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Magnetic properties and electronic structure of $Y_xGd_{1-x}Ni_5$ compounds

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Measurements of the magnetic susceptibility, crystal and electronic structure for $Y_xGd_{1-x}Ni_5$ ($x = 0.0$, 0.2, 0.5, 0.8, 1.0) compounds with a $CaCu_5$-type crystal structure are reported. The substitution of Y for Gd atoms results in a decrease of the unit cell volume and Curie temperature. In the paramagnetic range (300–650 K), the DC susceptibility follows the Curie–Weiss law for all investigated compounds. The effective moment deduced from the Curie constant decreases rapidly with Y concentration. The saturation magnetic moment for $GdNi_5$ exhibits a negative polarization of the Ni3d band, induced by interactions with Gd5d states. Both valence band and core level X-ray photoelectron spectra are analysed. The presence of satellite structure in the Ni2p core level suggests that the magnetic polarisation of Ni3d states, which dominates the valence band in all investigated compositions. The experimental investigations were complemented by the band structure calculations. In all cases, the calculations were based on the KKR and KKR–CPA methods. Satisfactory agreement between the recorded spectra and those obtained from the calculated electronic structure was achieved.

Key words: *rare earth–nickel intermetallics; magnetic properties; XPS; electronic structure*

1. Introduction

Intermetallic compounds RM_5 show interesting magnetic properties associated with both the localized moments of rare earth (R) and the itinerant electrons of 3d atoms (M). These compounds crystallize in a hexagonal $CaCu_5$-type crystal structure (space group *P6*/*mmm*) [1–4]. In this structure, the R atoms are located at 1a positions, and Ni atoms can occupy two positions, 2c and 3g [5]. Magnetic properties as studied by Gignoux [1] show that $GdNi_5$ is a ferromagnet with $T_C = 32$ K and a satura-

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tion magnetic moment of 6.2μ_B/f.u. This value is lowered with increasing yttrium concentration for $Gd_xY_{1-x}Ni_5$, and the magnetic properties correlate with negative Ni d-band polarization which is induced by interactions with Gd atoms [1, 2]. It has been reported that YNi_5 is a strong Pauli paramagnet exhibiting an effect of spin fluctuations in the temperature variation of susceptibility [6, 7].

In this work, we focus on the influence of the partial substitution of Gd by Y atoms on the magnetic properties and electronic structure of the $Y_xGd_{1-x}Ni_5$ system ($x = 0.0$, 0.2, 0.5, 0.8, 1.0). We report electronic structure analysis using experimental X-ray photoemission spectroscopy (XPS) and theoretical *ab initio* calculations.

2. Experimental and computing method

Polycrystalline samples of $Y_xGd_{1-x}Ni_5$ with $x = 0.0$, 0.2, 0.5, 0.8, and 1.0 were prepared by arc melting of high purity elements under an argon atmosphere. The purity of phases was checked by X-ray diffraction using a Siemens D5000 diffractometer. AC magnetic susceptibility measurements were done in the temperature range 4.2–300 K at the frequency of 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.

XPS measurements were performed with a PHI 5700/660 Physical Electronics spectrometer. The spectra were analysed at room temperature using monochromatised AlK_α radiation (1486.6 eV). The samples were fractured and measured in a vacuum of 6×10^{-10} Torr. After breaking in high vacuum, we observe only small amounts of carbon and oxygen. Band structure calculations were carried out using the spin-polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) band structure program [8]. The Local Spin Density Approximation (LSDA) exchange-correlation potential (XC) was used in the form given by Vosko et al. [9]. The crystal volume is divided into overlapping Wigner–Seitz (WS) spheres,, with the volume equal to the volume of a unit cell. The radii of the constituents were $r_{Gd} = 1.798$, $r_Y = 1.798$, $r_{Ni2c} = 1.508$, and $r_{Ni3g} = 1.328$ Å. XPS was simulated by convoluting the partial density of states with a Lorentzian (0.35 eV HW) and multiplying by the corresponding cross-section taken from [10].

