X-RAY PHOTOELECTRON SPECTROSCOPY AND MAGNETISM OF Al_2MnNi AND $Al_5Mn_3Ni_2$

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Abstract

The electronic and magnetic properties of Al_2MnNi and $Al_5Mn_3Ni_2$ alloys, obtained from X–ray photoelectron spectroscopy and magnetic measurements, are reported. The most important feature of the XPS spectra is the well-defined magnetic exchange splitting of about 5 eV of the Mn *3s* core levels of both alloys, arising from the exchange interactions between the core hole and open *3d* shell, giving a clear evidence of the existence of local moments in the Anderson's sense confined on Mn sites in Al-Mn-Ni alloys. For both alloys the Mn and Ni *3d* bands are filled by more than half, which leads to a ferromagnetic coupling between the neighboring local magnetic moments situated at Mn and Ni sites. By correlating the information from the XPS core level spectra and magnetic measurements in the ordered and paramagnetic states, the magnetic behavior of Al_2MnNi and $Al_5Mn_3Ni_2$ cannot be explained in the picture of ferromagnetic systems with a collinear arrangement of the local magnetic moments. We propose a canted ferromagnetism in the two alloys, which should be verified by further neutron diffraction investigations.

1. Introduction

The problem of local moments confined to the transition metals sites, i.e., localized behavior in some aspects of itinerant electrons, is one of the most important issues in the physics of the magnetic alloys and intermetallic compounds. It is already known that Mn-based Heusler alloys have a magnetic moment of about $\mu \approx 2.5\mu_B$-$4\mu_B$ localized at the Mn site [1]. Traditionally they are considered as ideal systems with local magnetic moments. In the phase diagram of the Al-Mn-Ni system there are three regions of solid solubility and a Heusler alloy: Ni_2MnAl. Al-Mn-Ni alloys are potential candidates to exhibit giant magnetic field induced strains [2]. The aim of this study is the investigation of local magnetic moments in Al-Mn-Ni alloys. We discuss the electronic and magnetic properties, obtained from X–ray photoelectron spectroscopy and magnetic measurements, of two alloys belonging to this system: $Al_2MnNi \equiv Al_{0.50}Mn_{0.25}Ni_{0.25}$ and $Al_5Mn_3Ni_2 \equiv Al_{0.50}Mn_{0.30}Ni_{0.20}$. These two alloys crystallize into the cubic ClCs structure type (Pearson symbol cP2, space group Pm-3m) with the lattice parameters a=0.2929 nm for Al_2MnNi and a=0.294 nm for $Al_5Mn_3Ni_2$. The Wyckoff positions of Al, Mn and Ni atoms in the unit cell are 1a, 1b and 1b respectively. The most important feature of the XPS spectra is the well-defined magnetic exchange splitting of about 5 eV of the Mn *3s* core levels of both alloys. The spectral splitting of *3s* core-level in transition metals and their compounds originates from the exchange interactions between the *3s* core hole and open *3d* shell [3]. This gives a clear evidence of the existence of local moments in the Anderson's sense confined on Mn sites in Al-Mn-Ni alloys [4]. The energy separation is

proportional to the magnetic moment according to the Van Vleck theorem [5], and hence can be used to estimate the magnetic moment due to unpaired *3d* electron spins in the solid.

2. Experimental

Polycrystalline samples were prepared by arc melting technique in a cold copper crucible under an argon atmosphere. The purity of the starting materials was 99.999% for Al, 99.99% for Mn and 99.9% in case of Ni. The weight loss of the final material was found to be less than 1 %. The homogeneity of the samples was checked by conventional X-ray powder diffraction with Cu K_α radiation, using a *Bruker D8 Advance* powder diffractometer. X-ray diffraction patterns show the presence of a single phase for each sample. Fig.1 shows the XRD pattern for the two alloys.

