MAGNETIC, ELECTRIC AND XPS STUDY OF $Gd_{1-x}R_xNi_3$ (R = Y, Ce) COMPOUNDS

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Abstract: We report studies of magnetic susceptibility, electrical resistivity, crystal and electronic structure of intermetallic $Gd_{1-x}R_xNi_3$ (R = Y, Ce) compounds. The effect of partial substitution Gd by Y and Ce is reflected in a change of the cell volume, the Curie temperature $T_C(x)$ and in the temperature dependence of magnetic susceptibility and electrical resistivity. For the $Gd_{1-x}Ce_xNi_3$ system the Ce(3d) XPS spectra show that Ce ions are in the intermediate-valence state. The filling of Ni 3d band in the investigated systems by charge transfer of Gd and Y conduction electrons is revealed by reduction of the satellite intensities in the Ni 2p core level spectrum. The XPS spectra in the valence band region show a hybridization of the states near the Fermi level. We conclude that this effect modifies the magnetic properties of the investigated compounds.

1. INTRODUCTION

The intermetallic compounds RT_3 (R – rare earth, T – transition metal) show very interesting magnetic properties. YNi_3 is a very weak itinerant electron ferromagnet with the Curie temperature about 30 K. The magnetic properties of YNi_3 are well described by the model developed by Stoner and Wohlfarth. Above the Curie point, the temperature dependence of the inverse susceptibility has a nonlinear variation. The diffraction experiments with polarized neutrons have shown that the magnetization in YNi_3 is localized on the nickel sites. The total magnetic moment on Ni is $0.20\,\mu_B$ [1]. $GdNi_3$ is ferrimagnetically ordered below Curie temperature ($T_C = 116$ K) with the magnetic moment about $6.55\,\mu_B$. The nickel magnetic moments are antiparallel oriented to those of gadolinium and the value of $\mu_{Ni} = 0.15\,\mu_B$ [2]. Both YNi_3 and $GdNi_3$ crystallize into the same rhombohedral $PuNi_3$ type structure (space group R-$3m$) $CeNi_3$ was reported to be a Pauli paramagnet [3]. This compound crystallizes in the hexagonal structure (space group $P6_3/mmc$).

In this paper we reporte the influence of partial replacement of Gd by Y and Ce atoms in $(Gd, R)Ni_3$ compounds.

2. EXPERIMENTAL DETAILS

Experiments were performed on the intermetallic compounds $Gd_{1-x}Y_xNi_3$ ($x = 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$) and $Gd_{1-x}Ce_xNi_3$ ($x = 0.0, 0.1, 0.2, 0.9, 1.0$). The samples were prepared from stoichiomertic amounts by arc melting constituent metals under argon atmosphere. The ingots were remelted several times in order to ensure homogeneity and after that annealed in quartz tubes at 950°C for 8 days. The crystal structure was established by powder X-ray diffraction technique. All $(Gd_{1-x}Y_x)Ni_3$ system and $(Gd_{1-x}Ce_x)Ni_3$ with $x = 0.0, 0.1, 0,2$

crystallized into the rhombohedral PuNi$_3$ structure. The compounds of (Gd$_{1-x}$Ce$_x$)Ni$_3$ with $x = 0.8$, 0.9, 1.0 exhibited the hexagonal CeNi$_3$ type structure.

AC-susceptibility measurements were made in the temperature range between 4.2 K and 295 K.

The electrical resistivity was measured by standard four-probe technique in the temperature range from 4.2 K up to room temperature.

The electronic structure of the samples was studied with the use of X-ray Photoelectron Spectroscopy (XPS). The measurements performed at room temperature by using a PHI 5700/660 Physical Electronics Spectrometer. Monochromatized Al K_α X-rays ($h\nu = 1486.6$ eV) were used as exciting radiation. The spectra were measured in vacuum of 5×10^{-10} Torr, immediately after cleaving the sample *in situ*. The fractured samples contain a small amount of oxygen and carbon. The oxidation of all samples were checked several times during measurements by observing the O (1s) spectra. No effects of oxidation during the acquisition time were observed.