3. Results and discussion

The X-ray powder diffraction measurements show the presence of only a hexagonal $CaCu_5$-type crystal structure for all the investigated $Y_xGd_{1-x}Ni_5$ compounds. The decrease of both lattice parameters and the volume unit cell with increasing yttrium concentration (Fig. 1) was observed. The Curie temperatures T_c (Fig. 1) obtained from AC measurements decrease from 34 K ($x = 0.0$) to about 5.5 K ($x = 0.8$) as a function of Y concentration.

The temperature dependence of reciprocal DC susceptibility exhibits the Curie –Weiss type behaviour in the paramagnetic range 300–650 K for all the investigated compounds. The effective moments deduced from the Curie constant decrease rapidly with Y concentration from 8.35μ_B/f.u. ($x = 0.0$) to 3.90μ_B/f.u. ($x = 1.0$). As has been previously reported for $GdNi_5$ [3] and YNi_5 [7], the value of the effective moment is higher above the characteristic temperature T^* in the paramagnetic range, where the system behaves as having local moments. Such behaviour was already analysed using the theory of spin fluctuations [3, 7]. For $GdNi_5$, the effective magnetic moment obtained up to 300 K is about 7.7μ_B/f.u., the same as that obtained by Gignoux [1]. The field dependence of magnetization for $GdNi_5$ obtained at 4.2 K saturates at the field of 9 T and the value of the saturation magnetic moment is equal to 6.77μ_B/f.u. [11].

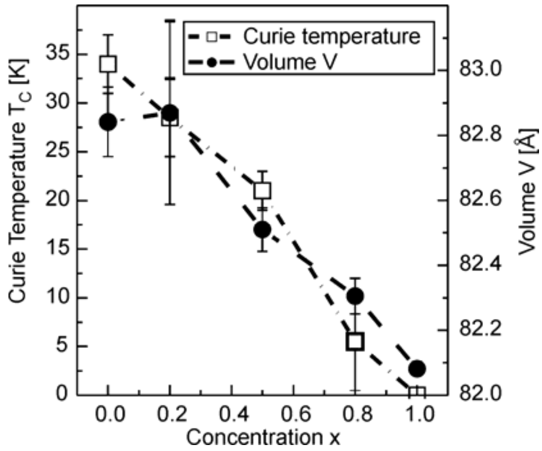

Fig. 1. Volume unit cell V and Curie temperature T_C for the $Y_xGd_{1-x}Ni_5$ system

