Magnetism in $DyNi_{1-x}Cu_xAl$ Pseudoternary Series

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Abstract. The $DyNi_{1-x}Cu_xAl$ pseudoternary series was studied from the point of view of magnetic behaviour. The results of magnetization, heat capacity and neutron diffraction experiments are summarised and discussed in context of other $RNi_{1-x}Cu_xAl$ pseudoternaries. The coexistence of AF and F order in the parent DyNiAl is adopted by the compounds with x = 0.1 and 0.2, but the sequence of ordering with respect to temperature is changed for x = 0.2. The compounds with $0.3 \leq x \leq 0.6$ exhibit AF order only while the compounds with $x \geq 0.9$ are ferromagnets. The compounds with $0.6 \leq x \leq 0.9$ exhibit signs of short-range correlations, especially the compound with x = 0.8 does not show any long-range magnetic order at all. It is in accordance with previously studied series.

Introduction

The DyNiAl and DyCuAl compounds belong to a large family of 1:1:1 rare-earth ternary compounds *RTX* (*R* = rare-earth, *T* = transition metal, *X* = *p*-metal) crystallizing in the hexagonal ZrNiAl-type structure, space group P-62m, no. 189. These compounds exhibit a lot of possible combinations and on the other hand a large variety of compounds crystallizing in the same structure type for systematic study.

In the past, several pseudoternary series with substitution on the position of transition metal - namely, the $TbNi_{1-x}Cu_xAl$ [Ehlers et al. *Europhys. Let.* 1997] and $ErNi_{1-x}Cu_xAl$ [Prchal et al. *J. Magn. Magn. Mater.* 2004] series - were studied. The evolution of magnetism in these substituted compounds was found to be quite complex. In both cases the change from antiferro (AF) to ferromagnetic (F) ordering was expected according to order in the parent compounds *R*NiAl and *R*CuAl. In the case of *R* = Tb and Er the F order appeared already for $x \geq 0.1$ and $x \geq 0.5$, respectively. In both series there was observed loss of the long-range magnetic order in the concentration range around $x = 0.8$. This effect was explained on basis of competition of two different types of exchange interactions for the Ni-rich and Cu-rich compounds due to change of the free 3*d*-electrons concentration in the system.

Contrary to the two above-mentioned systems, in the case of Dy-based series both parent compounds exhibit similar properties. This statement is based on bulk measurements. Neutron diffraction experiment performed on DyNiAl estimated a F order below $T_{ord} = 31$ K with magnetic moments aligned parallel to crystallographic *c* axis and additional AF component perpendicular to *c* that appears below $T_1 = 15$ K. The DyCuAl differs only slightly in the ordering temperatures $T_{ord} = 28$ K and $T_1 = 12$ K [Javorský et al. *J. Al. Comp.* 1998]. In this work we planned to confirm the existence of the region with LRO loss and check the evolution of magnetism within the series to check the influence of the transition-metal substitution to exchange interactions in these compounds.

Experimental

The measurements on the studied compounds were performed on polycrystalline samples. These were prepared by arc melting in the monoarc furnace under protection of the argon atmosphere after previous evacuation of the melting space. The initial materials with the purity of 3N for Dy, 4N for Ni, 4N5 for Cu and 5N for Al were used in the stoichiometric ratio. The samples were remelted five times to achieve better homogeneity.

The samples were then checked for the phase purity by the X-ray powder diffraction experiment and four of them were also checked for the composition by the microprobe.

The bulk measurements (heat capacity, magnetization) were performed using the Physical Property Measurement System (PPMS), Quantum Design, installed in the Joint Laboratory for Magnetic Studies, in the temperature range of 1.8-330 K and under external magnetic field up to 14 T.

The powder neutron diffraction was measured in the Institute Laue-Langevin in Grenoble in France, using the D1B diffractometer with standard banana-type multidetector, having resolution of 0.2°. The wavelength of the incident neutron beam was 2.44 Å. A standard orange cryostat with temperature range 1.6 – 300 K was used for cooling of the sample.

Results

After checking of the samples for their quality by X-ray powder diffraction and the microprobe experiment we have performed a systematic study of magnetic properties of the $DyNi_{1-x}Cu_xAl$ compounds with x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 0.9 and 1.0 (DyCuAl) The bulk properties like heat capacity and magnetization were measured and afterwards we have performed a powder neutron diffraction experiment as a microscopic method to determine magnetic structures in the studied compounds.

