

# Crystal structures and magnetic properties of nickel based compounds

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The  $RNi_5$  compounds where R is a rare-earth or yttrium crystallize in a hexagonal structure of  $CaCu_5$ -type. This structure is maintained in  $RNi_{5-x}M_x$  systems with  $M = Cu$  or  $Al$  up to  $x=2$ . Magnetic measurements and band structure calculations were performed in order to determine the magnetic moments at Ni sites in  $RNi_{5-x}M_x$  compounds with  $R=Nd, Tb, Dy$  and  $Ho$  as well as in  $Gd_xLa_{1-x}Ni_5$  one. The  $LaNi_{5-x}M_x$  are paramagnetic. A critical field of the order of 0.4 MOe is necessary to induce a Ni moment. Then, the nickel moments are linearly dependent on exchange fields. The magnetic behaviour of nickel in the above systems is analysed in models that take into account electron correlations effects in d bands.

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## 1. Introduction

The  $RNi_5$ -based compounds, where R is a rare-earth or yttrium have been intensively studied in correlation with their use as hydrogen storage materials [1]. The above compounds crystallize in a hexagonal structure of  $CaCu_5$ -type having  $P6/mmm$  space-group. In this structure the R atoms occupy 1a-type site and nickel ones are distributed on 2c and 3g positions. Generally, multicomponent hydrogen storage alloys, based on  $RNi_5$ , are used for practical applications. Among the elements replacing nickel, Co, Mn, Al and Cu are the most important.

In this paper we report the crystal structures, magnetic properties and band structure calculations on some  $RNi_{5-x}M_x$  compounds with  $M=Al$  and  $Cu$  as well as of  $Gd_xLa_{1-x}Ni_5$  system. The Curie temperatures of these alloys are very low, the maximum value  $T_c=35$  K, being reported for  $GdNi_5$  [1,2]. The magnetic behaviour of nickel in  $RNi_5$ -based compounds has been little analysed. In earlier studies on  $RNi_5$  systems, it was reported that nickel is not magnetic [1]. Analysing the magnetic properties of  $Gd_xA_{1-x}Ni_5$  with  $A=Y$  [2] or  $La$  [3] has been shown that nickel 3d band is polarized in  $GdNi_5$  and has a magnetic moment  $M_{Ni} \cong 0.16 \mu_B/\text{atom}$ . The  $LaNi_5$  and  $YNi_5$  are paramagnetic. Above a characteristic temperature,  $T^*$ , the reciprocal susceptibilities follow a Curie-Weiss behaviour [3].

The previous studies showed that  $RNi_{5-x}Cu_x$  compounds with  $R=La$  [4] and  $Nd$  [5], for  $x \leq 2$ , crystallize in a  $CaCu_5$ -type structure. In case of  $RNi_{5-x}Al_x$  with  $R=Nd, Gd$  [6],  $Dy$  [7,8] and  $La$  [9], the structure changes from  $CaCu_5$ -type to  $HoNi_{2.6}Ga_{2.4}$ -type, at  $x > 1.5$ , having also  $P6/mmm$  space group.

## 2. Experimental and computing method

The samples were prepared in an induction or arc furnace, in purified argon atmosphere. The samples were thermally treated in vacuum, at temperatures between 900 and 1000°C, during 5 up to 6 days. The composition dependences of lattice parameters for  $DyNi_{5-x}Al_x$  and  $NdNi_{5-x}Cu_x$  series are given in Fig. 1. For  $RNi_{5-x}Cu_x$  compounds with  $R=La, Nd$ , the presence of  $CaCu_5$ -type structure was shown for  $x \leq 2$ . For higher Cu content, a second phase was observed. In case of  $RNi_{5-x}Al_x$  with  $R=La, Tb, Dy, Ho$  and  $x \leq 1.5$  also a  $CaCu_5$ -type structure was shown. For  $2 \leq x \leq 3$ , the structure changes to a  $HoNi_{2.6}Ga_{2.4}$ -type. This structure is also hexagonal, but having a larger unit cell than  $CaCu_5$ -type. The unit cell parameters of the two types of structures are related by

$$a_{HoNi_{2.6}Ga_{2.4}} = \sqrt{3} a_{CaCu_5} \quad \text{and}$$

$c_{HoNi_{2.6}Ga_{2.4}} = c_{CaCu_5}$  [6]. In  $CaCu_5$ -type structure, the aluminium substitution takes place at the 3g site, situated in the  $z=1/2$  plane which does not contain R atoms. These sites allow greater Ni-Al distances. The total filling of the 3g site by Al is not possible since  $Ni(2c)-Ni(3g)$ ,  $Al(3g)-Al(3g)$  or  $Ni(3g)-Al(3g)$  distances are smaller than the sum of metallic radii  $r_{Ni}+r_{Al}$  or  $r_{Al}+r_{Al}$ . The occurrence of  $HoNi_{2.6}Ga_{2.4}$  superstructure induces an increase of the  $Al(3g)-Ni(6k)$  and  $Al(3f)-Al(6k)$  distances making the possibility to locate aluminium in 3f and 6k sites. In this structure nickel occupies completely 6l sites and aluminium 3f sites. The 6k sites are statistically occupied by Ni and Al.

