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Abstract. The magnetic properties of the LaNi$_{5-x}$Cu$_x$ system ($x \leqslant 1.5$) were investigated in the temperature range 1.7–300 K. The magnetic susceptibilities χ increase up to a characteristic temperature T_{max} and then decrease. At $T \leqslant 10$ K the χ-values of LaNi$_5$ follow a T^2-dependence. At temperatures above a characteristic temperature T^* a Curie–Weiss-type behaviour was observed for all samples investigated. The effective nickel moments decrease when increasing the Cu content. X-ray photoelectron spectroscopy measurements and a band-structure calculation show that the Fermi level is shifted towards a region with lower density of states when Cu is substituted for Ni. There is a weak hybridization between Ni and Cu d states. The magnetic properties were analysed in the spin-fluctuation model. The smaller values of the effective moments of nickel as compared to the free Ni^{2+} ion indicate that LaNi$_{5-x}$Cu$_x$ is a non-saturated spin-fluctuation system.

1. Introduction

Previously, we have shown that the magnetic behaviour of the exchange-enhanced paramagnets RCo$_2$ (R $=$ Y, Lu, Sc, Hf) [1–3], which exhibit strong exchange-enhancement factors ($s = 9$–10), is more complicated than the classical Pauli-type-paramagnet description. At low temperatures ($T < 10$ K) the susceptibilities χ follow a T^2-dependence, while at temperatures above a characteristic value T^* a Curie–Weiss behaviour was observed. The effective cobalt moments are close to those of Co^{2+} ions, considering only the spin contribution. The experimental data were discussed within the spin-fluctuation model [4].

The LaNi$_5$ compound was also considered to be at 4.2 K an exchange-enhanced paramagnet, having a magnetic susceptibility $\chi = 2.5 \times 10^{-3}$ emu/f.u. [5] or 2.27×10^{-3} emu/f.u. [6]. Since no corrections for the possible presence of magnetic impurities were made, the above values can be considered as upper limits. The estimated exchange-enhancement factor ($s = 5$–6) is lower than that reported for Laves-phase compounds. Thus, it is of interest to analyse the magnetic behaviour of systems which show exchange-enhancement factors intermediate between those reported for RCo$_2$ compounds and normal paramagnets. For this reason we have investigated the LaNi$_{5-x}$Cu$_x$ system. The experimental data were corrected for the possible presence of a small content of magnetic ordered impurities.

The LaNi$_5$ compound crystallizes in a hexagonal structure of CaCu$_5$ type. In this system nickel occupies 2c- and 3g-type sites. Different ranges of solid solutions for the LaNi$_{5-x}$Cu$_x$ system were reported in the literature, covering the composition range from $x = 1.5$ to 5 [7]. Copper has been reported to substitute for nickel at both 2c and 3g sites with a preference for the 2c sites [7, 8].

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In order to obtain more reliable information on the physical properties of the $LaNi_{5-x}Cu_x$ system, in addition to the magnetic measurements, x-ray photoelectron spectroscopy (XPS) measurements were performed. The experimental data were compared with computed band structures.

2. Experimental and computing methods

The samples were prepared in an induction furnace in a purified argon atmosphere and remelted several times to ensure a good homogeneity. A small excess of La ($\leqslant 1\%$) was added to compensate for weight loss during melting. The samples were thermally treated under vacuum at 1000 °C for one week. The x-ray analysis showed the presence of only one phase with a $CaCu_5$-type structure in the composition range $x \leqslant 1.5$. The composition dependence of the lattice parameters is given in table 1.

Table 1. Lattice parameters, paramagnetic Curie temperatures, effective nickel moments, computed densities of states (DOS) at the Fermi level (states eV^{-1}/supercell) and low-temperature magnetic susceptibilities of the $LaNi_{5-x}Cu_x$ system.

	Lattice parameters		$-\theta$	M_{eff} (Ni)		$10^3 \chi_p$ (emu/f.u.)	
x	a (Å)	c (Å)	(K)	(μ_B/atom)	DOS	Calculated	Experimental
0.0	5.0110	3.911	1104	2.15	17.620	1.88	1.93 (1.7 K)
0.5	5.0106	3.940	978	1.96	17.440	1.86	1.90 (4.2 K)
1.0	5.0100	3.980	577	1.41	12.810	1.38	1.60 (4.2 K)
1.5	5.0090	4.001	526	1.15	12.805	1.36	1.15 (4.2 K)

The magnetic measurements were performed in the temperature range 1.7–300 K and fields up to 8 T. For each temperature, the magnetic susceptibility has been determined from magnetization isotherms, according to a Honda–Arrott plot [9]:

$$\chi = \chi_p + \frac{cM_s}{H} \tag{1}$$

by extrapolation to $H^{-1} \to 0$. Here, c denotes a presumed impurity content and M_s is the saturation magnetization. By this method, any possible alteration of the χ-values as a result of the presence of small quantities of magnetic ordered impurities is avoided.

