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Magnetic properties, crystal and electronic structure of $GdNi_{5-x}Cu_x$ series

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ABSTRACT

The effect of Ni/Cu substitution on the magnetic properties, crystal and electronic structure of the polycrystalline $GdNi_{5-x}Cu_x$ series has been studied. All compounds crystallize in the hexagonal CaCu5 type of crystal structure (space group $P6/mmm$). The temperature dependence of magnetic phase transition (T_{mag}) estimated from $\chi_{AC}(T)$ susceptibility as well as magnetization $M(T)$ below room temperature indicates the maximum for $x = 1.0$ copper concentration. In the paramagnetic range (above 300 K) the magnetic susceptibilities follow a Curie–Weiss-type dependence. The effective magnetic moments are higher than theoretical value for free Gd^{3+}.

From X-ray photoelectron spectroscopy (XPS) data the valence band as well as the core level spectra have been analyzed. The filling of Ni3d band in the $GdNi_{5-x}Cu_x$ system by charge transfer of Gd conduction electrons is revealed by a reduction of the satellite intensities in the Ni2p core level spectrum. The obtained results exhibit that the valence bands at the Fermi level are dominated by hybridized Ni3d and Gd5d states, when Cu3d states are rather localized about 3 eV below the Fermi level. Quite good relation between the magnetic properties and electronic structure has been found.

1. Introduction

The RM_5 group of compounds where R is a rare earth and M is a 3d transition metal has been extensively studied in the past due to their interesting magnetic properties [1–17]. Almost all compounds with M = Ni crystallize in the hexagonal $CaCu_5$ type of crystal structure ($P6/mmm$ space group), but some of them with e.g. Al, Ga ($x > 2.0$) show an existence of a superstructure $HoNi_{2.6}Ga_{2.4}$ which is closely related to $CaCu_5$ structure [9,13–15]. It has been proved that RCu_5 series crystallize in two different crystal structures depending on the type of R atom. The RCu_5 compounds with light rare earths (R = La – Sm) crystallize only in $CaCu_5$ type of structure whereas those with heavy rare earths (R = Ho – Tm) occur only in cubic $AuBe_5$ type of structure. For middle rare earths (Gd, Tb, Dy) both structures can exist, depending on heat treatment given to the samples [6,11]. Different ranges of solid solutions for $LaNi_{5-x}Cu_x$ and $TbNi_{5-x}Cu_x$ show the presence of the $CaCu_5$ type of structure in which copper substitutes for nickel at both positions 2c and 3g with a preference the 2c sites [7,8].

One of the most popular is the $GdNi_5$ compound which indicates a ferromagnetic behaviour with ordering temperature $T_C = 32$ K and magnetic moment $6.2\mu_B$/f.u. [1,2,10,17]. Much more interesting is the $GdCu_5$ compound which shows an antiferromagnetic arrangement below $T_N = 26$ K and a quite unusual behaviour of $\rho(T)$ below 30 K. These features are probably connected with its helimagnetic-like structure [5]. The Ni/Cu substitution in the $RNi_{5-x}Cu_x$ series is reflected in the different magnetic properties depending on the type of R atom [3,4,7,8]. These properties are closely connected with crystal field effects, band magnetism and band structure. Those mechanisms are responsible for $T_C(x)$ as well as $M_S(x)$ dependencies. The maximum of $T_C(x)$ has been found for R = Gd and the minimum for R = Pr.

In our paper we present a study of magnetic properties as well as crystal and electronic structure as an influence of Ni/Cu substitution in the $GdNi_{5-x}Cu_x$ system. We analyze the relationship between magnetic behaviour and electronic structure in studied compounds.

2. Experimental

The $GdNi_{5-x}Cu_x$ (x = 0.0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 4.5, 4.8, 5.0) compounds have been prepared by arc melting under argon atmosphere. The purity of materials used for preparing samples were 99.99% for Ni and Cu and 99.9% for Gd. The crystal structures of all samples were checked by means of X-ray diffraction using Siemens D5000 diffractometer. The magnetic susceptibility has been measured by means of AC and DC methods. The AC method has been carried out at a frequency of 1 kHz in the temperature range 4.2–300 K using the precision HP LCR meter. The DC susceptibility measurements have been done above 300 K by standard Faraday method in the magnetic field 0.38 T. Additionally the magnetization (M) versus temperature has been measured in the temperature range at about 2–300 K in the magnetic field of 1000 kOe using MagLab 2000 System AC susceptometer/DC magnetometer (Oxford Instruments Ltd.). The field dependence of magnetization $M(H)$ has been measured at 4.2 K using the same system as $M(T)$ equipped with 9 T superconducting magnet.