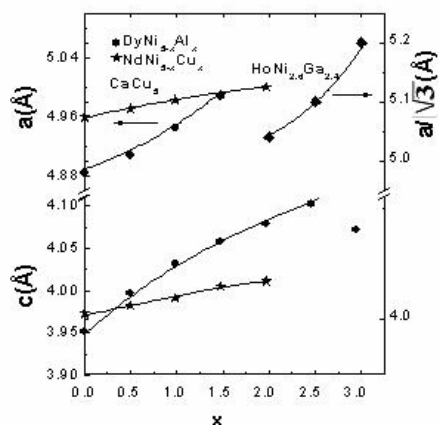


Fig. 1. Composition dependences of the lattice parameters for  $\text{NdNi}_{5-x}\text{Cu}_x$  and  $\text{DyNi}_{5-x}\text{Al}_x$  compounds.

Magnetic measurements were performed in the temperature range 1.7-300 K and fields up to 9 T. The saturation magnetizations,  $M_s$ , were determined from magnetization isotherms, according to approach to saturation law,  $M = M_s(1-a/H) + \chi_0 H$ , by subtracting the Pauli type contribution,  $\chi_0$  and extrapolating the measured values at  $H^{-1} \rightarrow 0$ . By  $a$  is denoted the coefficient of magnetic hardness. In the paramagnetic range, the susceptibilities,  $\chi$ , were determined from their field dependences, according to the relation  $\chi_m = \chi + bM_s H^{-1}$ , by extrapolating the measured values,  $\chi_m$ , to  $H^{-1} \rightarrow 0$ . By  $b$  is denoted a presumed magnetic ordered impurity content and  $M_s$  is their saturation magnetization.

Band structure calculations were carried out on  $\text{LaNi}_5$ ,  $\text{RNi}_5$  ( $M = \text{Cu}, \text{Al}$ ), and  $\text{RNi}_{5-x}\text{Al}_x$  ( $R = \text{Dy}, \text{Ho}$ ) systems, by using the ab initio tight binding linear muffin-tin orbitals method in atomic sphere approximation (TB-LMTO-ASA). The procedure of calculation was described elsewhere [10,11]. In the framework of the local density approximation (LDA), the total electronic potential is the sum of external, Coulomb and exchange-correlation potentials [12]. The functional form of the exchange correlation energy used was the free-electron gas parametrization of Von Barth and Hedin [13]. Relativistic correlations were included. For  $\text{NdNi}_{5-x}\text{Cu}_x$  and  $\text{TbNi}_{5-x}\text{Al}_x$  systems, band structure calculations were performed by using TB-LMTO method within LDA=U approach [14,15]. The LDA+U scheme is based on the Anderson impurity model in mean field (Hartree-Fock) approximation, that analyses the s- and p- electrons as noncorrelated, described by an orbital independent potential and d and f electrons are described by an orbital dependent potential [16]. In case of  $\text{RNi}_{5-x}\text{Cu}_x$  systems, the Cu atoms, for  $x=1$ , were supposed to occupy the 3g sites, while for higher Cu concentrations both 2c and 3g positions. For  $\text{RNi}_{5-x}\text{Al}_x$  compounds with  $x \leq 1.5$ , for band structure calculations, the Al was introduced in 3g sites. In case of  $\text{HoNi}_{2.6}\text{Ga}_{2.4}$  superstructure, one Al was located in 3f sites and one or two aluminium atoms were distributed on 6k sites.

### 3. Band structures

The total density of states as well as the Ni3d band projected DOS for some  $\text{RNi}_5$  compounds are plotted in Fig. 2. When R is a magnetic rare-earth, ordered Ni moments, at 0K, were shown. The Ni moments,  $M_{\text{Ni}}$ , are antiparallely aligned to R ones, for heavy rare-earth compounds ( $R = \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$ ), and parallelly oriented in case of light rare-earth (Nd) ones. The nickel is not magnetic in  $\text{LaNi}_5$  and  $\text{YNi}_5$  compounds. The Ni moments at 2c and 3g sites in  $\text{RNi}_5$  compounds with heavy rare-earths are plotted in Fig. 3 as function of De Gennes factor. Higher values were determined