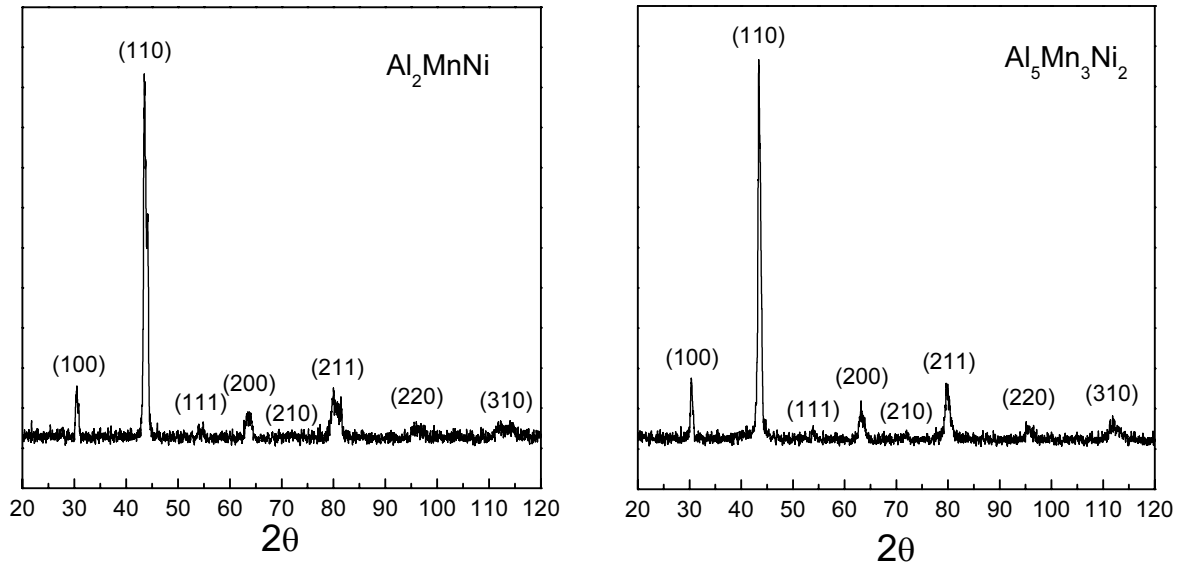

Fig. 1. X-ray diffraction pattern of Al_2MnNi and $Al_5Mn_3Ni_2$.

Rietveld analysis suggests a cubic ClCs crystalline structure type with a = 2.937 Å for $Al_5Mn_3Ni_2$ and a tetragonal crystalline structure with a = b = 2.965 Å and c = 2.929 Å for Al_2MnNi. The Mn and Ni atoms occupy the 1(b) positions, having in their first vicinity eight Al atoms situated at the 1(a) positions.

The magnetic measurements were performed with a vibrating magnetometer in the temperature range 4.2 – 850K and fields up to 90 kOe. The XPS spectra were recorded using a PHI 5600ci ESCA spectrometer with monocromatized AlK_α 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 crushed in situ. The surface cleanness was checked by monitoring the oxygen and carbon 1s levels.

3. Results and Discussions

3.1. Magnetic measurements

The temperature dependence of the spontaneous magnetization and of the reciprocal susceptibility of Al_2MnNi and $Al_5Mn_3Ni_2$ are shown in Figs. 2 and 3, respectively.

The values and variations of magnetization of Al_2MnNi and $Al_5Mn_3Ni_2$ with magnetic field and temperature suggest that both alloys have a ferromagnetic behavior below the Curie

temperatures 385K and respectively 401K, determined from the usual Arrot plots. The spontaneous magnetizations extrapolated to 0K have the values 1.53 μ_B/f.u. for Al_2MnNi and 5.03 μ_B/f.u. for $Al_5Mn_3Ni_2$.