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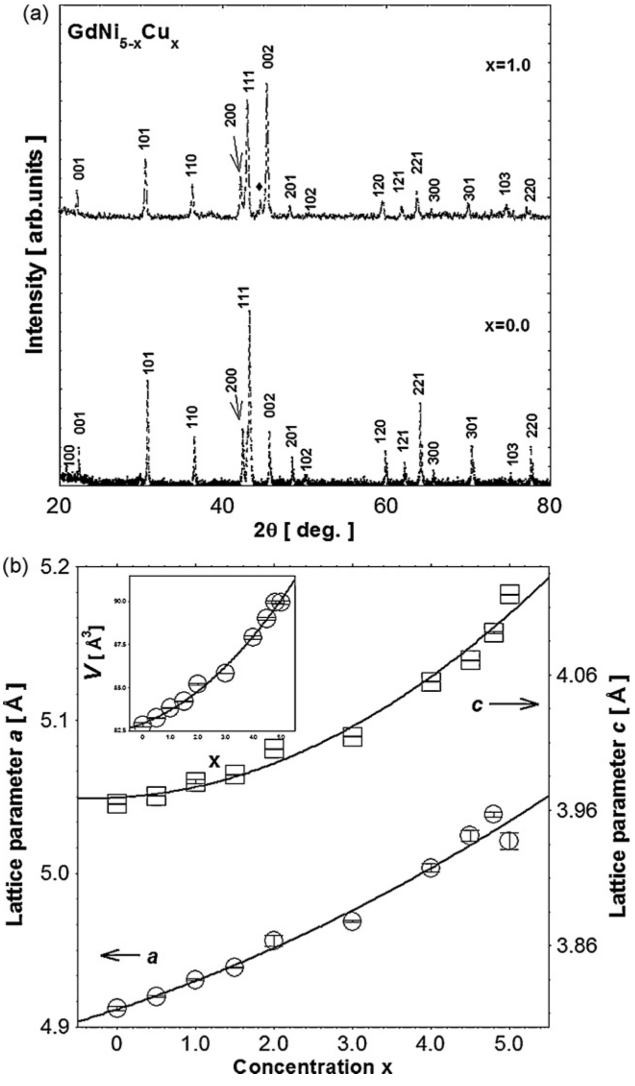

Fig. 1. (a) XRD patterns of for the $GdNi_{5-x}Cu_x$ series ($x = 0.0$ and 1.0). (b) The change of the lattice parameters for the $GdNi_{5-x}Cu_x$ series. Inset represents $V(x)$ dependence.

The X-ray photoemission spectra (XPS) have been obtained at room temperature with monochromatized Al Kα radiation (1486.6 eV) using a PHI 5700/660 (Physical Electronics) spectrometer. The energy spectra of emitted photoelectrons have been analyzed by hemispherical mirror analyzer with high energy resolution about 0.3 eV. The all spectra have been measured after breaking samples in vacuum about 5×10^{-10} Torr. Only small contamination of oxygen and carbon has been detected.

3. Results and discussion

3.1. XRD results

The X-ray diffraction measurements (XRD) performed for the $GdNi_{5-x}Cu_x$ system show that all samples crystallize in the hexagonal crystal $CaCu_5$-type of structure. In this structure the rare earth atoms are localized in 1a (0 0 0) position. There exist two crystallographic inequivalent Ni sites: 2c (1/3 2/3 0) in the basal plane layer $z = 0$ of mixed atoms (Gd + Ni) and 3g (1/2 0 1/2) in the interleaving layer (Kagome net) at $z = 1/2$. The different ranges of solid solutions for the $LaNi_{5-x}Cu_x$ and $TbNi_{5-x}Cu_x$ series show that copper substitutes for nickel at both positions 2c and 3g with preference to the 2c sites [2,7,8].

The additional small line at about 44° angle has been observed on the diffraction pattern for $x = 1.0$ (Fig. 1a) as well as for other compounds (not shown here). The origin of this line is unknown but could be correlated with the $AuBe_5$ structure, which has the strongest peak (3 1 1) in this range. It could be also a trace of the tetragonal Gd_2Cu_9 phase, for which the melting point (930 °C) is close to the melting point of the $GdCu_5$ phase (920 °C) [12]. Moreover, the temperature dependence of electrical resistivity $\rho(T)$ for the Gd_2Cu_9 compound studied by Alami-Yadri et al. [18] shows characteristic minimum at about 50 K. Close to this temperature we have observed a small additional contribution to the thermal variation of magnetic susceptibility and therefore we can conclude that this impurity trace may come from the Gd_2Cu_9 phase. However, in the studied system this small impurity equals only about several percent.

The intensity of the (2 0 0) Bragg peak is modified for compounds containing Cu, which is correlated with the preferred orientation due to the presence of platey crystallites in the samples. This kind of preferred orientation in the form given by Dollase [20] is described as a function:

$$P_k = [P1^2 \cos^2 \alpha_k + P1^{-1} \sin^2 \alpha_k]^{-3/2} \tag{1}$$

where $P1$ is the refineable parameter and α_k is the acute angle between the scattering vector and the normal to the crystallites (calculated internally from the Miller Index of the crystal platelet face). Typically, for high symmetry space groups, P_k is calculated as a sum over all equivalent reflections since the angle α_k can be different for each reflection.

The lattice parameters a, c and the volume of the unit cell V for the $GdNi_{5-x}Cu_x$ system are presented in Fig. 1b. The Ni/Cu substitution causes an increase of both lattice parameters. This behaviour is connected with different sizes of atomic radii for Ni (1.24 Å) and Cu (1.28 Å). However, the difference in atomic radius between these two elements is not so big as e.g. nickel and gallium or aluminum, therefore substitution Cu for Ni does not change type of crystal structure as in the case of the compounds containing e.g. Al, Ga,or Sn [2,7,13].

