14th Czech and Slovak Conference on Magnetism, Košice, Slovakia, July 6–9, 2010

Structural and Magnetic Properties of the $PrNi_{1-x}Cu_xAl$ Series

J. Fikáček[a,*], P. Javorský[a], M. Klicpera[a] and E. Šantavá[b]

[a]Charles University in Prague, Faculty of Mathematics and Physics, Department of Condensed Matter Physics
Ke Karlovu 5, 121 16 Prague 2, Czech Republic

[b]Institute of Physics ASCR, Na Slovance 2, 182 21 Prague 8, Czech Republic

Polycrystalline samples of $PrNi_{1-x}Cu_xAl$ series were studied by X-ray diffraction, magnetization and specific heat. The hexagonal ZrNiAl-type structure is preserved in the whole series. Compounds with x up to 0.4 order antiferromagnetically with the Néel temperatures between 3 and 5 K. The rest of the compounds (x = 0.5–0.9) exhibits a transition into a spin glass state below the freezing temperatures around 4 K. The analysis of the specific heat data reveals a quasi-doublet ground state well separated from higher crystal field levels in the whole series.

PACS numbers: 75.40.Cx

1. Introduction

The substituted $RNi_{1-x}Cu_xAl$ (R = Tb, Er, Dy) compounds, crystallizing in the hexagonal ZrNiAl-type structure, show very interesting development of magnetic behavior [1–3]. The loss of the long-range magnetic order in the concentration region around $x = 0.7$ was observed in all these series. It arouses questions about the nature of exchange interactions in these materials. The antiferromagnetic ground states and enhanced ordering temperatures of 7.9 and 6.5 K in PrNiAl [4] and PrCuAl [5], respectively, indicate that the behavior in the $PrNi_{1-x}Cu_xAl$ series could be different from the materials containing the heavy rare earth.

2. Experimental

Polycrystalline $PrNi_{1-x}Cu_xAl$ samples were prepared by the arc-melting stoichiometric amounts of pure elements. Crystal structure was analyzed by X-ray powder diffraction using the Cu K_α radiation. The magnetization measurements were performed using the PPMS and MPMS equipment (Quantum Design) between 2 and 300 K in magnetic fields up to 14 T. Powder samples (50–130 mg) consisting of randomly oriented grains fixed by a nonmagnetic glue were used. The specific heat was measured on polycrystalline samples (≈ 6 mg) by the relaxation method adopted by the PPMS instruments.

All the measured compounds keep the hexagonal ZrNiAl-type crystal structure. Both lattice parameters a and c increase monotonously with raising Cu content (see Table). The c/a ratios remain nearly unchanged, keeping the values above the forbidden gap (≈ 0.565–0.573) of this crystal structure [3].

TABLE

Structural and magnetic parameters characterizing the $RNi_{1-x}Cu_xAl$ series. T_{ord} refer to x = 0.1–0.4, whereas freezing temperatures T_f characterize compounds with x = 0.5–0.9.

x	a [pm]	c [pm]	T_{ord}, T_f [K]	θ_p [K]	μ_{eff} [μ_B]
0.0[4]	700.3(2)	408.5(2)	6.5	−23	3.80
0.1	704.9(7)	409.0(5)	5.0(5)	−9	3.58
0.2	705.2(8)	409.2(7)	4.7(2)	−12	3.50
0.3	707.6(4)	410.3(3)	3.4(2)	−10	3.58
0.4	709.3(5)	410.9(4)	4.6(3)	−9	3.54
0.5	710.8(4)	411.4(3)	4.0(2)	−6	3.57
0.6	712.4(4)	412.0(3)	3.8(2)	−9	3.59
0.7	713.9(6)	412.5(4)	3.4(2)	−4	3.48
0.8	715.6(4)	413.1(3)	3.8(2)	−6	3.61
0.9	715.5(5)	414.2(4)	4.5(2)	−5	3.66
1.0[5]	717.1(3)	414.8(1)	7.	−1	3.54

3. Results and discussion

The $M/H(T)$ dependences in the paramagnetic region follow the Curie–Weiss behavior and can be fitted to the formula

$$\chi = \frac{M}{H} = \frac{N_A \mu_0 \, \mu_B^2 \, \mu_{eff}^2}{3k_B(T - \theta_p)} + \chi_0 \, . \tag{1}$$

The determined paramagnetic Curie temperatures θ_p are all negative and the effective moments μ_{eff} are close to the Pr^{3+} free ion value of 3.58 μ_B (see Table). We can trace up some indistinct tendency of decreasing absolute values of θ_p with increasing Cu contents. The correction term χ_0 is of the order of 10^{-9} m^3/mol similarly to PrNiAl and PrCuAl [5].

The temperature dependences of magnetization and specific heat (see Figs. 1 and 2) reveal that there are two groups of compounds. The first one (x = 0.1–0.4) includes compounds exhibiting long range magnetic order below the ordering temperatures summarized in Table.

