X-ray photoelectron spectroscopy and magnetism of AlDyNi, AlDyNi$_4$ and AlDy$_3$Ni$_8$ compounds

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Abstract. The electronic and magnetic properties of AlDyNi, AlDyNi$_4$ and AlDy$_3$Ni$_8$ are studied using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), static and dynamic magnetic measurements. The three compounds AlDyNi, AlDyNi$_4$ and AlDy$_3$Ni$_8$ are single phases and crystallize in the Fe$_2$P, CaCu$_5$ and CeNi$_3$ structure types, respectively. All the investigated compounds order ferromagnetically below the corresponding Curie temperatures. The Curie temperature and the magnetic moments are 25 K and 6 $\mu_B$/f.u. for AlDyNi, 14 K and 6.9 $\mu_B$/f.u. for AlDyNi$_4$ and 22 K and 19.2 $\mu_B$/f.u. for AlDy$_3$Ni$_8$. At high temperature the magnetic susceptibility obey the Curie-Weiss law. The paramagnetic Curie temperature and the effective magnetic moments are 30K and 10.88 $\mu_B$/f.u. for AlDyNi, 28 K and 10.94 $\mu_B$/f.u. for AlDyNi$_4$ and 18 K and 18.33 $\mu_B$/f.u. for AlDy$_3$Ni$_8$. XPS valence band and Ni 2p spectra indicated the presence of small magnetic moment on Ni sites in AlDy$_3$Ni$_8$ and AlDyNi$_4$, and a complete filling of Ni 3d band in AlDyNi.

1. Introduction
The In the ternary metallic system Dy-Ni-Al ten intermetallic compounds with different crystallographic structure were reported [1].

The nearest neighbourhood of Dy and Ni ions, as well as, the distances Ni-Ni, Dy-Dy, Dy-Ni are different in each compound. This leads to different states of Ni ions and also influences the Dy-Ni interaction in these compounds.

The electronic 3d band width of the transition metals (T) is determined by the overlap between the d orbitals of adjacent atoms and depends on the number of nearest neighbours and the hopping integral J$_{hh}$, which is very sensitive to the T-T distances [2]. On the other hand, the hybridizations between the 3d Ni and 5d6s Dy states and 3d Ni and 3sp Al states may lead to a partial or complete filling of the Ni
3d band. In many rare-earth-nickel compounds, nickel atoms do not carry a magnetic moment because of charge transfer of rare-earth conduction electrons to the 3d band [3].

The aim of this paper is to study the magnetic properties of AlDyNi, AlDyNi$_4$ and AlDy$_2$Ni$_8$ and to correlate the results with the electronic structure obtained from XPS measurements. The three compounds AlDyNi, AlDyNi$_4$ and AlDy$_2$Ni$_8$ crystallize in the Fe$_2$P, CaCu$_5$ and CeNi$_3$ structure types, respectively [1].

2. Experimental
The investigated compounds of AlDyNi, AlDyNi$_4$ and AlDy$_2$Ni$_8$ were prepared by the standard arc-melting technique using a water-cold crucible in an argon atmosphere. The samples were melted repeatedly in the same atmosphere to ensure homogeneity. The weight loss of the final materials was found to be less than 1%. The purity of the starting materials was 99.9% for Dy, 99.99% for Ni and 99.999% for Al. X-ray powder diffraction measurement, performed using a Bruker D8 Advance diffractometer, showed that the compounds are single phases with the expected crystallographic structure type.

The magnetization measurements were performed with a vibrating sample magnetometer at temperature range 4 K and magnetic fields up to 10 T. The magnetic susceptibility measurements were performed using a Weiss balance starting from room temperature until 600 K. The AC susceptibility measurements were performed using a superconducting quantum interference device (SQUID magnetometer) from 4.2 to 300 K.

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 and discussions
3.1. Magnetic measurements
The magnetization as a function of magnetic field at $T = 4$ K for all the investigated compounds are shown in figure 1.

![Figure 1](image.png)

**Figure 1.** The magnetization dependence of the magnetic field at $T = 4$ K for AlDyNi, AlDyNi$_4$ and AlDy$_2$Ni$_8$ compounds.

The dependence of the magnetization with the magnetic field is characteristic for ferromagnetic materials. The spontaneous magnetization (table 1) was obtained by extrapolation to $H \to 0$ of the linear part (in the high fields range) of the $M(H)$ curve. The corresponding values of the magnetic moments per Dy atom in the ordered state are smaller than for free Dy$^{3+}$ ion (10 $\mu_B$). This is
characteristic for many Dy compounds [4] and may be explained taking into account the crystal field effect; the ground state of Dy$^{3+}$ ion is $^6H_{15/2}$ [5].