Bulk measurements

The magnetization and heat capacity measurements were performed to establish character of magnetic behaviour in the low temperatures.

In the paramagnetic region, the temperature dependence of susceptibility follows in all compounds the modified Curie-Weiss law (Eq. 1). Its fit on the measured data leads to values of the effective moments μ_{eff} that are close to the Dy^{3+} free-ion value of $10.65\mu_B$ (Table 1). Paramagnetic Curie temperatures θ_p are positive in all cases, indicating major F interactions. The value of χ_0 was found to be of the order of 10^{-9} m^3/mol in all cases, comparable to the values of temperature independent susceptibility of YCuAl and LuCuAl. [Ehlers et al. *Z. Phys. B* 1996].

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

Table 1. The ordering T_{ord} and additional phase-to-phase transition temperatures T_1 in the $DyNi_{1-x}Cu_xAl$ samples obtained from the low-temperature specific-heat and magnetization measurements, and the paramagnetic Curie temperatures θ_p and effective moments μ_{eff} as derived from the susceptibility data in the temperature range of 50-330 K.

x	T_{ord} (K)	T_1 (K)	θ_p (K)	μ_{eff}
0.0 [Ehlers et al. *Z. Phys. B* 1996]	31	15	17.3	10.9
0.1	25.0 (8)	13.0 (8)	16.6	10.76
0.2	21.0 (5)	11.5 (5)	13.3	10.75
0.3	19 .0 (5)	14 (1) ?	10.2	10.72
0.4	24.0 (5)	12 (1) ?	6.5	11.08
0.5	20.5 (5)	11 (1) ?	7.1	10.96
0.6	20 (1)	–	6.8	11.02
0.8	16 (1)	–	11.3	11.06
0.9	19 (1)	–	18.3	10.87
1.0 [Javorský et al. *J. Al. Comp.* 1998]	28	12	25.9	10.65

The low-temperature magnetization data show rather complicated evolution with x (see Fig. 1). The compound with $x = 0.1$ behaves probably very similarly to parent DyNiAl with F ordering at T_{ord} and AF order below T_1, but $x = 0.2$ is already basically different – there is AF ordering already at T_{ord} and F component (visible on magnetization curve at 2 K), then probably onsets below T_1. Similar low-temperature dependence of magnetization was observed in compounds with $x = 0.3 – 0.5$. Magnetization curves indicate consequent suppression of F component from $x = 0.2$ to 0.5 (Fig. 2). Weakening of ferromagnetism in this concentration region is corroborated by the minimum of θ_p (Table 1). The other phase-to-phase transition at T_1 for the compounds with $x = 0.3$ to 0.5 could be visible only on one of the probes – either by the heat capacity or the magnetization experiment but not using both complementary methods. These values are marked with a question mark in the Table 1 and as it will be shown below, these transitions were not confirmed by the neutron diffraction experiment.

The sample with $x = 0.6$ exhibits rather broader maximum in M/H vs. T dependence which can indicate loss of LRO as it was observed in the Tb- and Er-based series [Ehlers et al. *Europhys. Let.* 1997; Prchal et al. *J. Magn. Magn. Mater.* 2004]. Absolute values of magnetization at 2K (FC) are significantly smaller for $x = 0.6$.

The compounds with $x \geq 0.8$ exhibit already more F-like M/H vs. T dependencies, similar to DyCuAl [Javorský et al. *J. Al. Comp.* 1998]. Strengthening of F component from $x = 0.6$ to 1.0 can be deduced from magnetization curves. There is a small bend on magnetization curves visible in smaller fields (~0.2 T), which was also observed earlier in DyCuAl [Javorský et al. *J. Al. Comp.* 1998] (in accordance with expected AF component in the low-temperature phase; in analogy with DyNiAl).