Thus, in the $GdNi_{5-x}Cu_x$ series the $a(x)$ lattice parameter exhibits almost linear dependence according to Vegard's law. The $c(x)$ parameter as well as the volume of the unit cell indicates a deviation from linearity. This behaviour is probably connected with the substitution of copper in preferred position in transition metal sublattice.

3.2. Magnetic properties

The thermal variation of AC magnetic susceptibility $\chi_{AC}(T)$ for all studied samples is presented in Fig. 2. The values of the temperature of magnetic phase transition (T_{mag}) have been estimated from the derivative $d\chi_{AC}/dT$ (not shown here). The highest T_{mag} we have observed for the samples with $x = 0.5$, 1.0 and 1.5 (see Table 1). The maximum in T_{mag} has been found for $x = 1.0$. Similar behaviour has been already observed by Kuchin et al. [3,4]. Further increasing of copper concentration leads to the drop in T_{mag} to 13.5 K for $x = 4.8$.

The values of T_{mag} have been also estimated from thermal variation of magnetizations $M(T)$, which have been measured below the room temperature. A quite good agreement between T_{mag} obtained from $\chi_{AC}(T)$ as well as $M(T)$ measurements has been found. Thermal variation of magnetization $M(T)$ has been obtained in two modes. In the first mode the samples have been cooled from 300 K to 4.2 K in a zero magnetic field (ZFC). Then the magnetic field of 1 T has been applied and the magnetization has been measured with the increase of temperature up to 300 K. In the second mode the field–cooled curves (FC) have been obtained in a similar manner except that the samples have been cooled with the measuring field on.

The selected ZFC–FC curves (for the $GdNi_5$ and $GdCu_5$ samples) are presented in Fig. 3. The $\chi_{DC}(T)$ susceptibility in the paramag-

Table 1
Magnetic properties of $GdNi_{5-x}Cu_x$ compounds.

x	T_{mag} [K] from χ_{AC}	T_{mag} [K] from $M(T)$ $T < 300$ K	μ_{eff} [μ_B/f.u.] $T < 300$ K	θ_p [K] $T < 300$ K	$\chi_0 \times 10^{-3}$ [emu/Oe mol]	M_S [μ_B/f.u.]	M_S/3d atom [μ_B/f.u.]	μ_{eff} [μ_B/f.u.] $T > 300$ K	θ_p [K] $T > 300$ K
0.0	33.7	32.1	7.56	33.8	3.17	6.77	−0.05	8.35	7.24
0.5	37.4	–	–	–	–	–	–	8.67	16.6
1.0	37.6	38.5	7.21	51.5	6.21	7.10	−0.02	7.98	25.2
1.5	36.8	–	–	–	–	–	–	8.40	25.8
2.0	30.2	33.1	8.09	38.3	−1.91	8.05	0.21	8.27	47.6
3.0	25.6	29.7	7.87	41.4	3.5	8.61	0.32	8.26	32.7
4.0	32.8	36.1	8.28	35.3	−0.85	8.30	0.26	8.31	39.6
4.5	12.9	9.9	8.02	19.4	5.5	6.61	−0.08	8.32	15.4
4.8	13.5	16.3	7.71	9.14	9.44	5.62	−0.28	8.27	7.61
5.0	30.2	31.3	7.09	7.1	1.7	4.60	−0.48	8.56	3.20

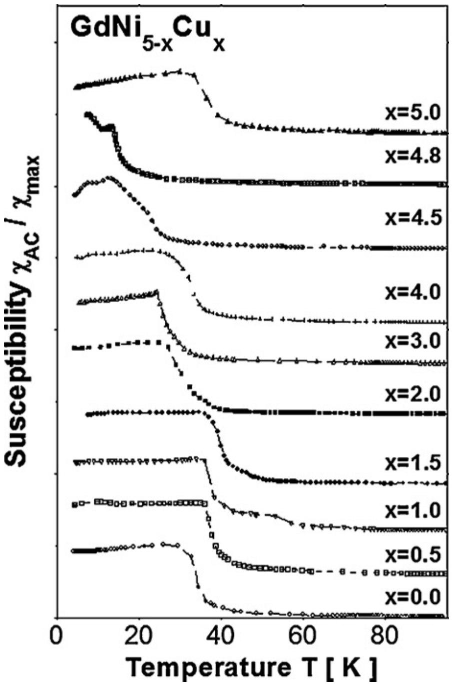

Fig. 2. The temperature dependence of χ_{AC} susceptibility for $GdNi_{5-x}Cu_x$ compounds.

netic range up to 300 K obeys the modified Curie–Weiss type of behaviour:

$$\chi_{DC} = \chi_0 + \frac{C}{(T - \theta_p)} \tag{2}$$

where C is the Curie constant, θ_p is the paramagnetic Curie temperature and χ_0 is the temperature independent element which includes the diamagnetic susceptibility of the core electrons, the Pauli paramagnetic contribution of the conduction electrons and eventually also a Van Vleck contribution. The values obtained from fitting $1/\chi_{DC}(T)$ dependence below 300 K with the use of Eq. (2) are listed in Table 1. For the $GdNi_5$ compound the effective magnetic moment μ_{eff} obtained from the Curie constant equals about $7.56\mu_B$/f.u. This value is smaller than μ_{eff} of free Gd^{3+} ion which may suggest the opposite arrangement of Gd to Ni moments. This behaviour can be related to the negative polarization of Ni3d band by Gd5d. Such an arrangement in the $GdNi_5$ compound has been already proved by the band structure calculations [22].