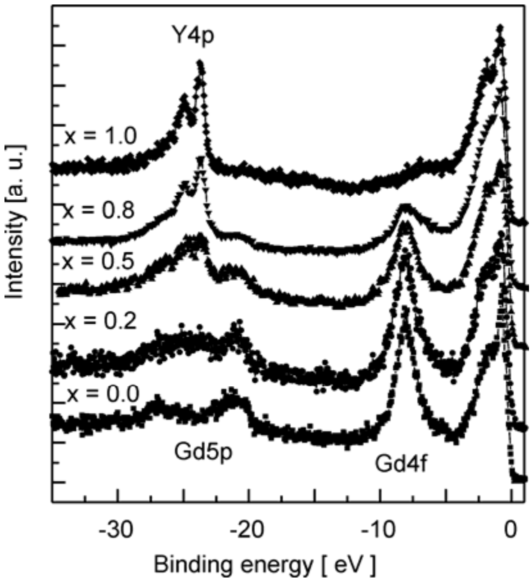

Fig. 2. XPS valence bands for a broad range for $Y_xGd_{1-x}Ni_5$ compounds

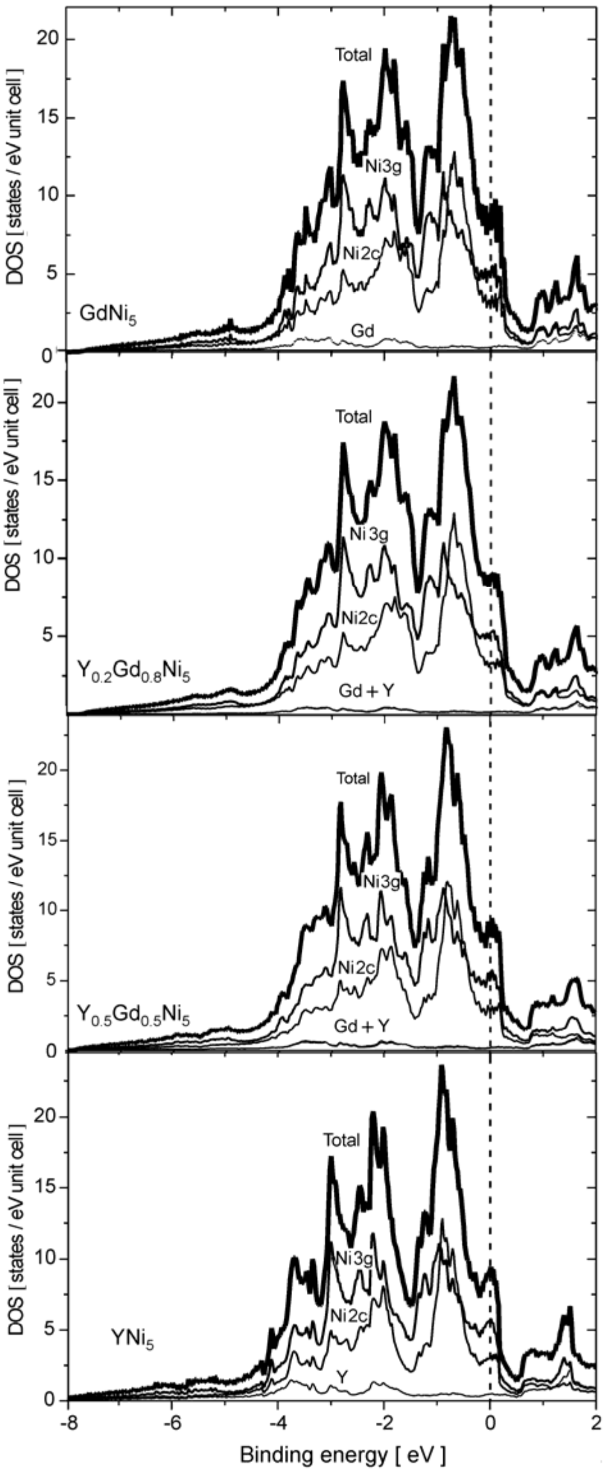

Fig. 3. Total density of states – thick solid lines (the highest density of states) and contributions coming from different types of atoms in the unit cell: Ni – solid lines (medium density of states), Y, Gd – solid lines (the smallest density of states). The vertical dashed line denotes the E_F level