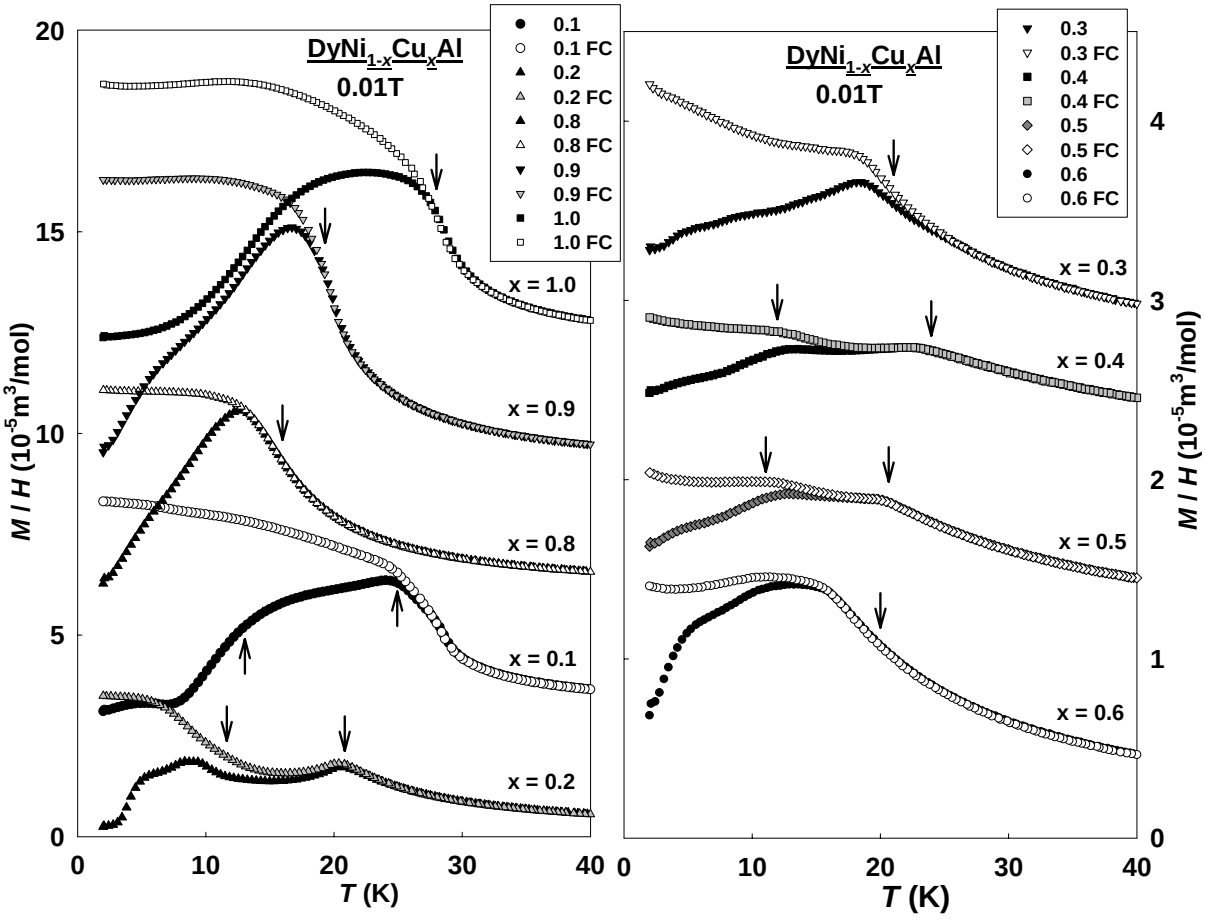

Figure 1. The low-temperature dependencies of the DyNi1-*x*Cu*x*Al compounds measured under small magnetic field of 0.01 T. The data are shifted for better view. The arrows indicate phase transitions as inferred from specific-heat data. The only exception for compounds with $x = 0.4$ and 0.5 where no anomaly was observed at the temperatures corresponding to the lower transitions at T_1 (see text).

