The Influence of Yb Substitution on the Magnetic, Electric Properties and Electronic Structure of $Yb_xGd_{1-x}Ni_5$ System

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The crystal and electronic structure, magnetic and electric properties of intermetallic compounds $Yb_xGd_{1-x}Ni_5$ ($x = 0.0$, 0.2, 0.4, 0.5) are presented. The whole series crystallize in the hexagonal $CaCu_5$ type of crystal structure. The ordering temperatures T_C and the effective magnetic moments decrease with increase in ytterbium concentration. The electronic structure studied by X-ray photelectron spectroscopy method shows the domination of Ni $3d$ states nearby the Fermi level. The multiplet structure visible in valence bands is typical of Yb^{3+} ions.

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1. Introduction

The RT_5 compounds, where R is rare earth and T is a transition metal, show very interesting magnetic properties due to the combination of $3d$ itinerant and $4f$ localized magnetism [1–11]. One of the most known series is RNi_5. The analysis of its magnetic properties shows that the Curie temperatures are very low. The highest value of T_C was evidenced for $GdNi_5$ compound [1–4] which was obtained for the first time in 1962 by Nesbitt et al. [6]. Latter studies showed that $GdNi_5$ is the ferrimagnet below $T_C = 32$ K and the value of magnetization extrapolated to 0 K equals 6.2 μ_B/f.u. [4, 7, 11]. This kind of behavior is connected with a negative polarization of the Ni $3d$ band by Gd atoms. The RT_5 compounds where R = Yb are very interesting due to possible existence of the intermediate valence state. The Yb ions in RT_5 systems often indicate the occurrence of the magnetic trivalent state Yb^{3+} with $4f^{13}$ localized electrons, but also the non-magnetic divalent Yb^{2+} state with non-localized $4f^{14}$ electrons or the intermediate valence state [8–10].

In this paper we present the influence of partially replacing of Gd by Yb atoms on the crystal structure, magnetic and electric properties as well as on the electronic structure in $Yb_xGd_{1-x}Ni_5$ system.

2. Experimental

Polycrystalline samples of the $Yb_xGd_{1-x}Ni_5$ series with $x = 0.0$, 0.2, 0.4, 0.5 were prepared by arc melting from high purity elements under argon atmosphere. The crystal structure of all samples was checked by means

of X-ray diffraction using Siemens D5000 diffractometer. The ac magnetic susceptibility measurements were done in the temperature range 4.2–300 K at frequency 1 kHz. The dc susceptibility was measured in the paramagnetic range 300–800 K using the Faraday method in the magnetic field of 0.38 T. The electrical resistance $R(T)$ was measured quasi-continuously at a slowly changing temperature (4.2–300 K) by a standard four-probe technique. The X-ray photoelectron spectroscopy (XPS) measurements were performed with the use of PHI 5700/660 Physical Electronics spectrometer. The spectra were analyzed at room temperature using monochromatized Al K_α radiation (1486.6 eV). The samples were fractured and measured in vacuum of 10^{-10} Torr.

3. Results and discussion

3.1. Crystal structure

The crystal structure of $Yb_xGd_{1-x}Ni_5$ samples was studied by X-ray powder diffraction (XRD). The analysis of XRD patterns obtained at room temperature confirms that all as-cast studied compounds crystallize in the hexagonal $CaCu_5$ structure. As it is shown in Table, the volume V of the unit cell decreases with rising Yb content up to $x = 0.4$. In parallel, the a lattice parameter decreases up to $x = 0.4$, while c parameter increases with a lower rate in the whole range of studied concentrations. This kind of behavior is probably connected with different ionic radii for gadolinium (Gd^{3+} — 1.02 Å) and ytterbium (Yb^{3+} — 0.86 Å). The anomalous expansion above $x = 0.4$ may be related to the occurrence of an Yb intermediate valence. Similar behavior was previously observed for $YbCu_{5-x}Al_x$ series [8]. The decrease

in a and the increase in c lattice parameters is possible in ternary compounds of $CaCu_5$ structure due to their layer structure.

