

XPS STUDY, MAGNETIC AND ELECTRIC PROPERTIES OF $\text{GdNi}_{5-x}\text{Cu}_x$ SYSTEM

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Abstract: Measurements of the magnetic susceptibility, electrical resistivity, crystal and electronic structure for $\text{GdNi}_{5-x}\text{Cu}_x$ system are reported. We find that all these compounds crystallize in the hexagonal CaCu_5 crystal structure. The influence of substitution of Ni for Cu atoms is reflected in an increase of the cell volume and in a weak dependence of the Curie temperature with the concentration x . The character of the electrical resistivity ρ versus temperature strongly depends on the composition. Especially for GdCu_5 compound, below 30 K, quite unusual behavior of $\rho(T)$ is observed. From X-ray photoelectron spectroscopy (XPS) data both valence band and core level spectra are analyzed. The filling of Ni $3d$ band in $\text{GdNi}_{5-x}\text{Cu}_x$ system by charge transfer of Gd conduction electrons is revealed by reduction of the satellite intensities in the Ni $2p$ core level spectrum. The obtained results also show that the valence band near the Fermi level is dominated by hybridized Ni $3d$ band and Gd $5d$ states, whereas Cu $3d$ states are rather localized about 3 eV below Fermi level.

1. INTRODUCTION

The RNi_5 compounds where R is a rare earth crystallize in a hexagonal CaCu_5 type of structure (P6/mmm space group). The R atoms in this structure occupy $1a$ (000) position while Ni atoms are located in two positions $2c$ ($1/3$ $2/3$ 0) and $3g$ ($1/2$ 0 $1/2$) [1-6]. The RCu_5 alloys with light rare earth elements ($R = \text{La-Sm}$) adopted CaCu_5 structure, whereas compounds with heavy rare earth elements ($R = \text{Ho-Tm}$) adopted cubic crystallographic structure AuBe_5 . In middle rare earths compounds (Gd-Dy) exist both structures, but CaCu_5 -type structure occurs in higher temperatures [3, 9, 10]. For the compound GdNi_5 was found hexagonal structure. Different ranges of solid solutions for $\text{LaNi}_{5-x}\text{Cu}_x$ and $\text{TbNi}_{5-x}\text{Cu}_x$ show that copper substitutes for nickel at both positions $2c$ and $3g$ with preference of the $2c$ sites [4-6].

Magnetic properties of GdNi_5 and GdCu_5 compounds were studied earlier. GdNi_5 is a ferromagnet with ordering temperature $T_C = 32$ K and magnetic moment $6.2 \mu_B/\text{f.u.}$ [4, 7, 8]. GdCu_5 shows antiferromagnetic behavior with $T_N = 26$ K and magnetic moment $7.5 \mu_B/\text{f.u.}$ [2]. For this compound variation of resistivity below 30 K is quite unusual and probably depends on helimagnetic-like structure. In a layer perpendicular to the c -axis, Gd moments form a triangular lattice. Between two layers, the Gd moments along c -axis make an angle about 80° . This magnetic structure arises from the weakly negative interaction between Gd nearest neighbours in two layers [2].

In this paper we present a study of magnetic, electric properties and electronic structure as an influence of substitution of Cu for Ni in $\text{GdNi}_{5-x}\text{Cu}_x$.

2. EXPERIMENTAL

The $\text{GdNi}_{5-x}\text{Cu}_x$ ($x = 0.0, 0.5, 1.0, 1.5, 3.0, 4.0, 5.0$) compounds were prepared by arc melting under argon atmosphere. Crystal structures of all samples were checked by means of X-ray diffraction using Siemens D5000 diffractometer. AC susceptibility measurements were done in the temperature range 4.2-300 K. The temperature dependence of the electrical resistivity $\rho(T)$ was measured by means of standard four-probe technique in temperature range 4.2-300 K.

XPS spectra were obtained with monochromatized Al K_{α} radiation (1486.6 eV) at room temperature using a PHI 5700/660 spectrometer. The energy spectra of emitted photoelectrons were analyzed by hemispherical mirror analyzer with high energy resolution about 0.3 eV. All spectra were measured after breaking samples in vacuum 5×10^{-10} Torr. Only small contamination of oxygen and carbon was observed.