3. RESULTS AND DISCUSSION

The substitution of Y and Ce for Gd in the Gd$_{1-x}$Y$_x$Ni$_3$ and Gd$_{1-x}$Ce$_x$Ni$_3$ compounds caused change of lattice parameters a and c. For both Gd$_{1-x}$Y$_x$Ni$_3$ and Gd$_{1-x}$Ce$_x$Ni$_3$ series a decrease of lattice parameters with concentration x was observed (Table 1).

In Figure 1 we can see the AC-susceptibility data of the Gd$_{1-x}$Y$_x$Ni$_3$ compounds as a plot of reduced χ/χ_{max} *versus* temperature T, where χ_{max} is the highest maximum value of χ. Curie temperature T_C decreases faster with increasing content of Ce then Y. The transition temperature for Gd$_{1-x}$Y$_x$Ni$_3$ and Gd$_{1-x}$Ce$_x$Ni$_3$ are summarized in Table 1.

Table 1. Lattice parameters, volume cell and transition temperature for the Gd$_{1-x}$Ce$_x$Ni$_3$ and Gd$_{1-x}$Y$_x$Ni$_3$ compounds

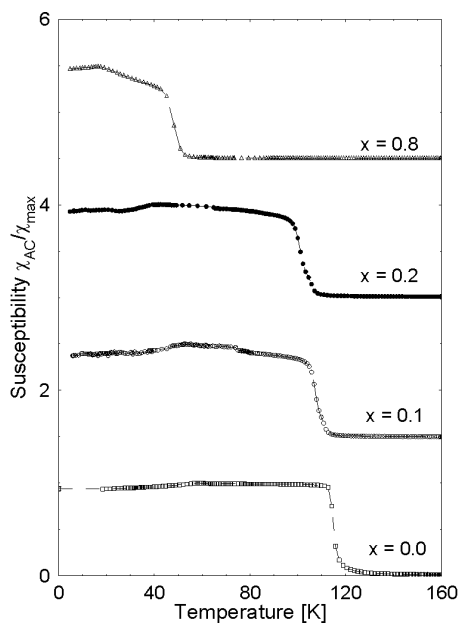| Gd$_{1-x}$Ce$_x$Ni$_3$ x	a [Å]	c [Å]	V [Å^3]	T_C [K]
0.0	5.005	24.618	534	115
0.1	4.992	24.576	530	88
0.2	4.981	24.495	526	69
0.8	4.986	16.551	356	22
0.9	4.981	16.559	355	~ 6
1.0	4.970	16.559	354	–
Gd$_{1-x}$Y$_x$Ni$_3$ x				
0.1	5.002	24.591	533	107
0.2	4.996	24.560	531	101
0.4	4.993	24.534	529	84
0.6	4.979	24.478	526	68
0.8	4.981	24.459	525	48
1.0	4.978	24.448	524	29

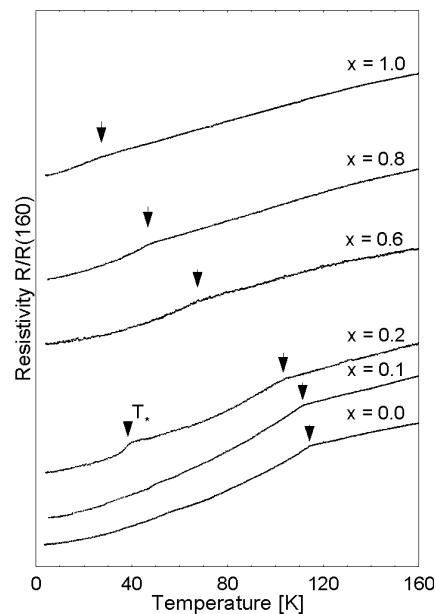Fig. 1. Thermal dependence of AC-susceptibility for $Gd_{1-x}Y_xNi_3$ compounds