TABLE

The crystal structure parameters, magnetic and electric properties of $Yb_xGd_{1-x}Ni_5$ system.

x	a [Å]	c [Å]	V [Å^3]	T_C [K]	μ_{eff} [μ_B/f.u.]	θ_p [K]	ρ_0 [$\mu\Omega$ cm]
0.0	4.9120	3.9647	82.84	33.7	8.35	7.24	27.28
0.2	4.8950	3.9727	82.44	24.3	8.07	−16.7	–
0.4	4.8807	3.9792	82.09	18.8	7.50	−17.3	12.29
0.5	4.8810	3.9857	82.23	13.3	7.14	−34.6	9.25

3.2. Magnetic properties

The magnetic properties of $Yb_xGd_{1-x}Ni_5$ series were studied using the temperature dependence of $\chi_{ac}(T)$ and $\chi_{dc}(T)$ magnetic susceptibility. From the plots of $\chi_{ac}(T)$ the values of the Curie temperature T_C were obtained. These values decrease from 33.7 K ($x = 0.0$) to 13.3 K ($x = 0.5$). The same behavior was noticed for the effective magnetic moment (μ_{eff}) obtained from $\chi_{dc}(T)$ measurements. The values of μ_{eff} deduced from the Curie constants decrease from 8.35 μ_B/f.u. ($x = 0.0$) to 7.14 μ_B/f.u. ($x = 0.5$). We can suppose that substitution of Yb with smaller effective moment (Yb^{3+} — 4.54 μ_B) in the place of Gd atoms causes the reduction of the total value of μ_{eff}. However, the fact that the value of μ_{eff} in $GdNi_5$ is higher than for free Gd^{3+} ion may be correlated with spin fluctuations as it was previously reported for different 1:5 compounds e.g. by Coldea et al. [3, 5]. With the substitution of Gd by Yb atoms the presence of the ferrimagnetic ordering was observed for all compounds, which was reflected in the negative values of paramagnetic temperatures (Table).

3.3. Electrical resistivity

The temperature dependence of electrical resistance $R(T)$ was measured for the whole $Yb_xGd_{1-x}Ni_5$ series. The values of the Curie temperature T_C obtained from the plots $R(T)$ were in good agreement with those derived from the magnetic measurements. Knowing the dimensions of samples we were able to obtain the thermal variation of electrical resistivity $\rho(T)$ besides the sample with $x = 0.2$ which had a lot of microcracks. The $\rho(T)$ dependence for $Yb_xGd_{1-x}Ni_5$ series shows a typical metallic behavior. The value of residual resistivity obtained experimentally at 4.2 K decreased with increase in Yb concentration from $\rho_0 = 27.28$ $\mu\Omega$ cm ($x = 0.0$) to $\rho_0 = 9.25$ $\mu\Omega$ cm ($x = 0.5$) (Table). The highest value of ρ_0 for $GdNi_5$ compound may be correlated with the microcracks which were observed for this compound. The decrease in ρ_0 with increase in Yb concentration is connected with different sizes of ionic radii for Yb^{3+} (0.94 Å)

and Gd^{3+}(1.02 Å) ions. This kind of behavior can suggest that Yb ions occur in trivalent state because the value of ionic radius for Yb^{3+} (0.94 Å) is smaller than Yb^{2+} (1.13 Å).

3.4. Electronic structure

The valence band (VB) spectra for $Yb_xGd_{1-x}Ni_5$ series in the energy range of $2 \div -12$ eV are presented in Fig. 1. The shape of VB spectra nearby the Fermi level (E_F) observed for $Yb_xGd_{1-x}Ni_5$ series is determined for
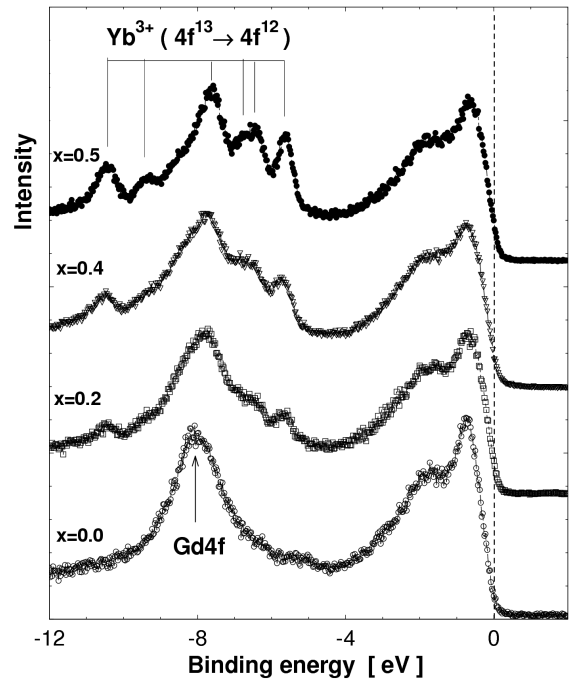

Fig. 1. The valence band spectra of $Yb_xGd_{1-x}Ni_5$ series in the energy range of $2 \div -12$ eV.