The real part of the ac susceptibility ($\chi'$) is constant in the temperature range 75-300 K, therefore in figure 2 was plotted only the temperature interval 4-75 K, in order to order to obtain a better resolution for Curie temperature ($T_C$) determination. The values for the $T_C$ are given in table 1. The value of the $T_C$ for AlDyNi is in good agreement with the earlier measurements [6].

In the high temperature range the magnetic susceptibility obey the Curie-Weiss law $\chi = C/(T-\Theta)$ (see figure 3).

![Figure 2](image.png)  **Figure 2.** The $\chi'$ dependence as a function of temperature of AlDyNi, AlDyNi$_4$ and AlDy$_3$Ni$_8$ compounds.

![Figure 3](image.png)  **Figure 3.** The reciprocal susceptibility versus temperature of AlDyNi, AlDyNi$_4$ and AlDy$_3$Ni$_8$ compounds.

The effective magnetic moment per Dy atom in AlDyNi compound, determined from the Curie constant, is bigger than the value for Dy$^{3+}$ free ion (10.6 $\mu_B$). This can be explained if we consider that the Dy 5d electrons are polarized by the exchange field from the localized 4f spins. Because this polarization is in the same direction as that of the localized 4f moments, an excess magnetic moment per Dy atom would be expected. This is in agreement with many experimental findings that the 5d electrons contribute to the total moment per rare-earth atom [7]. In addition to this contribution in AlDyNi$_4$ and AlDy$_3$Ni$_8$ compounds the Ni atoms carry also a small magnetic moment, confirmed by the XPS spectra.

|            | AlDyNi  | AlDyNi$_4$ | AlDy$_3$Ni$_8$ |
|------------|---------|------------|----------------|
| $T_C$ (K)  | 25      | 14         | 22             |
| $\mu$ ($\mu_B$/f.u.) | 6       | 6.9        | 19.2           |
| $\Theta$ (K) | 30      | 28         | 18             |
| $\mu_{\text{eff}}$ ($\mu_B$/f.u.) | 10.88   | 10.94      | 18.33          |

### 3.2. XPS measurements

The main contribution to the valence band spectra is given by the Ni 3d and Dy 4f electrons. The Ni 3d band is situated close to the Fermi level while Dy 4f band is more localized and split in several components (figure 4). The reference compound AlNi is a Pauli paramagnet with the Ni 3d band completely filled [8].
Ni 3d band centroids are shifted towards higher binding energy relative to metallic Ni, suggesting a partial filling of the Ni 3d band due to a strong hybridization between Ni 3d, Dy 5sp and Al 3sp states. The decrease in the satellite structure intensity of Ni 2p line compared to pure Ni confirms the partial filling of the Ni 3d band (figure 5).

Figure 4. Valence band spectra of AlDyNi, AlDyNi₄, AlDy₃Ni₈ and of reference Ni metal and AlNi.

Figure 5. Ni 2p core-level lines of investigated compounds together with Ni metal.

These spectra indicate also that Ni atoms carry a magnetic moment in AlDyNi₄ and AlDy₃Ni₈ compounds, which in the ordered state is orientated antiparallel to the Dy magnetic moment due to the 4f-5d-3d coupling. In the earlier investigation concerning the magnetic properties of AlDyNi₄, the magnetic contribution of Ni atoms was neglected [6]. Ni 2p satellite structure for AlDyNi disappears, suggesting that Ni 3d band is completely filled and Ni atoms have no contribution to the total magnetic moment. This is also confirmed by the position of the valence band centroid at ~1.5eV, close to that observed for the Pauli paramagnet AlNi.

Figure 6. Dy 4d core-level lines of AlDyNi, AlDyNi₄ and AlDy₃Ni₈.

In figure 6 are shown the Dy 4d lines for all the investigated compounds. A chemical shift smaller than 0.4 eV comparing to pure Dy [9] was evidenced. Furthermore the exchange splitting of Dy 4d
core level in all three compounds is similar with that found in pure Dy, suggesting that Dy 4f level is not affected by alloying.

4. Conclusions
The AlDyNi, AlDyNi$_4$ and AlDy$_3$Ni$_8$ compounds order ferromagnetically below the corresponding Curie temperatures. At high temperature the magnetic susceptibility obey the Curie-Weiss law. The strong hybridization between Ni 3d, Dy 5sp and Al 3sp states leads to a gradual filling of Ni 3d band. XPS core-level and valence band spectra indicated that Ni atoms carry a small magnetic moment in AlDyNi$_4$ and AlDy$_3$Ni$_8$ compounds. In AlDyNi compound the Ni 3d band is completely filled and Ni atoms do not carry a magnetic moment. The complete filling of Ni 3d band in AlDyNi compound is due to the high number of Al and Dy atoms in the Ni atoms first vicinity. The polarization of 5d electrons by the local exchange interaction 4f-5d gives rise to an excess magnetic moment of Dy ions in the paramagnetic state of AlDyNi compound.

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