The samples generally were shown to be free from magnetic impurities. A very small content of a magnetic ordered phase ($<0.1\%$) was evidenced only at low temperatures. This can increase the magnetic susceptibilities by up to 15%, if corrections are not made.

The XPS experiments were performed using a PHI 5600ci MultiTechnique system. The spectra presented here were recorded using the monochromatized Kα radiation of Al (1486.6 eV). The total-energy resolution of the electron spectra, as determined at the Fermi level of a gold foil, was about 0.3–0.4 eV. Binding energies are given with reference to the Fermi level. The $4f_{7/2}$ level of gold was found at 84.0 eV binding energy. The samples were fractured in the preparation chamber and then moved into the main chamber. All spectra were recorded in a vacuum below 5×10^{-10} mbar. All samples were studied in the same manner in order to facilitate a comparison. The fractured samples contained only tiny amounts of oxygen and carbon.

Band-structure calculations were carried out using the *ab initio* tight-binding linear muffin-tin orbitals method in the atomic sphere approximation (TB-LMTO-ASA). The detailed procedure of the calculations is described elsewhere [10–12]. In the framework of the local density approximation (LDA) the total electronic potential is the sum of the external, Coulomb

and exchange–correlation potentials [13]. The functional form of the exchange–correlation energy used in the present work was the free-electron-gas parametrization of von Barth and Hedin [14]. Relativistic corrections are included without the spin–orbit coupling. For band-structure calculations, an ordered structure is assumed. The ordered structure relates to the fact that there is a preferential substitution of Cu and consequently the compounds are crystallographically ordered. The Cu atoms were only placed at 2c-type positions, which were found to be the preferred sites.

3. Experimental data

3.1. Magnetic measurements

The temperature dependences of the magnetic susceptibilities χ are plotted in figure 1 and figure 2. The low-temperature χ-values for LaNi$_5$ are shown in the inset of figure 1 as a function of T^2. As evidenced in figure 1, at $T < 10$ K, the susceptibility of LaNi$_5$ follows a
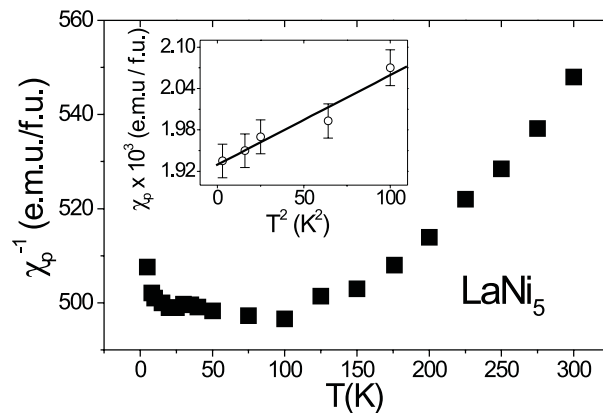

Figure 1. The temperature dependence of the magnetic susceptibility for LaNi$_5$ ($\chi_p \pm 1\%$). In the inset the low-temperature behaviour is plotted.
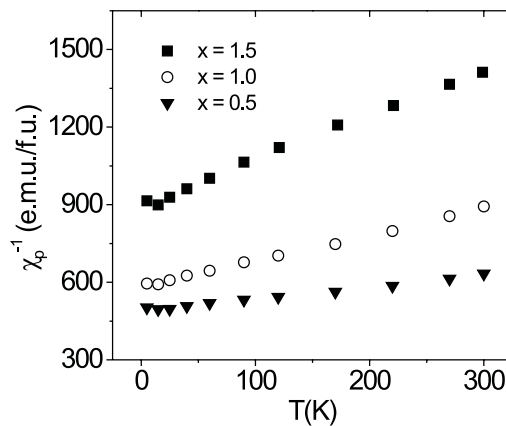

Figure 2. Temperature dependences of the magnetic susceptibilities for LaNi$_{5-x}$Cu$_x$ with $x = 0.5$, 1.0 and 1.5 ($\chi_p \pm 1\%$)

relation of the form

$$\chi_p = \chi_0(1 + aT^2) \tag{2}$$

with $a = 1.3 \times 10^{-3} \text{ K}^{-2}$.