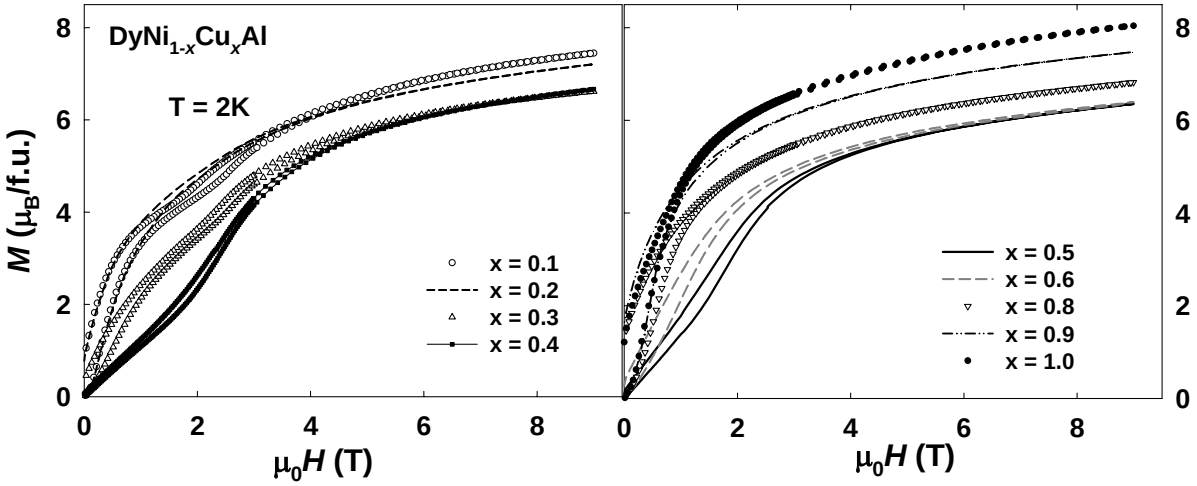

Figure 2. The magnetization curves of $DyNi_{1-x}Cu_xAl$ compounds at the lowest temperature.

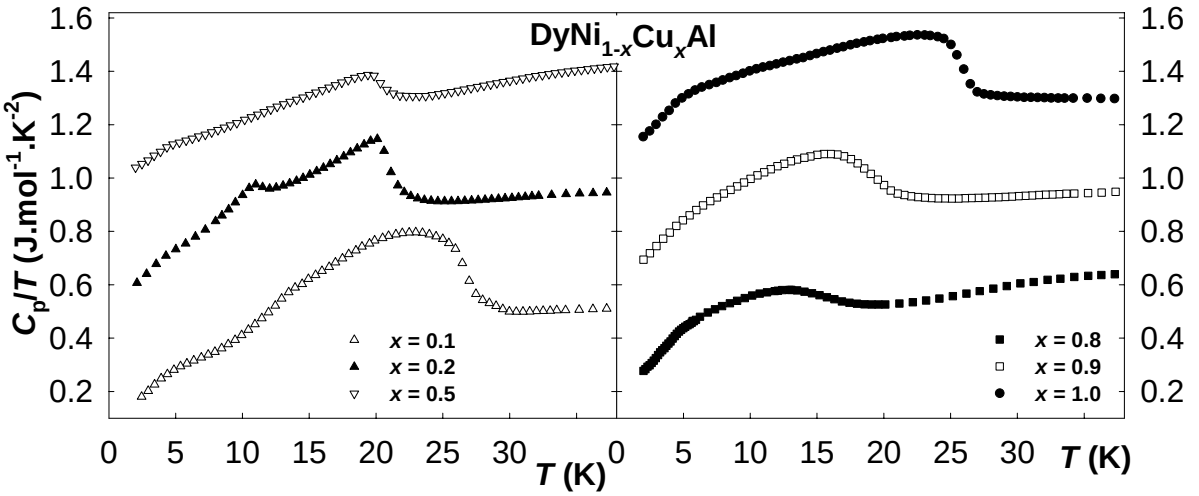

Figure 3. Temperature dependencies of the heat-capacity in the DyNi1-xCuxAl compounds. A radical change of character of the temperature evolution is visible between x = 0.1 and 0.2. A very broad anomaly corresponds to the sample with x = 0.8. The data are shifted for better view.

The Figure 3 displays temperature dependencies of heat-capacity data for selected compounds. One can see a radical change of temperature-dependency character between compounds with $x = 0.1$ and 0.2, connected with change from F to AF order at ordering temperature. Another interesting feature is observed for $x = 0.8$, where very broad anomaly is visible, indicating loss of the long-range magnetic order (see below).

Neutron diffraction

In the paramagnetic temperature the neutron diffraction pattern reflects the crystal structure based on the neutron scattering on the periodical structure of the nuclei. At low temperatures, additional magnetic reflections and/or intensities at the top of the nuclear reflections appear for all compounds, except for the compound with $x = 0.8$ where no magnetic structure was observed down to the lowest studied temperature of 1.6 K (see Fig. 4).