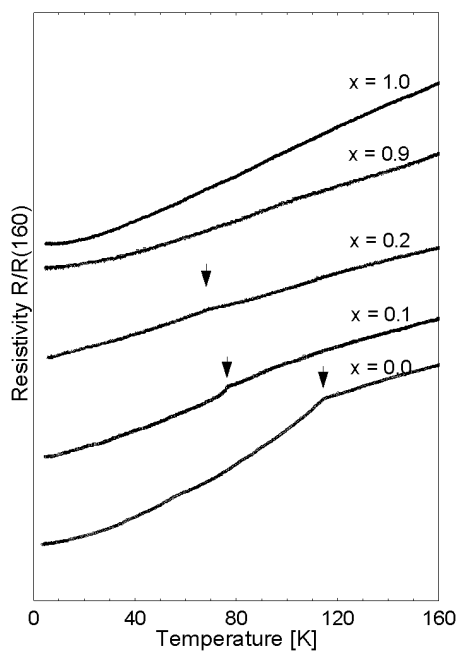Fig. 2. Termal variation of the resistivity for the $(Gd_{1-x}Y_x)Ni_3$ system

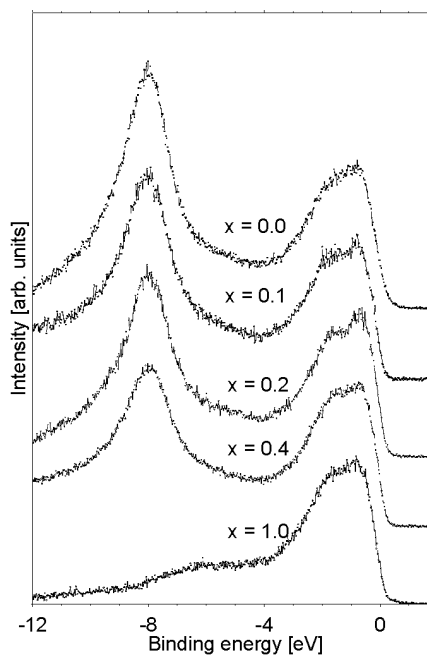Fig. 3. Termal variation of the resistivity for the $(Gd_{1-x}Ce_x)Ni_3$ system

Fig. 4. Valence band XPS spectra for $Gd_{1-x}Y_xNi_3$ compounds

The thermal variations of resistivity for (Gd, R)Ni$_3$ (R = Y, Ce) systems are shown in Figs. 2 and 3, respectively. Below T_C this variation is proportional to T^2. This behavior of the resistivity can be attributed to scattering of electrons by magnons. In case of Gd$_{0.8}$Y$_{0.2}$Ni$_3$ compound, except the para-ferromagnetic transition, the other transition at temperature $T^* = 39$ K is observed. The AC-susceptibility measurements indicate the existence of small anomalies at the same temperature T^* for this compound. Since the investigated sample exhibited a single PuNi$_3$ crystal structure we suppose that the anomaly is attributed to the spin reorientation processes.