For all samples, the susceptibilities increase up to a temperature T_{max} and then decrease. Above a characteristic temperature T^* a Curie–Weiss-type behaviour is observed. T_{max} and T^* are shifted to lower temperatures when increasing the copper content. Due to this shift, the region where the T^2-dependence is observed is diminished, and thus no reliable data on the T^2-dependence can be obtained for compounds with $x \geqslant 0.5$. The above data show a transition from Pauli-type paramagnetism to a Curie–Weiss behaviour as the temperature increases, similar to that found for cobalt-based compounds [1–3].

From the linear region of χ^{-1} versus T, the effective nickel moments $M_{eff}(\text{Ni})$ as well as the paramagnetic Curie temperature θ were determined. The values of $M_{eff}(\text{Ni})$ and θ were obtained directly from experimental data with or without considering the diamagnetic and paramagnetic contributions of the constituent ions. The differences between the values of $M_{eff}(\text{Ni})$ and θ obtained in the two cases are not significant.

The effective nickel moments and the absolute value of the paramagnetic Curie temperatures decrease in a similar way with increasing Cu content—see table 1. The θ-values are negative for all the compounds studied.

3.2. XPS measurements

The Ni $2p_{3/2}$, $2p_{1/2}$ and La $3d_{3/2}$ core-level lines of LaNi$_{5-x}$Cu$_x$ are presented in figure 3. The La $3d_{3/2}$ line overlaps with the Ni $2p_{3/2}$ line. We analysed to what extent the XPS data were affected by a possible oxidation. The 2p lines of a pure Ni sample fractured under UHV were measured under the same conditions as the lines of the LaNi$_{5-x}$Cu$_x$ system. We have identified one satellite for each Ni 2p line positioned at about 6 eV higher binding energy with respect to the parent lines. Another peak can be located at around 855 eV, which corresponds to oxidized La. The presence of this small degree of oxygen contamination can be explained by oxygen adsorption at the surface after cleaving the samples in the preparation chamber. The possibility of its presence due to fracturing along oxygen-rich grain boundaries, where oxygen had naturally segregated, is excluded. We conclude that the Ni states are not really affected
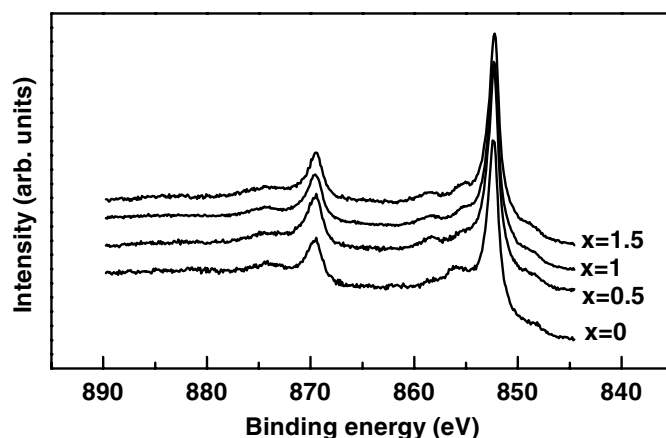

Figure 3. The Ni $2p_{3/2}$, $2p_{1/2}$ and La $3d_{3/2}$ core lines for LaNi$_{5-x}$Cu$_x$.

by this small level of oxygen contamination and also not during measurements.

The binding energies for the core levels of La, Ni and Cu show no chemical shifts for the different LaNi$_{5-x}$Cu$_x$ compounds within the experimental error bars. No chemical shift was found with respect to the pure metals.

The XPS valence bands recorded for the LaNi$_{5-x}$Cu$_x$ samples and for pure Ni are presented in figure 4. There is a similarity of the Ni 3d bands for pure Ni with those for LaNi$_5$. This fact evidences that the valence band of LaNi$_5$ is mainly derived from Ni d. The structure at about 6 eV binding energy is the well-known Ni satellite. The contribution of La states to the valence band of LaNi$_5$ is not visible in the spectra because of the low cross-sections of La. Alloying with Cu does not induce visible changes in the Ni d band. A rather independent Cu d band is formed at around 3.3 eV binding energy. By increasing the Cu content, the relative intensity of the Cu d band is increased. These Cu states are probably completely filled with electrons (d^{10} configuration). The width of the Cu line is not changed by increasing the Cu content.