The magnetic structure of $DyNi_{0.9}Cu_{0.1}Al$ is similar to that one found in DyNiAl [Ehlers et al. *Z. Phys. B* 1996]. This compound orders F with Dy moments parallel to the crystallographic *c*-axis (F||c) below $T_{ord} = 25$K. Additional AF component arranged within the basal plane (AF⊥c) adds to the F component below $T = 15$ K (see Fig. 5), in agreement with previous bulk study (see above). The AF component can be described by the propagation vector $\boldsymbol{k} = (½\ 0\ ½)$. For the compound with $x = 0.2$, previous bulk study revealed surprising change of the sequence of magnetic-order types with respect

to the temperature (see above). The compound orders first AF below T_c and the F component appears at lower temperatures – i.e. the F-AF coexistence is again present at the ground state. The neutron-diffraction data confirm this stating. As it can be seen from Fig. 5, the AF reflections start to appear around T_{ord} = 22 K and the F intensities at around T_1 = 10 K what is at similar temperatures to that ones estimated from the bulk data.

The compound with x = 0.3 showed also an AF ordering but due to weakness of the reflections and also due to low quality of the sample, that was caused probably by the existence of two different crystal phases (different *a,c* parameters due to forbidden *c/a* ratio [Prchal et al., *Czech. J. Phys.* 2004]), we were not able to determine the magnetic structure in more detail.

Table 2. The summary of amplitudes, orientation and propagation vectors of magnetic moments (or their components) in the DyNi1-xCuxAl compounds at 1.6K.

x	μ (μ_B)	Type	p.v.	R_{Bragg}
0.1	6.8	F‖c	(0 0 0)	9.2
	1.6	AF⊥c	(½ 0 ½)	69
0.2	4.8	F‖c	(0 0 0)	7.3
	2.8	AF⊥c	(½ 0 ½)	46
0.4	4.7	AF⊥c	(½ 0 q)	18
0.5	5.7	AF⊥c	(½ 0 ½)	10
0.6	4.1	AF⊥c + SRO	(½ 0 ½)	13
0.8	–	SRO	–	–
0.9	3.8	F‖c + SRO	(0 0 0)	3.7
1.0	5.8	F‖c	(0 0 0)	7.5

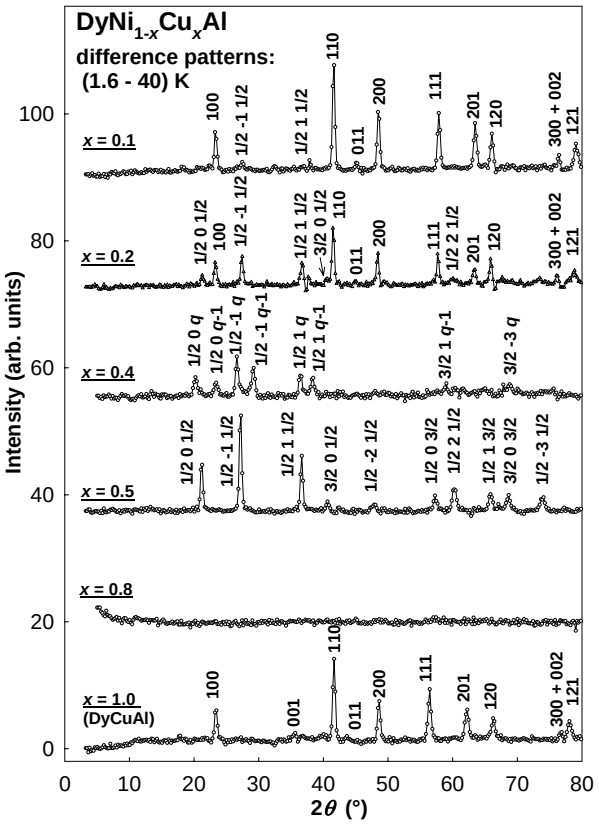

Figure 4. The difference patterns between the ordered state (or lowest studied temperature) and paramagnetic state of the compounds. The data are shifted for better view.