The experimental photoemission spectra of the valence band region for Gd$_{1-x}$Y$_x$Ni$_3$ and Gd$_{1-x}$Ce$_x$Ni$_3$ series are shown in Figs. 4 and 5, respectively. We do not observe any change in position of the 4f peak of Gd with the substitution Y or Ce atoms. The bands of width of an order of 3.5 eV near the Fermi level show dominating Ni 3d states hybridized with Gd 5d, Y 4d or Ce 4f states, for Gd$_{1-x}$Y$_x$Ni$_3$ and Gd$_{1-x}$Ce$_x$Ni$_3$, respectively.
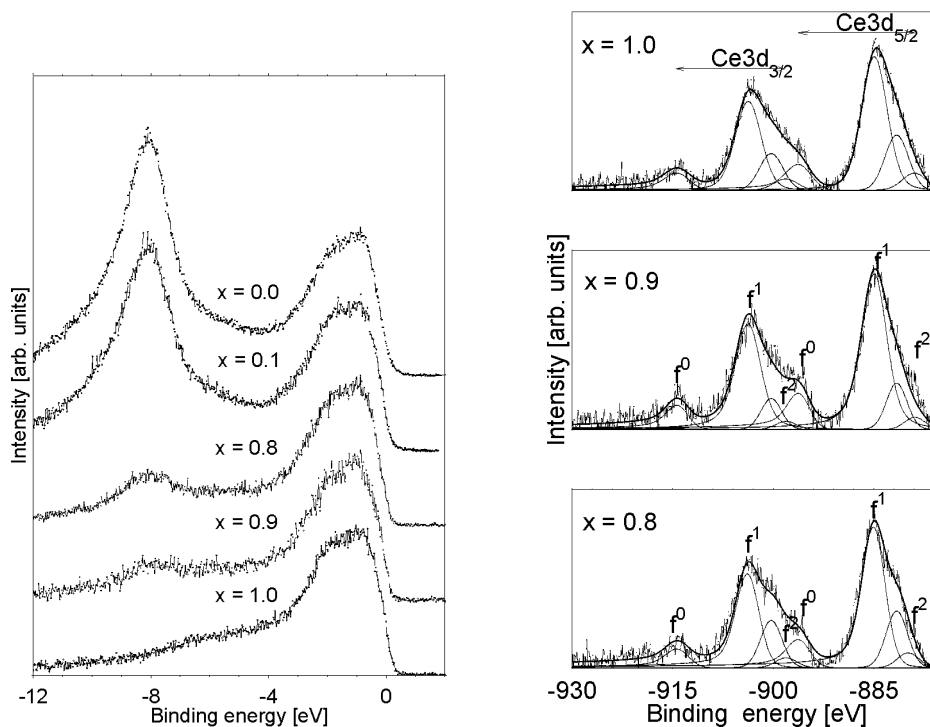

Fig. 5. Valence band XPS spectra for Gd$_{1-x}$Ce$_x$Ni$_3$ compounds

Fig. 6. The 3$d_{5/2}$, 3$d_{3/2}$ doublet of Gd$_{1-x}$Ce$_x$Ni$_3$ compounds. The background is subtracted in all figures. At 900.3 and 881.6 eV, peaks due to oxides are visible

Figure 6 shows the Ce(3d) XPS spectra obtained for Gd$_{1-x}$Ce$_x$Ni$_3$ (x = 0.8, 0.9, 1.0) series. The spin-orbit splitting dominates the spectral structure of the 3d XPS peaks of Ce intermetallics. At the low-binding energy side of the 3$d_{5/2}$ and 3$d_{3/2}$ lines are observed the shake down

satellites Ce $3d^9 4f^2$. The shift of the satellites in relation to the main peak is about 5 eV. The appearance of the $3d^9 4f^0$ satellites at higher energy with an energy separation of order 11 eV with respect to the main peak is clear evidence of mixed valence behavior of Ce. Based on the Gunnarsson–Schönhammer model [4], the intensity ratio $I(f^0)/[I(f^0) + I(f^1) + I(f^2)]$, which should be directly related to the *f*-occupation probability in the final states, indicates an *f*-occupation number n_f. The occupation number of the *f* shell n_f experimentally obtained from $3d$ Ce XPS spectra are 0.7, 0.72 and 0.74 for $x = 1.0$, 0.9 and 0.8, respectively. It implies that the *f*-level occupancy in this range of *x* concentration can be slightly modified.

4. CONCLUSIONS

1. The effect of the partial substitution Gd by Y and Ce is reflected in a drop of Curie temperature; T_C decreases faster with increasing content of Ce then Y.
2. The thermal variation of electrical resistivity for (Gd, R)Ni$_3$ (R = Y, Ce) systems below T_C is proportional to T^2.
3. The valence bands are dominated by the Ni $3d$ states hybrydised with Gd $5d$, Y $4d$ or Ce $4f$ states, for $Gd_{1-x}Y_xNi_3$ and $Gd_{1-x}Ce_xNi_3$, respectively.
4. The $(Gd_{1-x}Ce_x)Ni_3$ compounds with $x = 0.8$, 0.9 and 1.0 show a clear evidence of the deviation from the clean Ce^{3+} valence state.

References

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