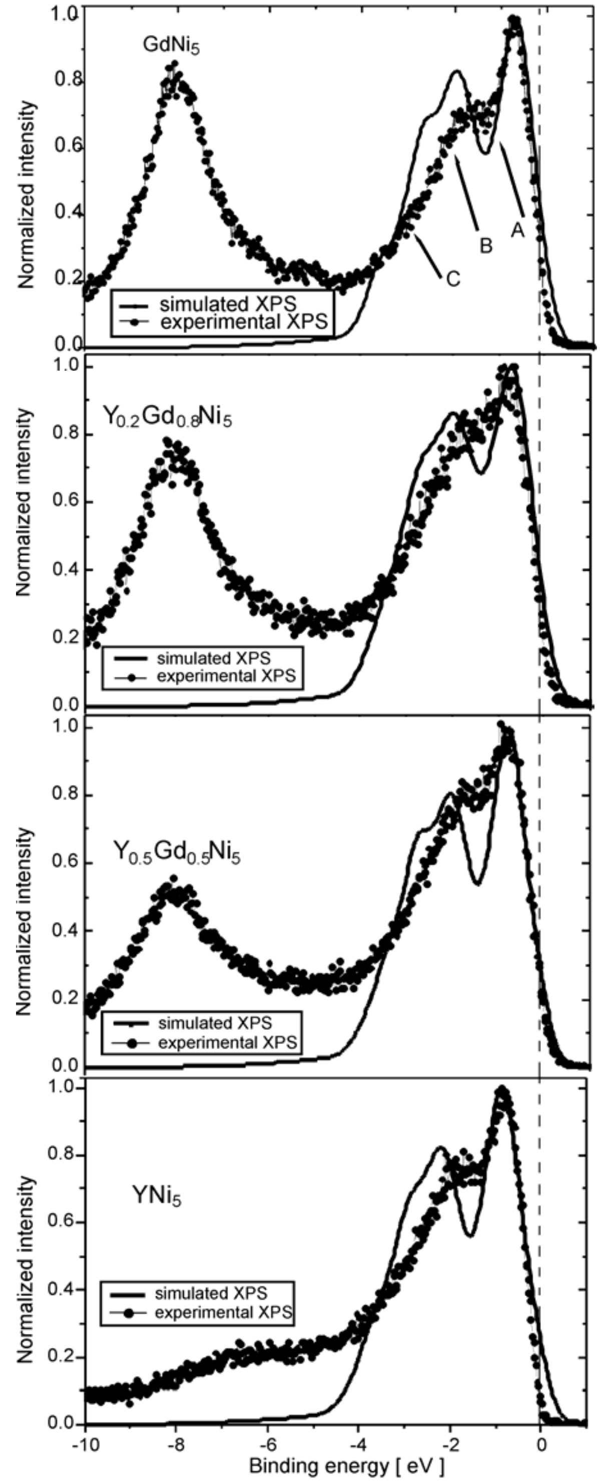

Fig. 4. Experimental (dotted lines) and simulated (solid lines) XPS valence bands. The vertical dashed line denotes the E_F level

In the valence bands (Fig. 2), we have observed the contribution of Gd5p states located at about 26 eV (Gd5p$_{3/2}$) and 21 eV (Gd5p$_{1/2}$). When replacing Gd by Y, a gradual vanishing of Gd5p peaks and appearance of Y4p peaks is observed. Y4p lines are located at about 23.7 eV (Y4p$_{3/2}$) and 24.8 eV (Y4p$_{1/2}$). The position of the Gd4f states is almost the same as in pure Gd. A gradual decrease of the Gd4f intensities with increasing Y content is observed.

From the valence bands near the Fermi level (Fig. 4) we conclude that Ni3d are dominant at E_F for all the investigated compounds. The main line located in the valence band spectrum consists of two visible peaks at about 0.7 eV (peak A) and 1.8 eV (peak B). One can also see a small contribution at 2.9 eV (peak C). When increasing Y concentration, a small shift in those peaks by about 0.11 eV towards higher binding energies is observed. The separation between peaks A and B is larger for $GdNi_5$ and YNi_5 than for the other compounds. This behaviour may be related to hybridization effects between Ni3d, Gd5d, and Y4d. About 6 eV below E_F one can observe a small satellite structure related to two-hole nickel final states: $3d^9 4s$ (main line) and $3d^8 4s^2$ (satellite line). A similar satellite structure at about 6 eV below the main line is observed for the core level spectra of Ni2p (not shown here). The existence of these satellites is usually associated with an incompletely filled Ni3d band. In our compounds, we have not observed these satellites vanish with an increasing number of Y atoms, contrary to other Ni compounds [3]. Therefore, we conclude that the Ni d band in $Y_xGd_{1-x}Ni_5$ is not completely filled.