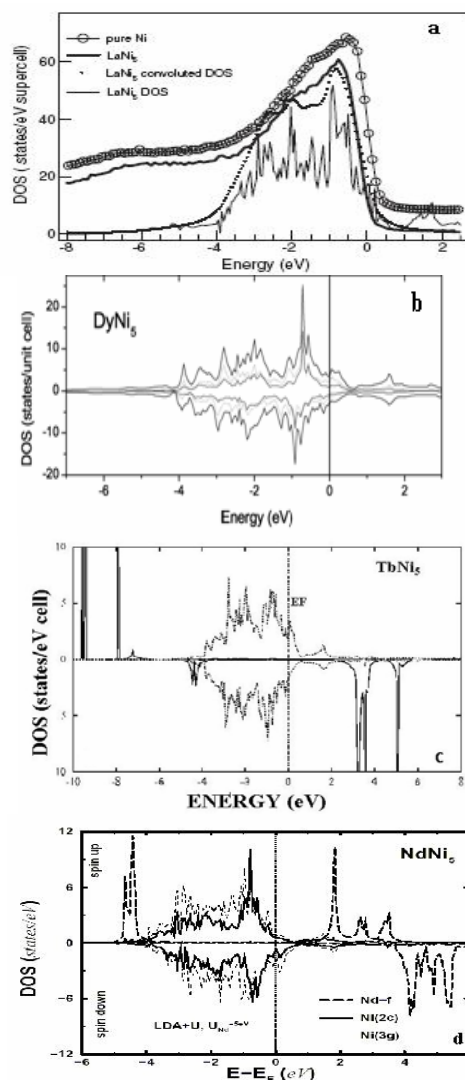


Fig. 2. Projected densities of states for  $\text{LaNi}_5$  (a),  $\text{DyNi}_5$  (b),  $\text{TbNi}_5$  (c) and  $\text{NdNi}_5$  (d). In (a) a comparison of the measured XPS valence (thick solid line) and convoluted DOS (by Lorentzian of half width of 0.4 eV taking into account proper cross sections for partial bands with different  $l$  symmetry; dashed line) for  $\text{LaNi}_5$ . The XPS valence band spectrum of Ni is also plotted.

for 3g sites. This behaviour can be attributed to different local environments. The 2c sites have 6Ni(3g) and 3Ni(2c) atoms as well as 3R ones, while 3g sites have 4Ni(2c), 4Ni(3g) and 4R atoms as nearest neighbours. The strength of exchange interactions between Ni and a magnetic R atoms is higher than between nickel ones, the Ni moments being essentially induced. Since the Ni3d(3g) sites have more R atoms as nearest neighbours, the exchange splitting of Ni3d(3g) band is greater than for Ni(2c) ones. As example, in NdNi<sub>5</sub>, the exchange splitting of Ni3d(3g) band, of 0.01 eV, is greater than that at Ni3d(2c) sites, of 0.0066 eV. As a general feature, we note that the contributions of Ni atoms to the magnetizations of RNi<sub>5</sub> compounds are relatively small, particularly in heavy rare-earth compounds.

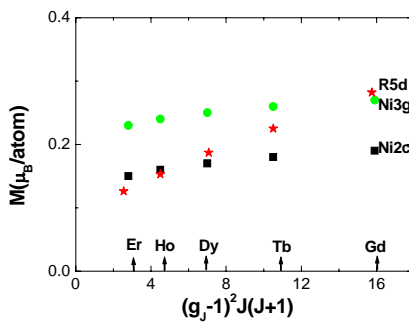


Fig. 3. The dependences of Ni moments at 2c and 3g sites as well as the R5d band polarizations in RNi<sub>5</sub> compounds with heavy rare-earths, as function of De Gennes factor.

The nickel moments, as well as the Gd5d and La5d band polarizations in Gd<sub>x</sub>La<sub>1-x</sub>Ni<sub>5</sub> system are plotted in Fig.4. An induced polarization on R5d bands is shown. This is in agreement with a model which considers that the exchange interactions can be described by the 4f-5d-3d path. In this model the 4f electrons of rare-earth polarize their 5d bands by local interactions and there are also 5d-3d short-range exchange interactions with Ni atoms. The 5d-3d degree of hybridization depends on the overlap matrix elements and on the energy separation between the 3d and 5d bands.

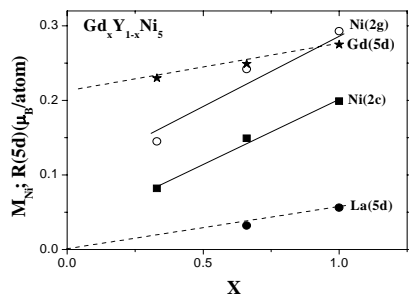


Fig. 4. Composition dependences of the Ni magnetic moments at 2c and 3g sites as well as of Gd5d and La5d band polarizations in Gd<sub>x</sub>La<sub>1-x</sub>Ni<sub>5</sub> compounds.