Ni $3d$ states. The substitution of Yb in the place of Gd causes the shift of the valence band into lower binding energies. These shifts reach the value of 0.1 eV for $x = 0.5$ and may be correlated with d–f interaction as well as with the presence of a small amount of Yb^{2+} states. The similar shift about 0.1 eV were also observed for the Ni $2p$ core level lines. The multiplet structure visible at about $-5 \div -12$ eV binding energy range for compounds with $x \geq 0.2$ is mainly coming from trivalent Yb $4f$ ions. It is connected with $4f^{13} \longrightarrow 4f^{12}$ transition and consists of six lines partly overlapping with Gd $4f$. About 6 eV below E_F one can observe small satellite structure related to two-hole nickel final states: $3d^9 4s$ (main line) and $3d^8 4s^2$ (satellite line). The analysis of Yb $4d$ core level lines (Fig. 2) shows the presence of multiplet structure connected with the interaction with core hole $4d$ and $4f$ electrons. There are visible several lines at about -184.5 eV, -192 eV and -199 eV which are typical of Yb^{3+} states. In contrast to $YbXCu_4$ compounds [9, 10] the core level Yb $4d$ spectra for $Yb_xGd_{1-x}Ni_5$

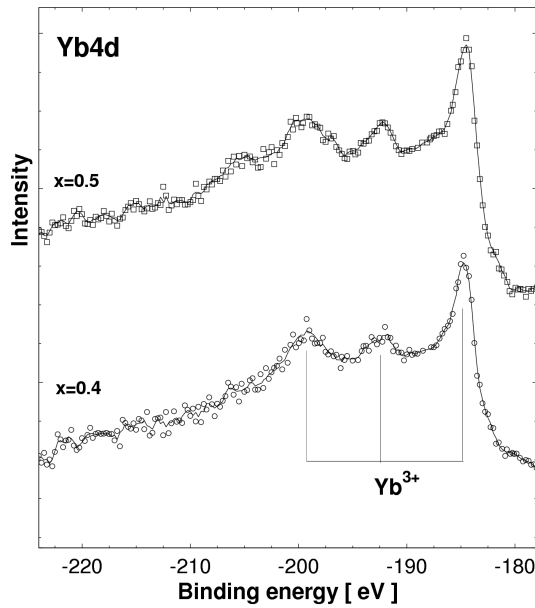Fig. 2. The Yb $4d$ core level lines for $Yb_{0.4}Gd_{0.6}Ni_5$ and $Yb_{0.5}Gd_{0.5}Ni_5$ compounds.

series do not show clearly the presence of ytterbium divalent states. For $YbXCu_4$ compounds the peaks typical of these states were observed at about -181.5 eV and -191 eV. We do not observe the first peak (-181.5 eV) which is typical of Yb^{2+} ions. In the Ni $2p$ spectra (not shown here) the satellite structures at about 6 eV above the main lines are visible for all investigated compounds. The presence of the satellites in this energy range is typical of the spectrum of pure Ni element with not fully filled $3d$ band and suggests that nickel atoms carry a magnetic moment, which is in agreement with band structure calculations for other RNi_5 compounds [7, 11].

4. Conclusions

The influence of Yb substitution is reflected in the magnetic and electric properties as well as in the crystal and electronic structure in $Yb_xGd_{1-x}Ni_5$ ($x \leq 0.5$) compounds.

The substitution of Gd/Yb causes the increase in $c(x)$ lattice parameter in the whole range of concentrations. This kind of change is connected with different ionic radii for gadolinium and yterrbium ions. The deviation from the linear change of $a(x)$ and $V(x)$ for $x > 0.4$ may be related to intermediate valence of Yb ions.

The Yb substitution causes the decrease in T_C as well as the value of μ_{eff} obtained from the Curie constant. The gradual decrease in ρ_0 was observed due to trivalent state of Yb ions which have smaller ionic radius than Yb^{2+} ions.

The XPS valence band nearby the E_F for the whole series are dominated by Ni $3d$ states. The multiplet structure visible in the valence bands is characteristic of Yb^{3+} states. With increase in Yb content there were observed small energy shifts into lower binding energies. It can be the result of d–f interaction but also the presence of small amounts of Yb^{2+} states. The valence of ytterbium can be also estimated from Yb $4d$ spectra. However, we suppose that the multiplet structure of Yb $4d$ core level line is rather characteristic of Yb^{3+} structure.

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