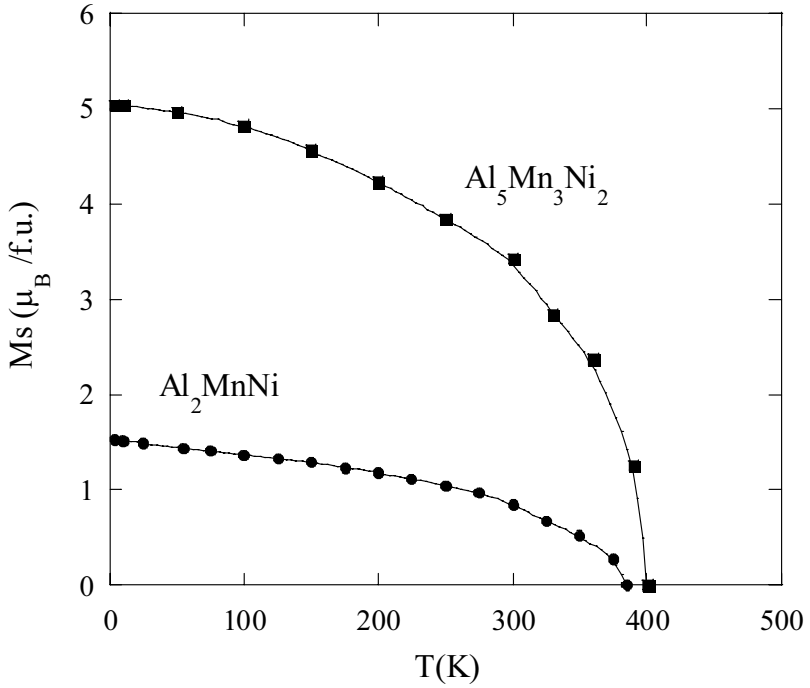

Fig. 2. Thermal variation of the spontaneous magnetization of Al_2MnNi and $Al_5Mn_3Ni_2$.

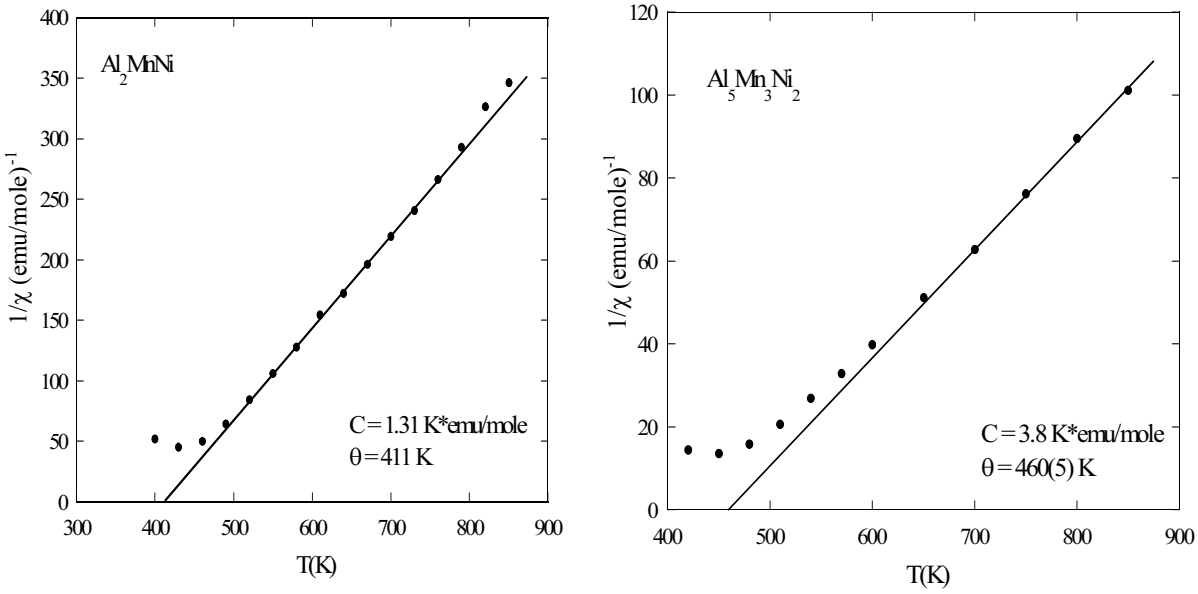

Fig. 3. Thermal variation of the reciprocal susceptibility of Al_2MnNi and $Al_5Mn_3Ni_2$

In the temperature range 300-900K, the magnetic susceptibilities obey the Curie-Weiss law, $\chi = C / (T-\theta)$, with the paramagnetic Curie temperatures $\theta = 411$K for Al_2MnNi and $\theta = 460$K for $Al_5Mn_3Ni_2$. The effective magnetic moments, determined from the Curie constants, have the values 3.25 μ_B/f.u. for Al_2MnNi and 5.53 μ_B/f.u. for $Al_5Mn_3Ni_2$.