3. RESULTS AND DISCUSSION

X-ray diffraction measurements show that all samples adopted hexagonal crystal CaCu_5 -type of structure. The additional small line observed on diffraction patterns at about 44° could be correlated with AuBe_5 structure, which has in this range the strongest (311) peak. This kind of impurity trace is only about several percent. The lattice parameters a , c and the volume V of the unit cell for $\text{GdNi}_{5-x}\text{Cu}_x$ system are presented in Table 1. Almost linear increase of both

Fig. 1. Lattice parameters a (\circ) and c (\square) for $\text{GdNi}_{5-x}\text{Cu}_x$. The insert shows increase the volume V of the unit cell with x concentration

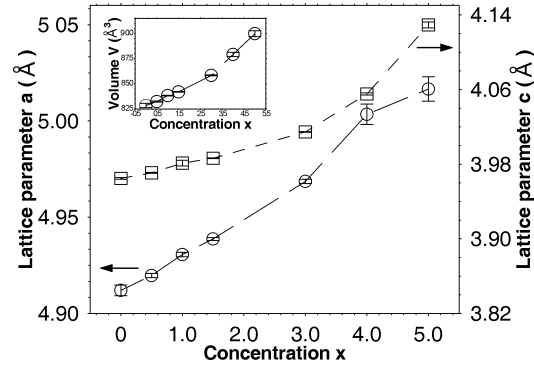


Table 1. Lattice parameters a , c and volume unit cell V the for $\text{GdNi}_{5-x}\text{Cu}_x$ system

x	a (Å)	c (Å)	V (Å ³)
0.0	4.9120	3.9647	82.84
0.5	4.9197	3.9707	83.23
1.0	4.9306	3.9811	83.82
1.5	4.9387	3.9863	84.20
3.0	4.9686	4.0145	85.83
4.0	5.0035	4.0552	87.92
5.0	5.0166	4.1291	89.99

parameters and volume with increasing Cu concentration was observed (Fig. 1). This behavior is a consequence of bigger atomic radius for Cu (1.28 Å) than for Ni (1.24 Å). But 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 [4, 5].

Figures 2a and 2b shows comparison between thermal variation of resistivity $\rho(T)$ and temperature dependence of AC susceptibility respectively for $GdNi_5$ and $GdCu_5$. Temperatures of magnetic ordering determined from AC susceptibility are given in Table 2. One can observe only weak influence of concentration for ordering temperature. The resistivity variations for both compounds $GdNi_5$ and $GdCu_5$ are quite different. For $GdNi_5$ is observed a weak peak at about 32 K which is correlated with Curie temperature. For $GdCu_5$ resistivity decrease with temperature decreasing to about 30 K, shows characteristic minimum and next increase to 4.2 K. Thermal variation of $\rho(T)$ for $GdCu_5$ below 30 K is quite unusual and probably is related to the incommensurate magnetic structure, which is characterized by weak negative interaction between Gd nearest neighbours.

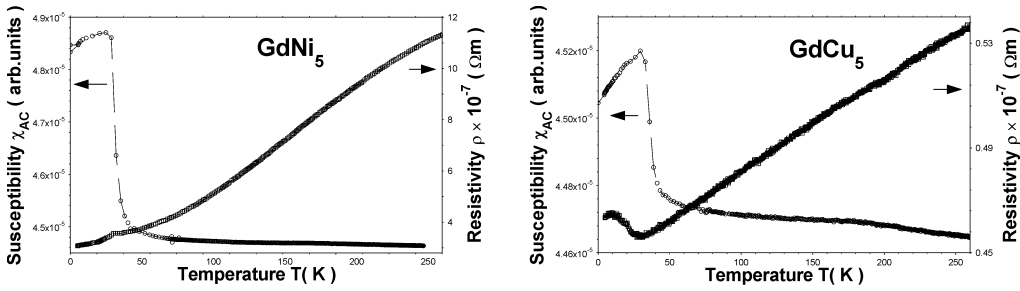


Fig. 2. Temperature dependence of AC susceptibility χ_{AC} and electrical resistivity $\rho(T)$ for a) $GdNi_5$, b) $GdCu_5$ compounds

Table 2. Data obtained from magnetic and electric measurement for $GdNi_{5-x}Cu_x$ compounds

x	T_C (K) from $\chi_{AC}(T)$	$\rho_r \times 10^7$ (Ωm)
0.0	31	3.087
0.5	37	—
1.0	37	0.644
1.5	36	—
3.0	24	1.235
4.0	32	1.134
5.0	29	0.464

Figure 3 shows the variation of the resistivity for all investigated compounds. The residual resistivity ρ_r determined at 4.2 K is about $3.09 \times 10^7(\Omega m)$ for $x = 0.0$ and is larger than $0.46 \times 10^7(\Omega m)$ for $x = 5.0$. This change may be connected with ionic radius, which is smaller

for Cu^{2+} (0.69 Å) than for Ni^{2+} (0.78 Å) but also with some substitutional disorder in the Ni/Cu sublattice.