The Ni/Cu substitution causes a slight change of the μ_{eff} values. The highest value has been evidenced for $x = 4.0$ (see Table 1, Fig. 3e). Further copper substitution is reflected in the quite different $M(T)$ behaviour in the low temperature range. For the Cu-rich compounds ($x \geq 4.5$) the difference between FC and ZFC curves is much more distinct. Thus, for ZFC curves at low temperature range the magnetization is smaller than in FC mode and exhibits a maximum. The ZFC–FC dependencies observed for Cu-rich compounds are probably related to the incomensurate magnetic structure which has been already found for the $GdCu_5$ compounds [5].

The reciprocal susceptibility for the $GdCu_5$ compound follows the modified Curie–Weiss law between 75 K and 300 K. The value of μ_{eff} for this compound is close to $GdNi_5$ and equals about $7.9\mu_B$/f.u. Below 75 K the $1/\chi_{DC}(T)$ decreases faster than linear variation but never vanishes and its value is small and quite constant below 25 K. This kind of behaviour has been already observed by Barandiaran et al. [5]. Additionally, the value of θ_p for $x = 5.0$ is much lower than for the others compounds. It may be connected with the change of magnetic interactions with the increase of copper content.

The temperature dependence of the reciprocal DC susceptibility $1/\chi_{DC}(T)$ measured in the paramagnetic range above 300 K follows the Curie–Weiss type behaviour for all investigated compounds. The values of effective magnetic moment μ_{eff} calculated from the Curie constant are higher than for free Gd^{3+} ion and equals $8.35\mu_B$/f.u. ($x = 0.0$) and $8.56\mu_B$/f.u. ($x = 5.0$). Similar enhancement of μ_{eff} was already observed in many compounds containing gadolinium [1,2,9]. It is the result of short-range correlations between Gd magnetic moments and spin fluctuations in d-electron sublattice. The $\mu_{eff}(x)$ change is not large, but the values of effective moments deduced from the Curie constant are a little bit higher than obtained bellow 300 K (see Table 1, Fig. 3c). Similar behaviour has been previously reported e.g. for the $Gd(Ni_{1-x}Al_x)_5$ compounds [9]. Two different values in two different temperature ranges are probably connected with the T^* temperature, where the system behaves as if having local moments. Usually above this characteristic point some intermetallic compounds indicate additional local moments coming from the spin fluctuations [1,2,7,9,21,22].

The field dependence of magnetization $M(H)$ obtained at 4.2 K is shown in Fig. 4. The value of $M(H)$ saturates at field 9 T for $x = 0.0$ and 1.0. The values of the saturation magnetic M_S moment have been estimated by applying extrapolation to the infinite field (see Table 1). The value of saturated magnetic moment for $GdNi_5$ ($6.77\mu_B$/f.u.) obtained from magnetic isotherm is similar to that obtain from theoretical calculations of band structure ($6.75\mu_B$/f.u.) which were based on KKR and KKR–CPA methods and were performed in the ground state [22]. Those calculations indicated that magnetic moments of Ni in 2c ($-0.02\mu_B$/atom) and 3g ($-0.06\mu_B$/atom) crystallographic positions are oriented antiparallel to Gd moments.

For middle copper concentration ($2.0 \leq x \leq 4.0$) the value of M_S is higher than for free Gd^{3+} ion ($7\mu_B$). Meanwhile, for the other Cu-rich compounds this value decreases and is lower than for free Gd^{3+} ion (see Table 1 and Fig. 4b). The $M_S(x)$ dependence is probably connected with the magnetic and electronic structure of those compounds. As it was already reported [5] in the $GdCu_5$ compound gadolinium moments form a triangular lattice in the layer perpendicular to c-axis and make an angle about 80 °C between Gd moments from the same column between the two layers. This kind