The M<sub>5d</sub> band polarizations in RNi<sub>5</sub> compounds—Fig.3—can be described by the relation M<sub>5d</sub>=M<sub>5d</sub>(0)+αG with α=1.4·10<sup>-2</sup> μ<sub>B</sub>. The above data suggest the presence of two contributions. The first one, proportional to G, is due to local 4f-5d exchange. The second one, M<sub>5d</sub>(0), can be attributed to 5d-3d and 5d-5d short range exchange interactions. As showed already [3], in RNi<sub>5</sub>-type compounds, there are also exchange interactions between R atoms through 5d<sub>3/2-1</sub> orbitals with lobes pointing along c-axis. The 5d-3d and 5d-5d exchange interactions act an internal field, H<sub>i</sub>, on the 5d band and induce an additional polarization to that determined by 4f-5d local exchange. By using the molecular field approximation, we already showed that M<sub>5d</sub>(0) = γM<sub>d</sub>, where M<sub>d</sub> is total d magnetization, M<sub>d</sub> = M<sub>3d</sub> + M<sub>5d</sub> [3,8]. According to the above relation, for more complex crystal structures, where R atoms are located in sites with different local environments, as in RCo<sub>4</sub>B compounds, the M<sub>5d</sub>(0) band polarization will be proportional to ∑ n<sub>k</sub> M<sub>k</sub>, where n<sub>k</sub> is the number of R and M atoms situated in the first coordination shell to a considered R atom, having M<sub>k</sub> magnetic moments. The M<sub>5d</sub>(0) values are plotted in Fig.5 as function of ∑ n<sub>k</sub> M<sub>k</sub> for some RNi<sub>5</sub> compounds and related RCo<sub>4</sub>B type structures. There is a linear dependence of M<sub>5d</sub>(0) on ∑ n<sub>k</sub> M<sub>k</sub>, in agreement with computed trend. According to the above analysis, we determined the M<sub>5d</sub>(0) induced polarizations in Gd<sub>x</sub>La<sub>1-x</sub>Ni<sub>5</sub> system. Values M<sub>5d</sub>(0) = 0.07; 0.05 and 0.035 μ<sub>B</sub> were obtained for compounds with x = 1.0; 0.67 and 0.33. Admitting that the 4f-5d contribution to the Gd5d band polarization is ≅ 0.20 μ<sub>B</sub>, as showed in Fig.3, total 5d polarizations of 0.27; 0.25 and 0.235 μ<sub>B</sub> were determined, in agreement with those obtained from band structure calculations. Considering the La5d-Ni3d as well as Gd5d-La5d short range exchange interactions we evaluated the polarizations of La5d bands in Gd<sub>x</sub>La<sub>1-x</sub>Ni<sub>5</sub> compounds. Values M<sub>5d</sub>(0) = 0.057 μ<sub>B</sub> (x=0.67) and 0.039 μ<sub>B</sub> (x=0.33) were obtained, also in agreement with computed data.

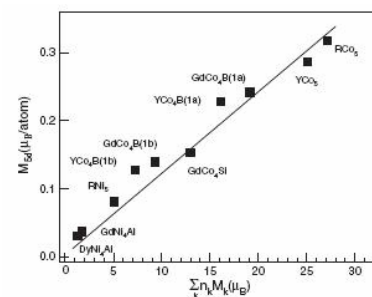


Fig. 5. The M<sub>5d</sub>(0) contributions to 5d band polarizations due to 5d-3d and 5d-5d short range exchange interactions as function of ∑ n<sub>k</sub> M<sub>k</sub>.

#### 4. Magnetic measurements

Representative magnetization isotherms, at 1.7 K, for DyNi<sub>5-x</sub>Al<sub>x</sub> and NdNi<sub>5-x</sub>Cu<sub>x</sub> compounds are plotted in Fig.6. The saturation has been not attained in DyNi<sub>5-x</sub>Al<sub>x</sub> compounds with relatively high Al content, even in field

of 9 T. In addition, the magnetizations decrease when increasing Al content. This behaviour is different from that expected considering an antiparallel alignment of Dy and Ni moments. As the Ni moments decrease, when Ni is gradually replaced by Al, the saturation magnetizations must to increase, different from experimentally observed trend. The above behaviour can be attributed to a micromagnetic type contribution superposed on an essentially ferromagnetic ordering, in aluminium doped samples. The Curie temperatures decrease gradually from  $T_c=13$  K ( $x=0$ ), when increasing Al content.

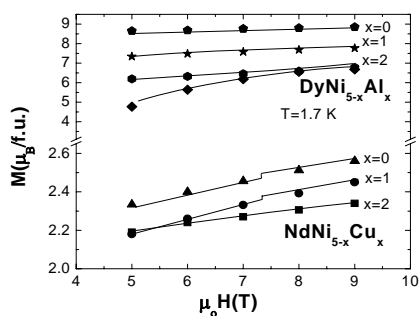


Fig. 6. Magnetization isotherms, at 1.7 K, for  $\text{DyNi}_{5-x}\text{Al}_x$  and  $\text{NdNi}_{5-x}\text{Cu}_x$  compounds.

The magnetization isotherm, at 1.7 K, for  $\text{NdNi}_{5-x}\text{Cu}_x$  system and  $x=0$  suggests the presence of relatively high anisotropy. The  $M=f(H)$  curves saturate at lower fields as the copper content increases. The coefficient of magnetic hardness decreases gradually from  $a=0.92$  ( $x=0$ ) to  $0.32$  ( $x=1.0$ ) and finally at  $0.03$  ( $x=1.5$ ). This suggests that Cu substitutes also nickel in 2c sites, which have the largest orbital moment. The magnetization isotherms for compounds with  $x=0$  and  $0.5$  show small discontinuities between 7 and 8 T. This may be correlated with a possible itinerant metamagnetic transition at some Ni sites. The Curie temperature of  $\text{NdNi}_5$  is  $T_c=9$  K and decreases to 6 K from  $x=1.0$ .