The computed densities of states describe rather well the general features of the experimental spectra—see figure 4. In agreement with the XPS data, separated Cu and Ni d bands were shown. Thus the DOS of LaNi$_{5-x}$Cu$_x$ compounds can be described as a
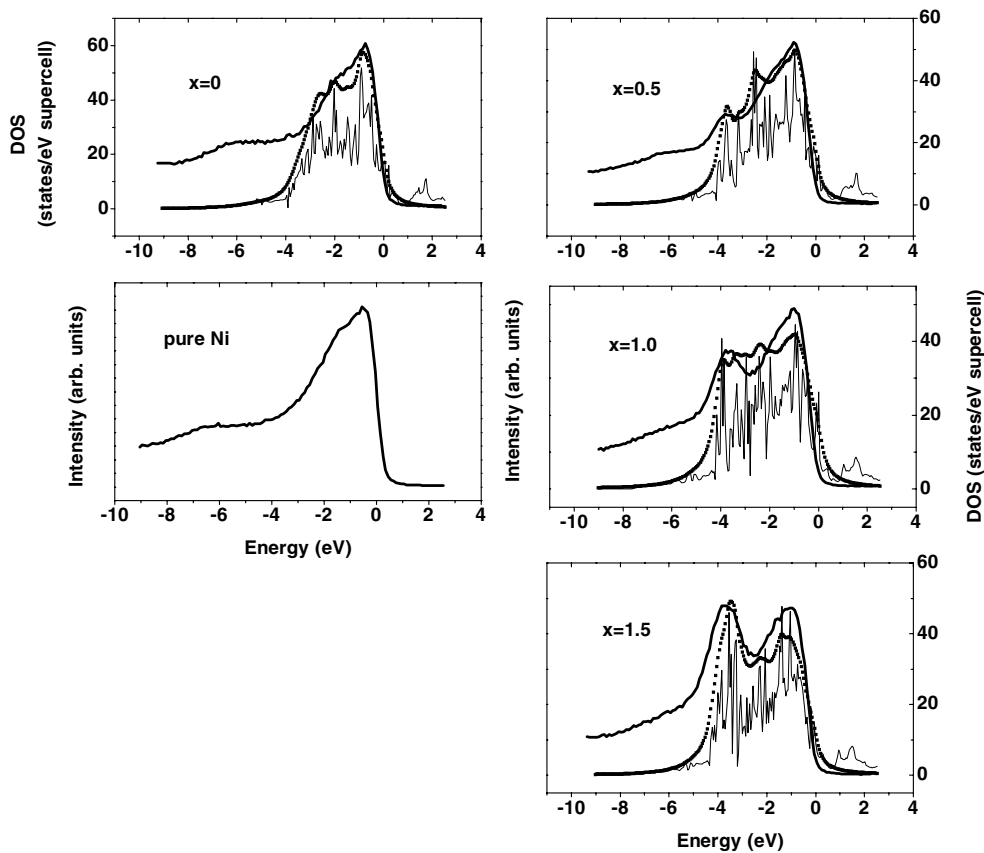

Figure 4. Comparison of the measured XPS valence bands (thick solid line), the calculated total DOS (solid line) and the convoluted DOS (with Lorentzians of half-width 0.4 eV and taking into account appropriate cross-sections for partial bands with different *l*-symmetry; dashed line) for LaNi$_{5-x}$Cu$_x$.

superposition of independent atomic densities of states separated by 2 eV. The general features of the computed and experimental densities of states show that there is a weak hybridization between the Cu d and Ni d bands.

There are also minor differences between the experimental and computed band structures. Some explanations can be given for the discrepancies evidenced in figure 4. Thus, in computing the density of states, room temperatures lattice parameters were used. The comparison was made with XPS spectra obtained at room temperature. In addition, d–d correlation effects were not considered in computing the density of states. The inelastic scattering background present in the XPS spectra was not extracted.

We note that, assuming an ordered lattice, the Ni 3d band becomes narrower when Ni is replaced by Cu, as a result of dilution effects as well as the simultaneous change in the lattice parameters. The Cu d band retains the characteristic bandwidth.

From the analysis of the band structure we conclude that a rigid-band model is not suitable for describing the properties of $LaNi_{5-x}Cu_x$ and a model which leaves the Cu and Ni electronic configuration unchanged in the alloy is more appropriate [15].