In Figure 3, the total density of states (DOS) and contributions coming from different crystallographic positions of each atom are shown. Their partial densities of states are multiplied by their number in the unit cell. The dominating features of the total DOS plots have their counterparts in the simulated XPS spectrum (Fig. 4).

The contributions from Ni atoms in the inequivalent positions 2c and 3g are significantly different due to different environments. The contribution from Ni atoms is dominant, and it originates mainly from 3d states. This is simply due to the fact that there are 5 times as many Ni atoms than Gd or Y atoms in the unit cell. E_F is located at the top of the Ni3d band. The 4f bands of Gd give relatively high and unphysical peaks at –4 eV and 1.5 eV. Their binding energies are twice smaller than the measured binding energy, which is a well known deficiency of the local density approximation. This deficiency can be corrected by using the LDA + U or SIC (self interaction corrected) method. The Gd4f states were removed for clarity and the remaining states were used to obtain the XPS spectra.

These simulated and measured XPS spectra are very similar, except for the Gd4f bands positions noted above. The positions of other peaks are in a good agreement with the experimental ones. The slight shift of the peak at 1 eV in the direction of higher binding energies with increasing yttrium concentration is reflected in both experimental and simulated spectra. This peak originates from Ni3d bands and is caused mainly by Ni atoms in 2c positions. The next peaks, at 2 and 4 eV, also arise from Ni3d bands, but from Ni atoms in the 3g positions. The widths of the peaks are in good agreement with the experimental data.

The magnetic moments of Ni in 2c and 3g positions are oriented antiparallel to Gd and Y moments in all samples (Table 1). Quite interesting is the fact that the value of Gd5d moments, equal to 0.132μ$_B$/f.u. for $GdNi_5$, is larger than Ni3d moments at both lattice positions. Ni polarization is very small due to its almost fully filled 3d band. The substitution of Gd atoms by Y is reflected in the slight growth of the Ni moment, which can be correlated with the arrangement of Gd5d moments, oriented parallel to Gd4f moments. Very small changes in Gd4f moments with Y concentration were also observed. The total magnetic moment decreases rapidly with increasing Y concentration, from 6.75μ$_B$ for $x = 0.0$ to 0.181μ$_B$ for $x = 1.0$.

Table 1. Total and partial magnetic moments obtained from band structure calculations for $Y_xGd_{1-x}Ni_5$

x	M_Y [μ$_B$/atom]	M_{Gd} [μ$_B$/atom]	M_{Ni2c} [μ$_B$/atom]	$M_{Ni(3g)}$ [μ$_B$/atom]	Total M [μ$_B$/f.u.]
0.0	–	6.97	–0.02	–0.06	6.75
0.2	0.02	6.97	–0.02	–0.05	5.39
0.5	0.01	6.98	–0.01	–0.02	3.42
1.0	–0.01	–	0.03	0.04	0.17

4. Conclusions

From the results of our measurements for $Y_xGd_{1-x}Ni_5$ compounds, the following conclusions can be drawn. The decrease of the Curie temperature and effective magnetic moment with increasing Y concentration were observed. From the analysis of XPS valence band spectra, the domination of Ni3d states at E_F is observed. Hybridization effects between Ni3d, Gd5d, and Y4d states are evident from the experimental spectra as well as from the band structure calculations. In addition, the Ni3d band remains almost unchanged for all $Y_xGd_{1-x}Ni_5$ compounds. The observed satellite structure in Ni2p core level lines can be correlated with the incompletely filled Ni3d bands. The agreement found between the experimental and simulated XPS valence bands is quite good. The calculations have shown three visible contributions coming from Ni2c and Ni3g states near the Fermi level. The positions of these contributions are almost the same in the experimental spectra (peaks A, B, and C). The different values for Ni2c and Ni3g magnetic moments obtained from band structure calculations can be attributed to different local environments.

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