3.2 XPS spectra

The electronic structure of the two alloys is studied by analyzing the valence band and core level spectra.

The Mn 3s spectra for Al_2MnNi and $Al_5Mn_3Ni_2$ are shown in Fig. 4. Both spectra exhibit a well-defined magnetic exchange splitting of about 5 eV, arising from the exchange interactions between the *3s* core hole and open *3d* shell. The magnitude of the 3s spectral splitting according to the Van Vleck theorem [5] is determined by:

$$\Delta E_{ex} = \frac{1}{2l+1}(2S+1)G^2(3s,3d),$$

where *S* is the total spin of the ground state of the *3d* electrons, *l* is the orbital quantum number and $G^2(3s,3d)$ is the Slater exchange integral. The energy separation is proportional to the total spin of the ground state of the *3d* electrons, and hence it can be used to estimate the magnetic moment due to unpaired *3d* electron spins in the solid.

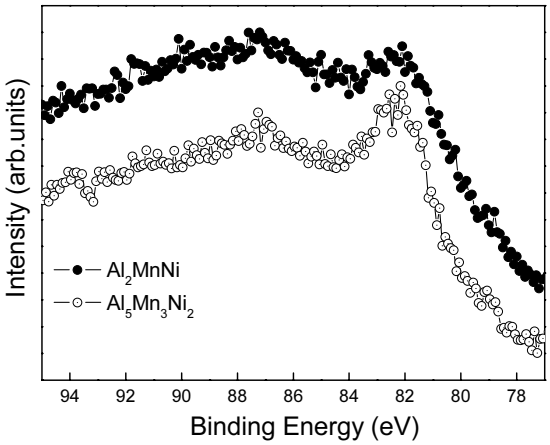

Fig. 4. XPS Mn 3s core level spectra of Al_2MnNi and $Al_5Mn_3Ni_2$.

By fitting the Mn *3s* spectra with two exchange components, after background subtraction, we found a separation value of 5.1 eV in Al_2MnNi and 5 eV in $Al_5Mn_3Ni_2$ corresponding to a magnetic moment of about 3 μ_B /Mn.

In Fig. 5 the Ni *2p* core level spectra of Al_2MnNi and $Al_5Mn_3Ni_2$ in comparison to pure metallic Ni are shown.

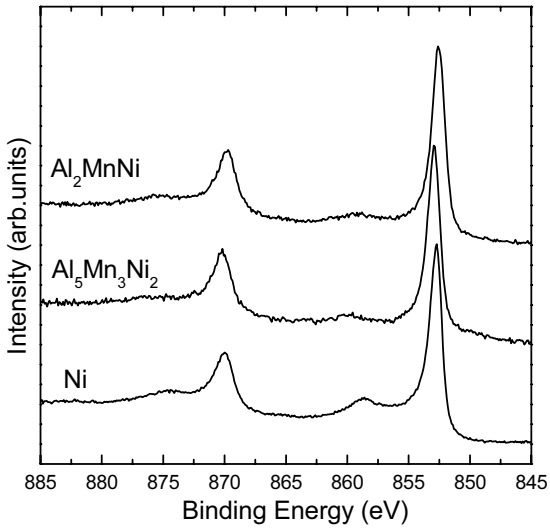

Fig. 5. XPS Ni 2p core level spectra of Al_2MnNi, $Al_5Mn_3Ni_2$ and metallic Ni.

The presence of satellites in the Ni *2p* core level spectra of Al_2MnNi and $Al_5Mn_3Ni_2$, at ~6.5 eV higher binding energy than the main line, implies the presence of *d* character in the unoccupied bands. By comparing the Ni *2p* core level spectra of Al_2MnNi and $Al_5Mn_3Ni_2$ 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 intensities of the Ni satellites are known to be proportional to the number of holes in the Ni *d* band [7]. After fitting the *2p* core level spectra and considering a number of 0.6 holes per Ni atom for metallic Ni, we estimated ~0.3 holes per Ni atom for both Al_2MnNi and $Al_5Mn_3Ni_2$. The partial filling of the Mn *3d* and Ni *3d* states, indicated by the XPS core level spectra, is attributed to the hybridization of the Al states with Mn and Ni states.