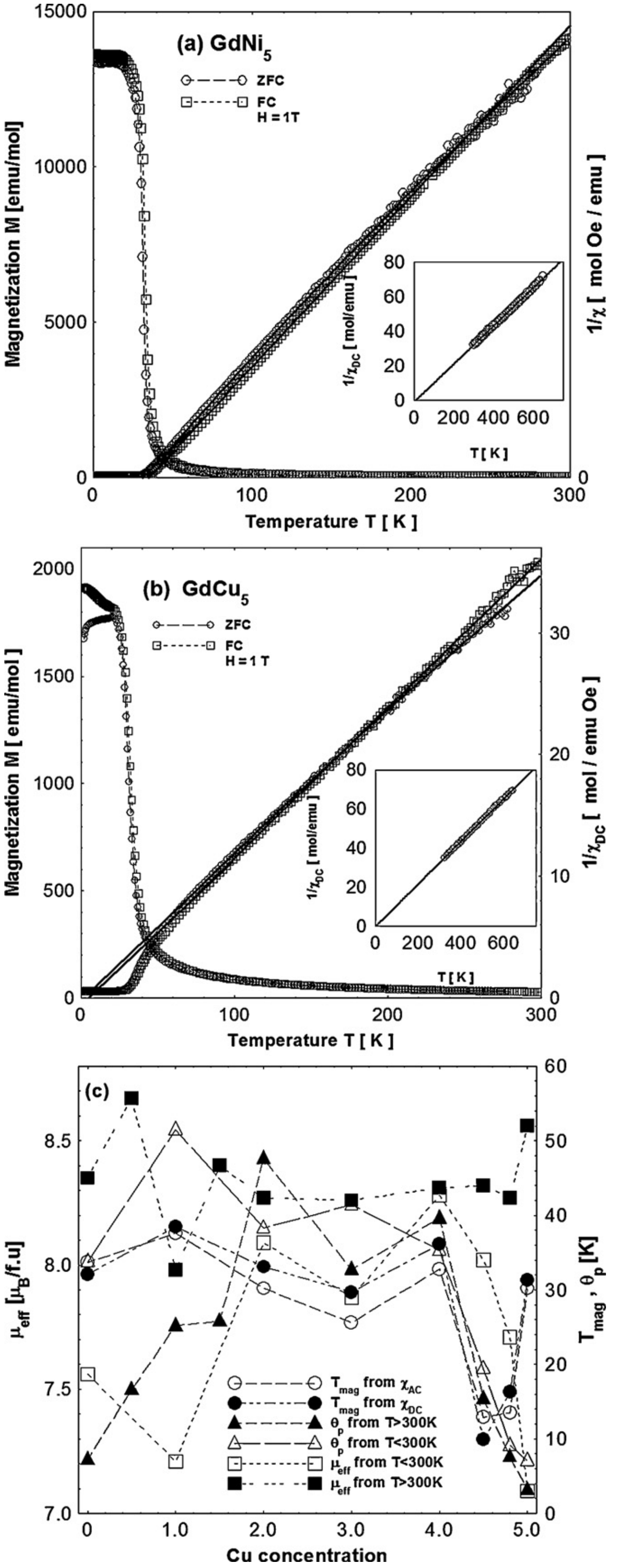

Fig. 3. Thermal variation of magnetization $M(T)$ and reciprocal susceptibility $1/\chi_{DC}(T)$ for: (a) $GdNi_5$, (b) $GdCu_5$ compounds. Insets represent the reciprocal susceptibility above 300 K. (c) Magnetic properties of the $GdNi_{5-x}Cu_x$ compounds estimated below and above room temperature.

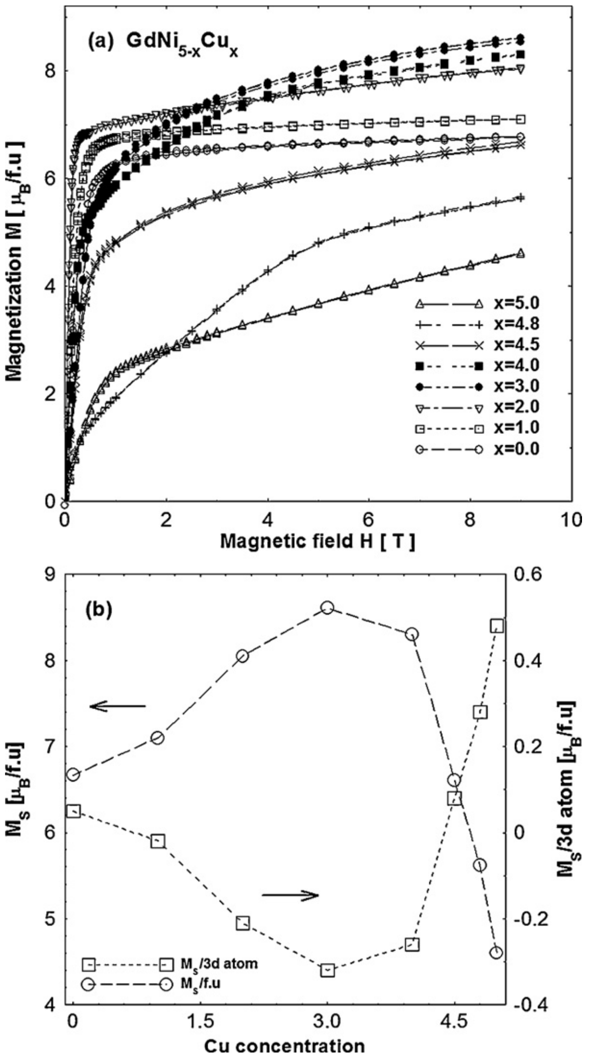

Fig. 4. (a) Magnetic field dependence of the magnetization M for the $GdNi_{5-x}Cu_x$ series where $x = 0.0$, 1.0, 2.0, 3.0, 4.0, 4.5, 4.8 and 5.0. (b) The change of magnetic moment per M_S/f.u. and M_S/3d atom in the $GdNi_{5-x}Cu_x$ system.

of structure is correlated with the presence of extra band gaps and therefore below T_{mag} the conduction electrons feel a new magnetic ordering potential besides the usual lattice potential. It is reflected in thermal variation of resistivity [5,19]. The value $M(H)$ for the $GdCu_5$ compound equals $4.60\mu_B$/f.u. and is close to that obtained by Barandiaran et al. [5].