* corresponding author; e-mail: fikacekjan@seznam.cz

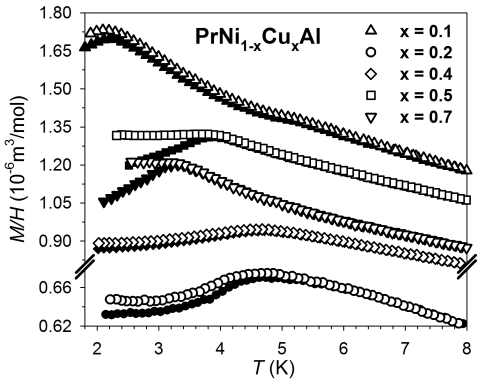

Fig. 1. $M/H(T)$ dependences of $PrNi_{1-x}Cu_xAl$ compounds measured in the field of 0.03 T. Empty and full symbols represent FC and ZFC curves, respectively.

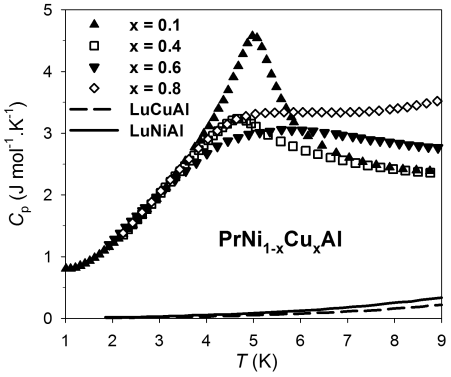

Fig. 2. Specific heat of selected compounds from the $PrNi_{1-x}Cu_xAl$ series.

The presence of maxima in both zero field cooled (ZFC) and field cooled (FC) curves points on an antiferromagnetic type of order. $PrNi_{0.9}Cu_{0.1}Al$ is the only studied compound which undergoes two magnetic phase transitions — at 5 K and 2.1 K. The magnetization curves measured at 2 K show that compounds with $x = 0.1$ and 0.2 undergo a metamagnetic transition between 3 and 6 T, analogously to parent PrNiAl, see Fig. 3. The

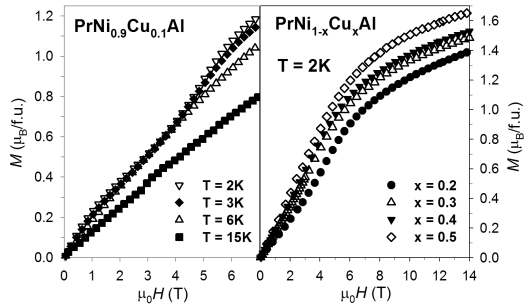

Fig. 3. Magnetization curves of selected $PrNi_{1-x}Cu_xAl$ compounds.

microscopic details of the magnetic structure development could be very complex as in other R(Ni,Cu)Al series and can be revealed by neutron scattering studies only. The second group of compounds ($x = 0.5$–0.9) is characterized by much broader anomalies in the $C_p(T)$ and $M(T)$ dependences, the enhanced irreversibility between ZFC and FC regimes with the maxima present in ZFC curves only and no metamagnetic transitions in their $M(H)$ curves. Similar behavior was observed in the $ErNi_{1-x}Cu_xAl$ series for Cu concentrations where the loss of long range magnetic order had been revealed by neutron scattering experiments [2]. The detailed investigation of these $PrNi_{1-x}Cu_xAl$ compounds by AC-susceptibility, which will be subject of a separate paper, points to a transition into a spin glass state below the freezing temperatures around 4 K.

The crystal-field energy schemes were evaluated from the magnetic part of the specific heat which was obtained from the measured data after subtraction of nonmagnetic contributions using specific heats of LuNiAl ($x = 0.1$–0.4) and LuCuAl ($x = 0.6$ and 0.8) and with the following formula

$$C_{\mathrm{Sch}} = \frac{-\partial^2(k_{\mathrm{B}}T\ln Z)}{\partial T^2}\,, \quad Z = \sum_i \mathrm{e}^{-E_i/k_{\mathrm{B}}T}, \qquad (2)$$

where E_i are the determined crystal field levels. Although this approximation was not accurate at higher temperatures (> 60 K), it gave us information about the lower part of the energy schemes. The quasi-doublet ground state ($\Delta_1 \approx 10$ K) is well separated from further excited levels ($\Delta_2 > 40$ K) in the whole series.

Acknowledgments

This work is a part of the research program MSM 0021620834 financed by the Ministry of Education of Czech Republic. The work of J.F. was supported by the grant SVV-2010-261303.

References

[1] G. Ehlers, D. Ahlert, C. Ritter, W. Miekeley, H. Maletta, *Europhys. Lett.* **37**, 269 (1997).

[2] J. Prchal, P. Javorský, V. Sechovský, M. Dopita, O. Isnard, K. Jurek, *J. Magn. Magn. Mater.* **283**, 34 (2004).

[3] J. Prchal, P. Javorský, M. Dopita, O. Isnard, V. Sechovský, *J. Alloys Comp.* **408-412**, 155 (2006).

[4] N.C. Tuan, V. Sechovský, M. Diviš, P. Svoboda, H. Nakotte, F.R. de Boer, N.H. Kim-Ngan, *J. Appl. Phys.* **73**, 5677 (1993).

[5] P. Javorský, V. Sechovský, L. Havela, H. Michor, *J. Magn. Magn. Mater.* **177-181**, 1052 (1998).