The Fermi level shifts to a region with a smaller density of states as the Cu content increases. The computed DOS at the Fermi level follows the same trend as the $M_{eff}(Ni)$ values—see table 1.

4. Discussion

The experimentally observed magnetic behaviour of $LaNi_{5-x}Cu_x$ may be analysed in the self-consistent renormalization (SCR) theory of spin fluctuation [4]. The model is based on the concept of temperature-induced local moments for systems having a strongly enhanced paramagnetic susceptibility. The wavenumber-dependent susceptibility χ_q of a nearly ferromagnetic alloy has a large enhancement due to electron–electron interaction for small q-values. The temperature dependence of χ_q is significant only when the q-values are small. The spin fluctuations in this case have a local character in the reciprocal space.

The average amplitude of local spin fluctuation

$$\langle S_{loc}^2 \rangle = 3k_B T \sum_q \chi_q \tag{3}$$

is a temperature-dependent quantity and increases with temperature until it reaches an upper limit determined by the charge-neutrality condition at a temperature T^*. The spin fluctuations are saturated and the effective moments correspond to a given electron configuration only for systems which show a strong exchange-enhanced susceptibility. Below T^* the temperature variation of the local amplitude of the spin fluctuations (longitudinal components) determines the magnetic susceptibility. Above T^* only the transverse components of the spin fluctuation contribute to the Curie constant. Thus, at $T > T^*$, the alloy behaves like one having local moments. The maxima in the χ-versus-T curves observed for the systems studied may be considered as crossovers between the low-T regime governed by longitudinal spin fluctuations and the classical regime determined by transverse spin fluctuations.

The experimentally determined nickel moments are smaller than the value characteristic for Ni^{2+} ions, considering only spin contributions (2.83 μ_B/ion), and decrease with increasing Cu content. Two mechanisms may be considered. The first supposes that the values of $\langle S_{loc}^2 \rangle$ at $T > T^*$ are not saturated even for $LaNi_5$ and that the saturation decreases as a result of diminution of the exchange-enhancement factor when Ni is replaced by Cu. The second mechanism considers a gradual hybridization of the Ni 3d band with Cu states as a result of increasing Cu content. In this case the electronic configuration of nickel must be

gradually modified.

Only weak hybridization effects between Ni and Cu d states were evidenced from the analysis of the XPS spectra as well as from the band-structure calculations. The Cu states behave almost like separate impurity atoms in a LaNi$_5$ lattice. In addition, the Ni d band remains almost unchanged when the composition is modified. Thus, the smaller effective nickel moments as compared to that of the Ni^{2+} ion and their decrease when changing the composition cannot be attributed to a gradual filling of the Ni 3d band. The experimentally observed trend may be correlated with the exchange-enhancement factors which are not sufficiently high, even for LaNi$_5$, to lead to the saturation of the spin fluctuations $\langle S_{loc}^2 \rangle$ and which decrease as Ni is replaced by Cu. A similar behaviour was evidenced in Y(Co$_{1-x}$Ni$_x$)$_2$ compounds [3].

By using the computed densities of states we estimated the low-temperature magnetic susceptibilities. The calculated values as well as those determined experimentally are given in table 1. As a function of composition, the same trend is observed. The differences in χ-values may be attributed to the same factors as were mentioned above when analysing the experimental and computed band structures.

The temperature factor a of the LaNi$_5$ low-temperature susceptibilities was computed according to the relation [16]

$$a = \frac{\pi^2}{6} \left[\left(2\frac{N''}{N} - 1.2\frac{N'^2}{N^2} \right) \bigg|_{E_F} \right] s^2 \tag{4}$$

where s is the Stoner enhancement parameter; N, N', N'' are the density of states at the Fermi level and its first and second derivatives, respectively.

The value determined, $a = 1.22 \times 10^{-3}$ K^{-2}, is in good agreement with that observed experimentally, $a \cong 1.3 \times 10^{-3}$ K^{-2}.

Finally, we concluded that LaNi$_{5-x}$Cu$_x$ is a non-saturated spin-fluctuation system. The exchange-enhancement factors are not high enough to lead to the saturation of the values of $\langle S_{loc}^2 \rangle$. The XPS measurements and the band-structure calculations show that there is a weak hybridization between Cu d and Ni d bands. The magnetic susceptibilities determined at low temperatures are in rather good agreement with those obtained from the computed densities of states.

Acknowledgments

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