The values of the transition magnetic moment per 3d atom are presented in Table 1. These 3d moments have been calculated from the values given for the saturation moment after substraction the value of the free Gd^{3+} ion. The calculations have shown the existence of a very small magnetic moment on Ni atoms in the $GdNi_5$ compound. With the further increase of Cu concentration the value of 3d moment increases up to $0.32\mu_B$/3d for $x = 3.0$ and next decreases. For the $GdCu_5$ compound M_{3d} equals $-0.48\ \mu_B$/3d. The negative values of the magnetic moment per 3d atom for the Ni-rich and Cu-rich compounds can mean the opposite arrangements of magnetic moments in 4f and 3d sublattices. For $1.0 \leq x \leq 4.0$ copper concentration the values of M_{3d} are positive. It means that in this range we have observed ferromagnetic-like structure. Generally, the magnetic moment as well as the temperature of phase transition depends on f–d exchange interactions. We can assume that for the whole studied copper concentrations the 4f–4f and 4f–3d interactions are dominant. It is reflected in the change of all magnetic

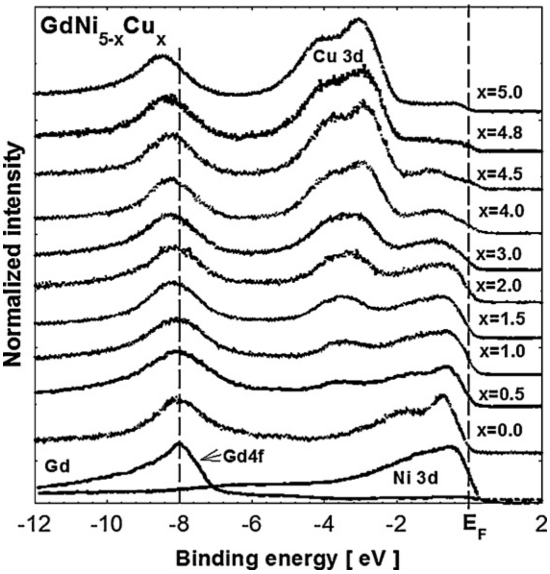

Fig. 5. The XPS valence bands for $GdNi_{5-x}Cu_x$ compounds and for Gd and Ni elements.

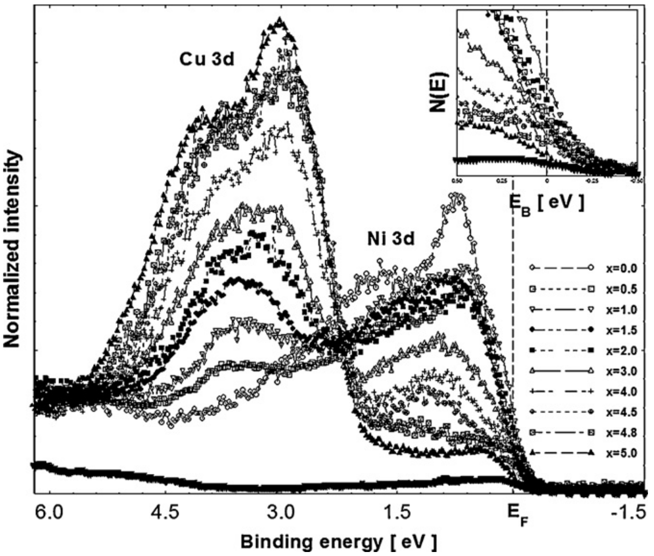

Fig. 6. The XPS valence bands near by Fermi level for $GdNi_{5-x}Cu_x$ compounds.

parameters with the increase in Cu content. It seems to be that for middle copper content 3d–3d interactions play an important role. It is reflected in the $M_{3d}(x)$ change. However, this dependence can be also the consequence of the charge transfer from Gd to 3d atoms.

3.3. Electronic structure

The XPS analysis indicates that Ni/Cu substitution has a big influence on electronic structure of the investigated $GdNi_{5-x}Cu_x$ system. The XPS valence bands (VB) normalized to Gd4f peak are shown in Fig. 5. For the $GdNi_5$ compound the VB near by the Fermi level (E_F) is dominated by Ni3d states, which have the maximum at about 0.7 eV. The shape of VB observed for this compound is typical for other RNi_5 compounds where Ni states are dominant at E_F [9,23]. For the Ni-rich and Cu-rich compounds there is visible an exchange splitting of 3d band. This splitting gradually vanishes with the increase of copper content. As a consequence in the $GdNi_{5-x}Cu_x$ system the valence bands near by E_F indicate a significant change. The more intense lines are located at about 8 eV (Gd4f), 3 eV (Cu3d) and 1 eV (Ni3d) binding energies. With the increase of copper content the intensity of Cu3d states and respectively decreasing of the intensity of Ni3d states is visible. The highest intensity of states at the Fermi level $N(E_F)$ has been observed for $x = 1.0$ concentration (Fig. 6). Simultaneously, the T_{mag} is the highest for this copper concentration. So, the $N(E_F)$ dependence for the studied system strongly depends on f–d interactions and can be connected with the change of $T_{mag}(x)$.