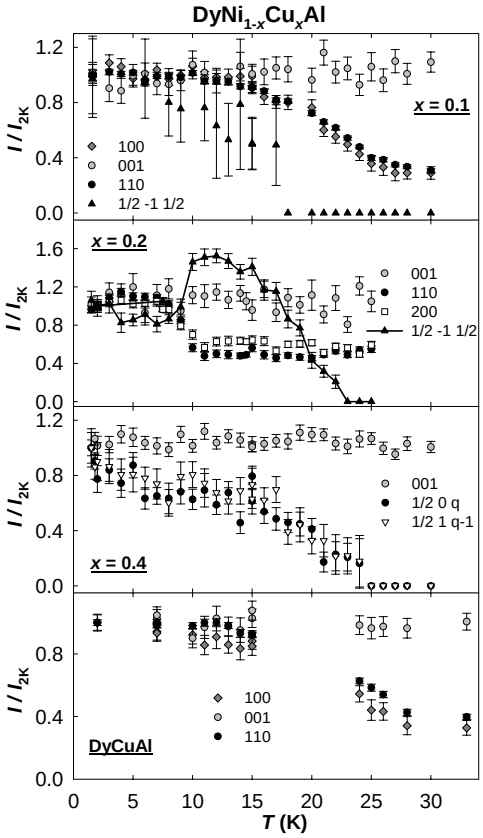

Figure 5. The intensities of selected reflections for four of the $DyNi_{1-x}Cu_xAl$ compounds.

The $DyNi_{0.6}Cu_{0.4}Al$ compound exhibits the AF incommensurate order with the $\boldsymbol{k}$ = (½ 0 q), where q = 0.448, while the samples with x = 0.5 and 0.6 order again with the commensurate propagation $\boldsymbol{k}$ = (½ 0 ½) and moments adjusted within the basal plane. Moreover, with increasing Cu-concentration, the ordered magnetic moment is getting smaller and the long-range order (LRO) becomes weaker resulting in the total loss of the LRO for x = 0.8. Similar loss of LRO was observed in the Tb- and Er-based systems [Ehlers et al. *Europhys. Let.* 1997; Prchal et al. *J. Magn. Magn. Mater.* 2004]. The low-temperature pattern of $DyNi_{0.2}Cu_{0.8}Al$ at T = 1.6K can be described by the nuclear structure only. The $DyNi_{0.1}Cu_{0.9}Al$ and DyCuAl compounds were found to be simple ferromagnets with moments aligned along the *c*-axes. The simple F order in DyCuAl is in contradiction with the bulk data that indicated similar behavior to DyNiAl, i.e. with two magnetic phases and the AF component in the ground state. Strong dependence of magnetic properties on the sample quality could be an explanation and was discussed e.g. for isostructural HoNiAl [Javorský et al. *J. Al.Comp.* 2001].

The summary of refined magnetic moments, types and directions of the moments as well as the propagation vectors are shown in the Table 2. The agreement factors for the AF component for the compounds with x = 0.1 and 0.2 are enhanced due to low intensities of the AF reflections at 1.6K.

Discussion and Conclusions

Contrary to the fact that parent compounds DyNiAl and DyCuAl exhibit similar bulk behavior, the magnetic behavior of the substituted compounds is quite complicated. Namely the change of the sequence of the magnetic-ordering type between x = 0.1 and 0.2 as confirmed by both – bulk and neutron scattering data – is surprising. It expresses importance of the Ni-Cu composition as the key parameter in determining of the type of magnetic interactions between the rare-earth atoms. This fact is also confirmed by the region around x = 0.8 where the LRO is lost similarly to other $RNi_{1-x}Cu_xAl$ pseudoternaries with R = Tb and Er. The loss of the long-range magnetic order in this concentration region can be explained either by similar way as it was done already by Ehlers [Ehlers et al. *Europhys. Let.* 1997] and other possibility if strong frustration of the moments leading to loss of long-range order in extreme case. This idea confirms the fact that the established magnitudes of the ordered moments is getting smaller when approaching to this critical concentration (see Table 2).

Moreover in our experiment we found out that the parent compound DyCuAl does not exhibit the AF component like the DyNiAl does what is in contradiction to presumption of similar behavior determined from bulk data. Nevertheless, we cannot exclude the possibility of sample (or sample-quality) dependence of the results that could cause the discrepancy of our neutron-diffraction results made on the DyCuAl sample with that ones performed on the same compound by previous study [Javorský et al. *J. Al. Comp.* 1998].

The accuracy for the phase-ordering temperatures are less precise for the neutron diffraction experiment in comparison to that ones determined from bulk data because it is not always clear when the intensity of the reflection starts to increase, other reason is especially caused by the fact that the temperature dependence is not usually performed with so small temperature steps as for the bulk measurements where the measuring time and cost for one point is much smaller than for neutron experiment.

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