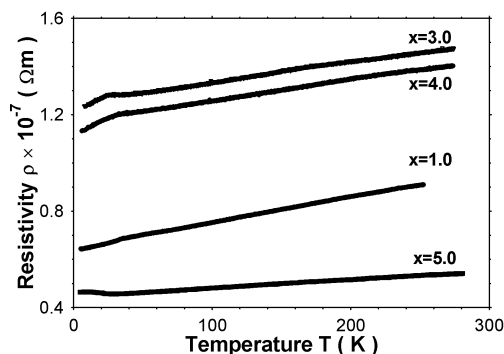


Fig. 3. Temperature dependence of electrical resistivity $\rho(T)$ for $\text{GdNi}_{5-x}\text{Cu}_x$.

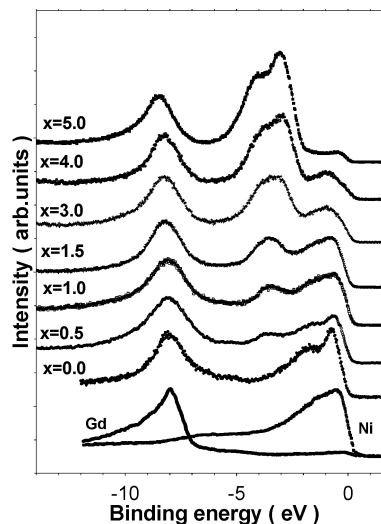


Fig. 4. The XPS valence bands in broad range for $\text{GdNi}_{5-x}\text{Cu}_x$.

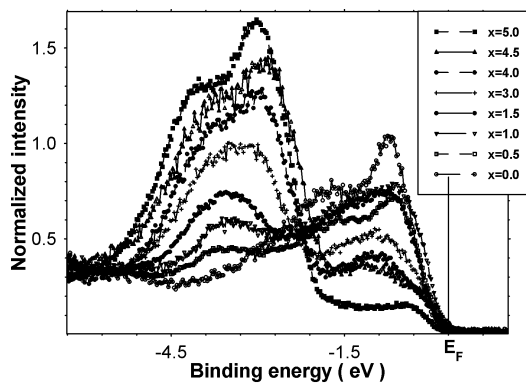


Fig. 5. The XPS valence bands for $\text{GdNi}_{5-x}\text{Cu}_x$ near Fermi level

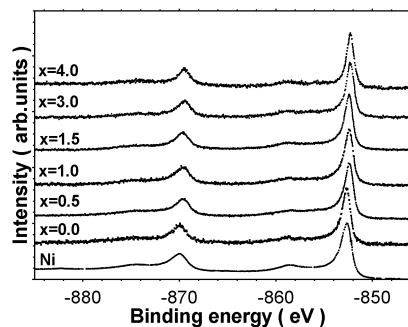


Fig. 6. The Ni $2p_{3/2}$ and $2p_{1/2}$ lines for $\text{GdNi}_{5-x}\text{Cu}_x$.

The XPS valence bands for $\text{GdNi}_{5-x}\text{Cu}_x$ are plotted in Figs. 4 and 5. The more intense lines are located at about 8 eV ($4f$ of Gd), 3 eV ($3d$ of Cu) and 1 eV ($3d$ of Ni) binding energies. There were observed small shifts in $4f$ of Gd line positions as compared to pure Gd and GdNi_5 . For $x = 0.0$ position $4f$ of Gd is about 8.08 eV and is shifted to higher energies and for $x = 5.0$ is about 8.45 eV. These shifts may be correlated with modification of electron concentration when Ni is replaced by Cu atoms.

The density of states at Fermi level is drastically reduced with increasing Cu concentration and the relative intensity of the Cu band (around 3 eV) is increased. This result is a consequence of the hybridization effect and increasing number of d electrons. For d -metals and their

alloys $3d$ states are shifted to higher binding energies when increase d -state occupancy. In consequence is observed a decrease of density of states at Fermi level. Thus, $3d$ band is probably completely filled in $GdCu_5$.

The $2p$ of Ni core level lines are plotted in Fig. 6 together with pure Ni line. When replacing Ni by Cu the core lines are shifted to lower binding energies from about 852.7 eV ($x = 0.0$) to about 852.2 eV ($x = 4.0$). These shifts can be correlated with changes of Ni $3d$ band structures. In pure Ni the satellite line located about 6 eV below main line $2p_{3/2}$ is correlated with not fully filled $3d$ band of Ni [11]. In all investigated samples these satellite lines are still observed but their intensity is smaller then for pure Ni.

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