On the basis of model proposed by Campbell [24,25] and its reinterpretation made by e.g. Brooks et al. [24,26] the 4f–3d interactions involve 4f–5d and 4f–4f local interaction at R atom, 3d–3d exchange and 3d–5d hybridization. This hybridization causes the polarization of mixed 3d band which influences on f–f interactions. Therefore the change of T_{mag} may be connected with enhancement of f–f interactions, the decrease of the effective exchange constant of f–d interactions (Γ) and the reduction of polarization of mixed 3d band with the increase of Cu concentration. The variation of $T_{mag}(x)$ for the $GdNi_{5-x}Cu_x$ system should be the result of a band structure effect via Γ and the density of states $N(E_F)$ at the Fermi level according to the following expression:

$$T_{mag} \sim (g-1)^2 J(J+1)\Gamma^2 N(E_F) \quad (3)$$

where $(g-1)^2 J(J+1)$ is de Gennes factor. From our measurements we have observed the highest value of T_{mag} for $x = 1.0$ and simultaneously the intensity of states at the Fermi level determined from XPS investigations for these compounds is the highest (Fig. 5). For the other compounds some rough scaling between T_{mag} and $N(E_F)$ can be found, but also the influence of Ni/Cu substitution on the effective exchange constant Γ which describes a function of the filling degree of the Ni3d band should be taken into account.

For $x > 1.0$ the states at E_F mainly have s–p character with the small contribution of hybridized Ni3d–Gd5d states. The significance increase of s states on E_F is closely related to the charge transfer from Gd to Cu because this transfer concerns the most outer electrons. In the $GdCu_5$ compound d states on E_F mainly comes from Gd5d. The visible reduction of d states on E_F with the increase of Cu concentration and their shift to the higher binding energy is typical for d–metals and their alloys when d-state occupancy is increasing. In consequence the decrease of states at Fermi level is observed. This kind of behaviour can be the proof of gradual filling of 3d band.

The position of the Gd4f states in $GdNi_5$ is almost the same as in pure Gd. 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). Similar satellite structure at about 6 eV below the main line is observed for the Ni2p core level spectra. The energy shift of Gd4f line to higher binding energies as compared to $GdNi_5$ has been evidenced for all studied compounds (see Table 2). Thus, the position of Gd4f line changes from about 8.1 eV ($x = 0.0$)

Table 2
The measured chemical shifts of Gd4f, Cu2p and Ni2p photoelectron lines in relation to pure elements.

x	Gd 4f 8 eV	Cu $2p_{3/2}$ 932.7 eV	Ni $2p_{3/2}$ 852.65 eV
0.0	+0.07	0.00	0.00
0.5	+0.09	0.00	+0.20
1.0	+0.10	−0.40	+0.23
1.5	+0.17	−0.33	+0.25
2.0	+0.20	−0.31	+0.34
3.0	+0.26	−0.29	+0.41
4.0	+0.28	−0.27	+0.45
4.5	+0.30	−0.25	+0.46
4.8	+0.35	−0.22	+0.48
5.0	+0.45	−0.10	–