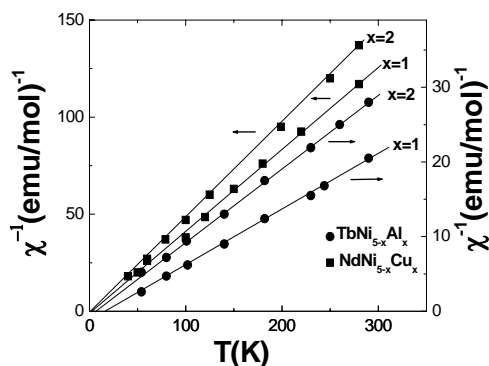


Fig. 7. Thermal variations of reciprocal susceptibilities for some  $\text{TbNi}_{5-x}\text{Al}_x$  and  $\text{NdNi}_{5-x}\text{Cu}_x$  compounds.

The thermal variations of reciprocal susceptibilities for  $\text{TbNi}_{5-x}\text{Al}_x$  and  $\text{NdNi}_{5-x}\text{Cu}_x$  are plotted in Fig.7. The experimental data were analysed considering a modified Curie-Weiss law  $\chi=\chi_0+C(T-\theta)^{-1}$ , where  $\chi_0$  is a Pauli paramagnetic term,  $C$  is the Curie constant and  $\theta$  is the paramagnetic Curie temperature. The Curie constants are somewhat higher than those of free  $R^{3+}$  ions. This suggests the presence of nickel contribution to  $C$  values. According to additional law of magnetic susceptibilities and supposing that the effective moments of  $R$  elements are given by the free ion values, we determined the effective nickel moments. The  $M_{\text{effNi}}$  values decrease when increasing Al or Cu content, particularly in aluminium doped systems – Fig.8. This suggests a strong hybridization of Ni3d and Al3p bands, in agreement with band structure calculations.

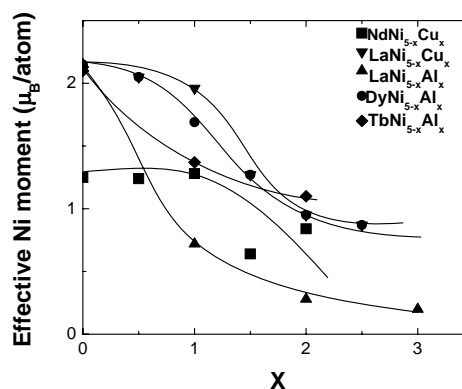


Fig. 8. Composition dependences of the effective nickel moments.

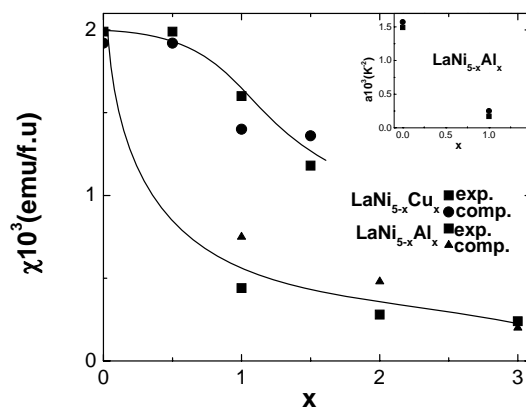


Fig. 9. Composition dependences of the susceptibilities, determined at 1.7 K, in  $\text{LaNi}_{5-x}\text{M}_x$  with  $M = \text{Cu}$  or  $\text{Al}$  and those obtained from band structure calculations. In inset the determined and computed a values for  $\text{LaNi}_{5-x}\text{Al}_x$  with  $x = 0$  and  $1.0$  are given.

The magnetic behaviour of paramagnetic  $\text{LaNi}_{5-x}\text{M}_x$  compounds with  $\text{M}=\text{Cu}$  or  $\text{Al}$  were also studied [4]. The magnetic susceptibilities, at 1.7 K,  $\chi(0)$  decrease as result of substitutions – Fig. 9. The  $\chi(0)$  values were also determined from state densities at the Fermi level. There is a good agreement between experimentally determined values and the computed ones. At  $T < 10$  K, the susceptibilities follow a  $T^2$  dependence described by the relation  $\chi=\chi(0)[1+\alpha T^2]$  – Fig. 10. The  $\alpha$  values determined in  $\text{LaNi}_{5-x}\text{Al}_x$  are plotted in Fig. 9 inset. From band structures we evaluated also the  $\alpha$  parameter by considering the paramagnon model [18]:

$$\alpha = \frac{\pi^2}{6} \left[ 2 \frac{N''(E_F)}{N(E_F)} - 1.2 \left( \frac{N'(E_F)}{N(E_F)} \right)^2 \right] S^2 \quad (1)$$

We denoted by  $s$  the Stoner enhancement factor and  $N(E_F)$ ,  $N'(E_F)$  and  $N''(E_F)$  are the density of states at the Fermi level and their first and second derivative, respectively. We selected a symmetric energy interval around the self-consistent value at the Fermi level and we used a mean square interpolation scheme in order to analytically evaluated the energy dependence of the density of states. This approach allowed us to evaluate the first and the second derivative of the DOS at the Fermi level. The  $\alpha$  values, obtained according to relation (1), agree reasonable with those experimentally determined – Fig. 9 inset.

