exchange-enhanced Pauli paramagnets). The average amplitude of the local spin fluctuations on Ni sites $< S_L^2 >= 3k_B T \sum_q \chi_q$ increases with temperature until it reaches an upper limit determined by the charge neutrality condition. The temperature dependence of χ at low temperatures is the result of the increase of local moments with increasing temperature. The amplitude $< S_L^2 >$ of thermally excited longitudinal spin fluctuations saturates at certain temperature T* above which the susceptibility is governed by local moment type fluctuations and therefore a Curie-Weiss behavior is observed.

5. Conclusions

The substitution of Mn by Al in $MnNi_3$ in the range of solid solubility leads to no significant changes in the crystallographic structure, but has significant effect on the magnetic properties and electronic structure of the two investigated alloys. The hybridization between the *3d* Ni and *3sp* Al states leads to an incomplete filling of the Ni *3d* band, as indicated by the XPS core level and valence band spectra. The magnetic properties of $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$ alloys are dominated by the local magnetic moments on Mn sites, the Ni magnetic moments having a key role in the magnetic interactions between the magnetic atoms. The investigated alloys, $AlMnNi_6$ and $Al_7Mn_3Ni_{30,}$ order ferromagnetically as the parent compound MnNi3, with different values for Curie temperatures, paramagnetic Curie temperatures and magnetic moments on Mn and Ni sites. The temperature dependence of the reciprocal susceptibility for $AlMnNi_6$ and $Al_7Mn_3Ni_{30}$ alloys could be explained in terms of the self-consistent renormalization theory of spin fluctuations.

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