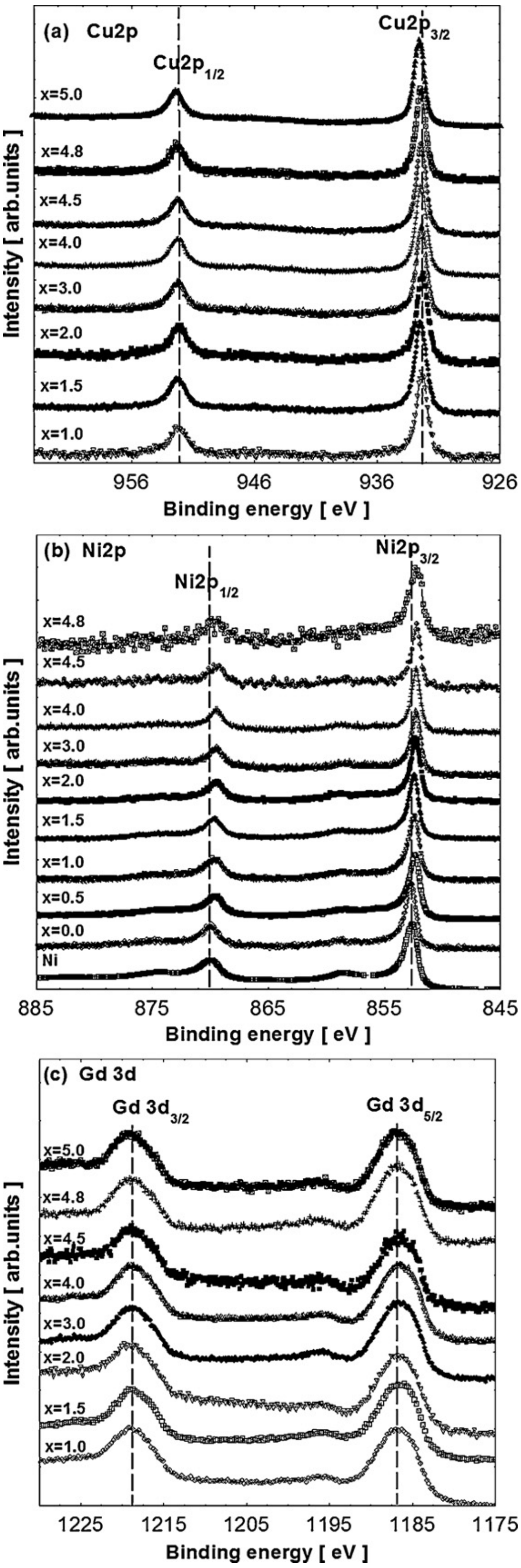

Fig. 7. The core level spectra in the $GdNi_{5-x}Cu_x$ system: (a) Cu2p core level; (b) Ni2p core level line and (c) Gd3d level line.

to 8.45 eV ($x = 5.0$). This shift may be correlated with the change of local environment of gadolinium atoms and is connected with the charge transfer from Gd to neighbouring ions. Similar behaviour has been already evidenced for other Gd–Cu compounds [27]. We have also observed some changes in Cu3d band as an influence of Cu concentration. For the Cu-rich compounds one can observe the presence of two broadened peaks at about 3 eV and 3.9 eV connected with the exchange splitting of the 3d band. The spectral weight of Cu3d shows a small shift to lower binding energy in relation to pure Cu which is in contrary to Cu2p level. This can be caused by the overlapping wave functions from neighbouring atoms.

The increase of Cu concentration in the $GdNi_{5-x}Cu_x$ series causes the chemical shifts of core levels Cu2p to a higher binding energy (Fig. 7a). At the same time the decrease of Ni concentration gives the shift of core level lines Ni2p (Fig. 7b) to lower binding energy from about 852.65 eV ($x = 0.0$) to about 852.19 eV ($x = 4.5$). This kind of shift is also connected with the charge transfer from Gd to Cu which causes the change of local environment of Ni atoms. So, we can assume that the change of magnetic properties is caused by f–d exchange interaction as well as the charge transfer from Gd to Cu which is confirmed by the energy shifts of Gd4f as well as Cu2p and Ni2p lines.

For the core level lines Gd3d we have not observed any shifts (Fig. 7c) because Gd3d level lies deeply and is good isolated. All studied core level lines exhibit spin–orbit (L–S) splitting. In the case of Cu2p line the L–S parameter (Δ) equals about 19.8 eV. For Ni2p line this parameter is about 17.3 eV and for Gd3d around 32.1 eV. With increasing copper content Δ is almost unchanged for all measured lines. The satellite lines located about 6 eV below main $Ni2p_{3/2}$ line are observed in all investigated samples and are correlated with not fully filled d band of Ni. Thus, the change in the magnetic properties for the $GdNi_{5-x}Cu_x$ series can be easily correlated to the electronic structure.

4. Conclusions

In this work we present magnetic properties, crystal and electronic structure of the $GdNi_{5-x}Cu_x$ series. From all performed measurements the following conclusions can be drawn:

In the present work it has been proved that the substitution of Ni/Cu substitution causes the increase of both lattice parameters as well as the volume of the unit cell. The *a* lattice parameter exhibits almost linear dependence according to Vegard's law whereas the *c* lattice parameter shows the deviation from the linearity.

The value of the magnetic phase transition temperature T_{mag} increases from 33.7 K ($x = 0.0$) up to 37.6 K ($x = 1.0$). For higher copper concentration T_{mag} decreases gradually to 13.5 K ($x = 4.8$). For $GdCu_5$ compound the value of T_{mag} equals 30.2 K. The values of saturation magnetization M_S are smaller than for free Gd^{3+} ion ($7\mu_B$) only for Ni-rich ($6.77\mu_B$/f.u. – $x = 0.0$) and Cu-rich ($4.60\mu_B$/f.u. – $x = 5.0$) compounds. For the $1.0 \leq x \leq 4.0$ copper content the magnetizations are higher than $7\mu_B$. The $T_{mag}(x)$ and $M_S(x)$ dependencies are correlated with f–d interactions, magnetic and electronic structure of studied series. The values of the effective magnetic moment in the paramagnetic range are higher than for Gd^{3+} ion.

The magnetic properties of studied system are closely related to the electronic structure. The XPS results show the gradual reduction of Ni3d and at the same time the increase of Cu3d states close to the Fermi level. The $N(E_F)$ indicates maximum for $x = 1.0$. Moreover, T_{mag} indicates the maximum for the same copper content. The chemical shifts of Gd4f, Cu2p and Ni2p lines are connected with the charge transfer from Gd to Cu which concerns the most outer s electrons. Such energy shifts are correlated with the change of local environment of Gd ions with the increase of Cu concentration.

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