The susceptibilities of  $\text{LaNi}_{5-x}\text{M}_x$  compounds increase up to a temperature  $T_{\max}$  and at  $T > T^*$ , the  $\chi^{-1}$  vs  $T$  values follow a modified Curie-Weiss behaviour – Fig.11. The effective Ni moments determined from Curie constants are given in Fig. 8.

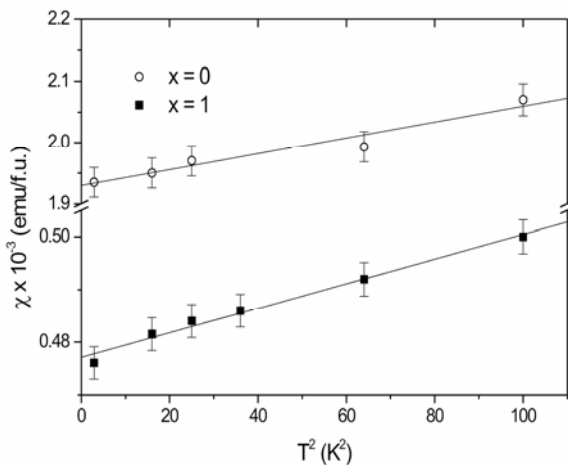


Fig. 10. Thermal variations of magnetic susceptibilities for  $\text{LaNi}_{5-x}\text{Al}_x$  with  $x = 0$  and  $1.0$ , at  $T \leq 10$  K.

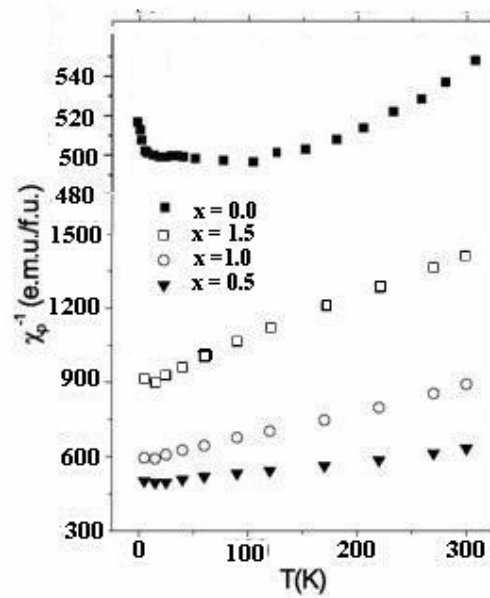


Fig. 11. Thermal variations of reciprocal susceptibilities for some  $\text{LaNi}_{5-x}\text{Cu}_x$  compounds.

## 5. Magnetic behaviour of Ni in $\text{RNi}_5$ -based systems

The nickel moments, at 1.7 K, is nil in  $\text{LaNi}_5$  and has finite values in compounds with magnetic rare-earth. Thus, there seems to be a transition from nonmagnetic state to magnetic one as the exchange interactions increase as result of nonmagnetic rare-earth substitution by a magnetic one. We studied the transition of nickel to magnetic ordered state in  $\text{Gd}_x\text{La}_{1-x}\text{Ni}_5$  system. The correlation between  $M_{\text{Ni}}$  at 2c and 3g sites and the exchange splitting of Ni3d band,  $\Delta E_{\text{exch}}$ , is plotted in Fig. 12. The nickel moments are linearly dependent on the exchange splitting, starting from a value  $\Delta E_{\text{exch}}=3 \cdot 10^{-3}$  eV. This corresponds to a critical field of 0.5 MOe. The critical field for the appearance of induced nickel moment was estimated also from magnetic data. By using the molecular field model we determined the exchange parameters characterizing the interactions inside  $J_{\text{NiNi}}$ ,  $J_{\text{GdGd}}$ , as well as between  $J_{\text{GdNi}}$ , magnetic sublattices. Starting from the above parameters we evaluated the exchange fields acting on nickel atoms. There is also a linear dependence of mean nickel moments as function of exchange fields – Fig. 13. A critical field of  $\cong 0.3$  MOe was estimated, somewhat smaller than that obtained from band structure calculations. Analyzing the data from Figs.12 and 13 we conclude that Ni3d band splitting is linearly dependent on the exchange fields. This shows that nickel moments are essentially induced by exchange interactions. The difference between the critical field values determined above, may be attributed to the fact that in first case we used the values of local 2c and 3g moments and in the another one the mean nickel moments. Also, the exchange interaction coefficients were evaluated from paramagnetic data. Since the Ni moments, at 1.7 K, and the effective moments are different, the molecular

field analysis may lead to some differences in the determined  $J_{ij}$  values. In spite of the above approximation, the estimated critical fields for the appearance of a nickel moment are in reasonable agreement,  $H_{cr} = 0.4 \pm 0.1$  MOe.