The XPS valence-band spectra for the two alloys are shown in Fig. 6:

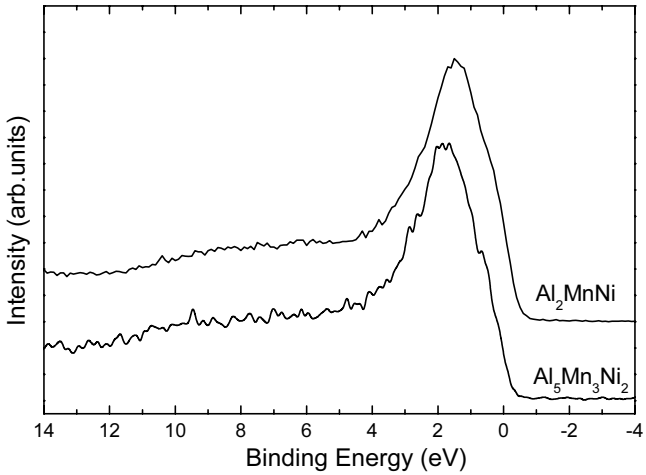

Fig. 6: XPS valence-band spectra of Al_2MnNi, $Al_5Mn_3Ni_2$

At Al K_α radiation, the Ni *3d* cross section is about four times larger than the Mn 3d cross section, i.e., the valence-band of Al_2MnNi and $Al_5Mn_3Ni_2$ are dominated by the Ni *3d* states. The valence band spectra of both alloys exhibit satellites at ~6.5 eV higher binding energy than the centroid, confirming 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 pure metallic Ni, suggesting a partial filling of the Ni *3d* band.

The XPS core level spectra of Al_2MnNi and $Al_5Mn_3Ni_2$ indicate a partial filling of the Mn *3d* and Ni *3d* states, attributed to the hybridization of the Al *3sp* states with Mn and Ni *3d* states. For both alloys the Mn and Ni *3d* bands are filled by more than half, which leads to a ferromagnetic coupling between the neighboring local magnetic moments situated at Mn and Ni sites [8]. We cannot correlate the data obtained from the magnetic measurements in the ordered and paramagnetic domains considering a ferromagnetic system with a collinear arrangement of the local magnetic moments. A canted ferromagnetism could explain the magnetic behavior of Al_2MnNi and $Al_5Mn_3Ni_2$.

4. Conclusions

The well-defined magnetic exchange splitting of about 5 eV of the Mn *3s* core levels of Al_2MnNi and $Al_5Mn_3Ni_2$ gives a clear evidence of the existence of local moments in the Anderson's sense confined on Mn sites in Al-Mn-Ni alloys. The hybridization of the Al states with Mn and Ni states leads to a partial filling of the Mn *3d* and Ni *3d* states, as indicated by the XPS core level and valence band spectra. By correlating the experimental data obtained

both from ordered and paramagnetic states correlating, the magnetic behavior of Al_2MnNi and $Al_5Mn_3Ni_2$ cannot be explained in the picture of ferromagnetic systems with a collinear arrangement of the local magnetic moments. We propose a canted ferromagnetism in the two alloys, which should be verified by further neutron diffraction investigations.

References

[1] P.J. Webster and K.R.A. Ziebeck, In: Alloys and Compounds of d-Elements with Main Group Elements, Part 2, edited by H.R.J. Wijn, Landolt-Börnstein, New Series, Group III, vol. 19, 75, Springer-Verlag, Berlin, 1988.
[2] A. Fujita, K. Fukamichi, F. Gejima, R. Kainuma and K. Ishida, Appl. Phys. Lett., 77, 3054, (2000).
[3] C.S. Fadley, D.A. Shirley, A.J. Freeman, P.S. Bagus and J.V. Mallow, Phys. Rev. Lett., 23, 1397, (1969).
[4] P.W. Anderson, Phys. Rev., 124, 41, (1961).
[5] J.H. Van Vleck, Phys. Rev., 45, 405, (1934).
[6] T. Moriya, Solid State Commun., 2, 239, (1964).
[7] J.C. Fuggle and Z. Zolnierek, Solid State Commun., 38, 799, (1981).