The  $\text{LaNi}_{5-x}\text{M}_x$  compounds with  $\text{M}=\text{Cu}$  or  $\text{Al}$  show an interesting magnetic behaviour. There is a transition of magnetic susceptibilities from a  $T^2$  dependence to a Curie-Weiss behaviour, as temperature increases. At  $T > T^*$  the system behaves as having local moments. The same behaviour can be shown also in compounds where Ni show a weak ferromagnetism or is not magnetic as in  $\text{RNi}_{5-x}\text{M}_x$  with magnetic rare-earths. Above  $T_c$ , the nickel atoms contribute to Curie constants. This suggests that nickel atoms behave, at high temperatures, as in systems having local moments. In order to obtain more information on this behaviour, XPS measurements were performed at room temperature, at  $T > T^*$ , respectively. A comparison of the computed density of states for  $\text{LaNi}_5$  and the measured XPS valence band spectra of  $\text{LaNi}_5$  and of pure Ni is shown in Fig.2a. The computed density of states describe rather well the XPS spectrum. There is also a similarity of the Ni3d band for pure Ni and that of  $\text{LaNi}_5$ . This fact evidences that the valence band of  $\text{LaNi}_5$  is mainly derived from Ni3d one. The structure at 6 eV, as in Ni, suggests, that in  $\text{LaNi}_5$  nickel 3d band is not completely filled. The Ni2p core level lines of  $\text{NdNi}_{5-x}\text{Cu}_x$  system are plotted in Fig. 14 [5]. The positions of the  $2p_{3/2}$  and  $2p_{1/2}$  lines are situated at  $852.5 \pm 0.1$  eV and  $826.9 \pm 0.1$  eV, respectively and do not change with composition. These

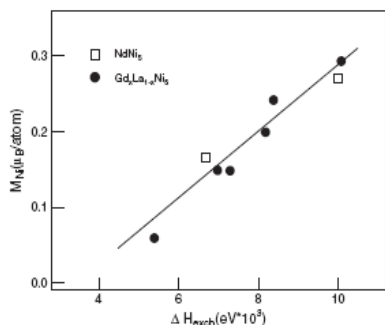


Fig. 12. The correlation between Ni moments at 2c and 3g sites and exchange splitting of their 3d bands.

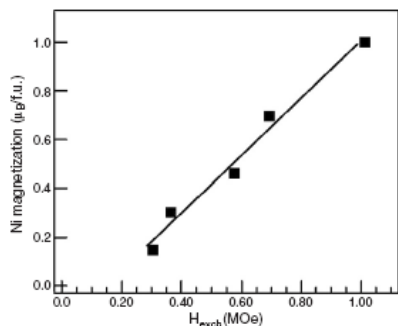


Fig. 13. Dependence of nickel magnetization at, 1.7 K, on exchange field.

lines are located at the same binding energies as for nickel ( $852.7 \pm 0.1$  eV and  $869.97 \pm 0.1$  eV). The 6 eV satellite is located at  $858.5 \pm 0.1$  eV, as in pure Ni. Although the intensity of 6 eV satellite decreases as the Ni is gradually replaced by Cu, still exist, confirming the presence of Ni3d holes.

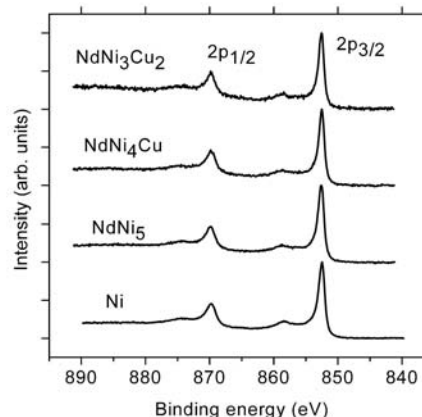


Fig. 14. The Ni $2p_{3/2}$  and  $2p_{1/2}$  core lines for  $\text{NdNi}_{5-x}\text{Cu}_x$  compounds.

The nickel magnetic behaviour may be analysed in models which take into account the electron correlations effects in d-band as spin fluctuation model [19] or dynamical field theory [20]. These models reconcile the dual character of electron which as particle requires a real space description and as a wave, a momentum space description. The spin fluctuation model considers the balance between the frequencies of longitudinal spin fluctuations which are determined by their lifetime and of transverse fluctuations which are of thermal origin. These effects lead to the concept of temperature induced moment. For a weak ferromagnet or an exchange enhanced paramagnet, as Ni in the above systems, the wave number dependent susceptibility,  $\chi_q$ , has a large enhancement due to electron-electron interaction for small q-values. The  $\chi_q$  shows a significant temperature dependence only for q values close to zero. The average amplitude of spin fluctuations  $\langle S_{\text{loc}}^2 \rangle = 3k_B T \sum \chi_q$  increases with temperature and reaches the upper limit at temperature  $T^*$ , determined by charge neutrality condition. For  $T > T^*$ , a Curie-Weiss behaviour is predicted as in systems having local moments. The moments are localized in q-space. The effective nickel moments decrease as result of 3d-3p hybridizations in aluminum substituted samples or as result of decreasing electron correlations in copper doped ones.

The magnetic behaviour of nickel in  $\text{RNi}_5$ -based compounds, may be also analysed in dynamical mean field theory, DMFT [20] combined with the standard LDA band calculations (LDA+DMFT) [21]. In a strongly correlated

system, leading Curie-Weiss behaviour, at high temperatures, is predicted. For an itinerant electron system, the time dependence of the correlation function results in a temperature dependence of  $\langle S_{\text{loc}}^2 \rangle$ .

Fluctuating moments and atomic like configurations are large at short time. The moments are reduced at larger time scales, corresponding to a more band like less correlated electronic structure at the Fermi level. By using a numerically exact quantum scheme, in the LDA+DMFT, was possible to reproduce the 6 eV satellite in DOS spectrum of nickel, at  $T = 0.9 T_c$ . This satellite was shown to have substantially more spin-up contribution. The diminution of the 6 eV satellite intensity, as evidenced by XPS measurements, in samples where Ni was substituted by Al or Cu is in agreement with partial filling of Ni3d band due to hybridization effects.

## 6. Conclusions

The  $R\text{Ni}_{5-x}\text{Cu}_x$  compounds with  $R=\text{La, Nd}$  form solid solutions having  $\text{CaCu}_5$  type structure in composition range  $x \leq 2.0$ . In  $R\text{Ni}_{5-x}\text{Al}_x$  systems with  $R=\text{La, Tb, Dy}$ , the structure changes to  $\text{HoNi}_{2.6}\text{Ga}_{2.4}$  type for  $x \geq 2$ .

Band structure calculations on  $R\text{Ni}_5$  compounds with magnetic rare-earths show the presence of nickel ordered moments. The Ni moments are antiparallely aligned to heavy rare-earth ones and parallelly oriented in case of a light rare-earth, as Nd. The magnetic behaviour evidenced by band structure calculations is in agreement with the result of magnetic measurements. The effective nickel moments decrease when Ni is replaced by Al or Cu.

The magnetic susceptibilities of  $\text{LaNi}_{5-x}\text{M}_x$  with  $M = \text{Cu or Al}$ , at  $T \leq 10 \text{ K}$  show a  $T^2$  dependence, while at higher temperatures than a characteristic value,  $T^*$ , a Curie-Weiss behaviour was shown. The above behaviour can be described in models which take into account the electron correlation effects in d-band.

The transition of Ni from nonmagnetic to magnetic state was also analysed in  $\text{Gd}_x\text{La}_{1-x}\text{Ni}_5$  system. A field of  $0.4 \pm 0.1 \text{ MOe}$  is necessary to induce a magnetic moment. Then, the nickel moments vary linearly with the exchange field.

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## References

- [1] E. Burzo, A. Chelkovski, H. R. Kirchmayr, Landolt Börnstein Handbuch, Vol. III/19d2, Springer Verlag, 1990
- [2] D. Gignoux, D. Givord, A. del Moral, Solid State Commun. **19**, 891 (1976).
- [3] E. Burzo, L. Chioncel, I. Costina, S. Chiuzaibaian, J. Phys.: Condens. Matter **18**, 4861 (2006).
- [4] E. Burzo, S. G. Chiuzaibaian, L. Chioncel, M. Neumann, J. Phys.: Condens. Matter **12**, 5897 (2000)
- [5] E. Burzo, T. Crainic, M. Neumann, L. Chioncel, C. Lazar, J. Magn. Magn. Mater. **290-291**, 571 (2005).
- [6] J. L. Bobet, S. Pechev, B. Chevalier, B. Darriet, J. Alloys. Compounds **267**, 136 (1998)
- [7] S. Sorgic, A. Dasner, Z. Blazina, J. Phys.: Condens. Matter **7**, 7209 (1995).
- [8] E. Burzo, S. G. Chiuzaibaian, M. Neumann, M. Valeanu, L. Chioncel, I. Creanga, J. Appl. Phys. **92**, 7362 (2002).
- [9] E. Burzo, S. G. Chiuzaibaian, M. Neumann, L. Chioncel, J. Phys.: Condens. Matter **14**, 8057 (2002).
- [10] O. K. Anderson, Phys. Rev. **B12**, 3060 (1975).
- [11] O. K. Anderson, O. Jepsen, Phys. Rev. Letters **53**, 2571 (1984).
- [12] R. O. Jones, O. Gunnarson, Rev. Mod. Phys. **61**, 689 (1989).
- [13] U. von Barth, L. Hedin, J. Phys. C: Solid State Physics **5**, 1629 (1972)
- [14] V. I. Anisimov, J. Zaanen, O. K. Anderson, Phys. Rev. **B44**, 943 (1991); A. I. Lichtenstein, J. Zaanen, V. I. Anisimov, Phys. Rev. **B 52**, R5467 (1995).
- [15] V. I. Anisimov, I. V. Solovyev, M. A. Korotkin, T. H. Cyzyk, G. A. Sawatzky, Phys. Rev. **B48**, 16929 (1993)
- [16] V. I. Anisimov, F. Aryasetivan, A. I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767, (1997).
- [17] I. A. Campbell, J. Phys. F.: Metal Phys. **2**, L149 (1972).
- [18] M. T. Beal-Mond, Physica B **139-140**, 1837 (1982).
- [19] T. Moriya, J. Magn. Magn. Mat. **100**, 201 (1991).
- [20] A. Georges, G. Kothar, W. Krauth, M. J. Rosenberg, Rev. Mod. Phys. **68**, 13 (1996).
- [21] A. I. Lichtenstein, M. I. Katsnelson, G. Kothar, Phys. Rev. Letters **87**, 672205 (2001).

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