ELSEVIER

Journal of Alloys and Compounds 408–412 (2006) 155–157

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Structure and magnetism in $RNi_{1-x}Cu_xAl$ (R = Er, Dy) compounds

Jiří Prchal [a,*], P. Javorský [a], M. Dopita [a], O. Isnard [b], V. Sechovský [a]

[a] *Charles University, Faculty of Mathematics and Physics, Department of Electronic Structures, Ke Karlovu 5, 12116 Prague 2, Czech Republic*
[b] *Institut Max von Laue Paul Langevin, rue Jules Horowitz and University J. Fourier Grenoble, 38042 Grenoble Cedex 9, France*

Available online 3 June 2005

Abstract

Results of crystal and magnetic structure study of $DyNi_{1-x}Cu_xAl$ quasiternary compounds are presented and discussed in context with results of previous investigations of analogous compounds with Tb and Er. This allows to draw conclusions with more general validity for this type of materials with heavy rare earths showing common anomalies of lattice parameters (a and c) and evolution of magnetism with respect to the composition of the Ni,Cu sublattice. The opposite steps in the $a(x)$ and $c(x)$ dependences compensate and have no effect on the lattice volume. On the other hand, these anomalies yield discontinuity of the c/a concentration dependence and manifest existence of a "forbidden" c/a ratio around c/a (≈0.56–0.57) in RTX compounds with the hexagonal ZrNiAl structure. The loss of magnetic long-range order, which is generally observed around $x = 0.8$, is not coupled with the structure anomaly but the number of 3d electrons in the Ni, Cu sublattice seems to be the crucial parameter.

Keywords: Rare-earth; RNiAl; RCuAl; Exchange; Neutron diffraction; Incommensurate structure

1. Introduction

The RNiAl and RCuAl compounds belong to a large group of the RTX compounds (R = rare-earth, T = transition metal, X = p-metal) crystallizing in the ZrNiAl-type hexagonal structure (space group No. 189). This structure consists of two types of basal plane layers alternating along the c-axis: one containing all the rare-earth atoms and one-third of the transition-metal atoms, and second, a nonmagnetic layer formed by all the p-metal and the rest of the T-atoms. Magnetic properties and structures have been found complex in many of these materials (eg. [1,2]). Majority of the RNiAl compounds are antiferromagnets (AF), whereas the RCuAl analogs are usually ferromagnetic (F) in low temperatures.

In the pseudo-ternary $TbNi_{1-x}Cu_xAl$ [3], the transition from antiferromagnetism to ferromagnetism (Tb moments are parallel to the c-axis both in TbNiAl and TbCuAl) happens already with quite small Cu substitution for Ni, however in the concentration region of $x \in (0.6;0.8)$ no long-range magnetic order (LRO) was indicated. In the $ErNi_{1-x}Cu_xAl$ series, the parent compounds exhibit not only different type of magnetic order but also different magnetocrystalline anisotropy. In particular, the Er moments locked in the basal plane are arranged antiferromagnetically in ErNiAl whereas ferromagnetism with Er moments along the c-axis holds in ErCuAl. Consequently, a more complex AF–F transition has been observed within the $ErNi_{1-x}Cu_xAl$ series in the concentration range of $x \in (0.2; 0.4)$. In this region, a commensurate propagation vector (1/2 0 1/2) with an incommensurate (IC) one (1/2 0 q), $q < 0.5$ coexist, and the Er magnetic moment rotates from basal plane to the c-axis with increasing Cu concentration. Lack of LRO and signs of short-range order (SRO) were also found in the concentration interval of $x \in (0.6; 0.8)$ [4]. In this work, we present results of powder neutron diffraction experiments performed on selected the $DyNi_{1-x}Cu_xAl$ compounds and discuss in a common context with the above mentioned phenomena in order to get a more general scenario of physics of all these pseudoternaries. DyNiAl exhibits ferromagnetic order with moments parallel to the c-axis below the ordering temperature T_{ord} and additional AF component arranged within the basal plane, which emerges below another phase-transition temperature $T_1 < T_{ord}$ [5]. Since the magnetization as a function of temperature and magnetic field

* Corresponding author. Tel.: +420 221911457; fax: +420 224911061.
E-mail address: prchal@mag.mff.cuni.cz (J. Prchal).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.04.115

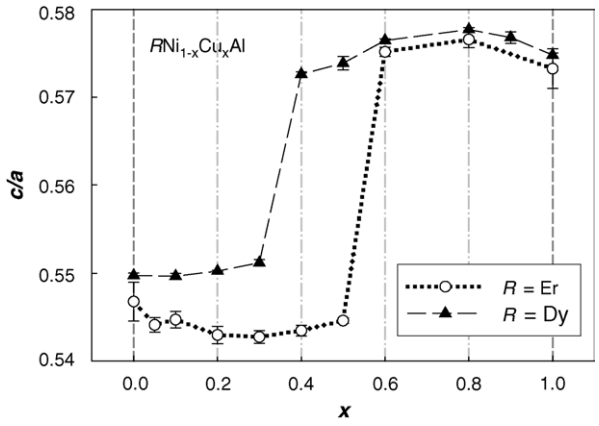

Fig. 1. Structure discontinuity observed in $DyNi_{1-x}Cu_xAl$ and $ErNi_{1-x}Cu_xAl$ series.

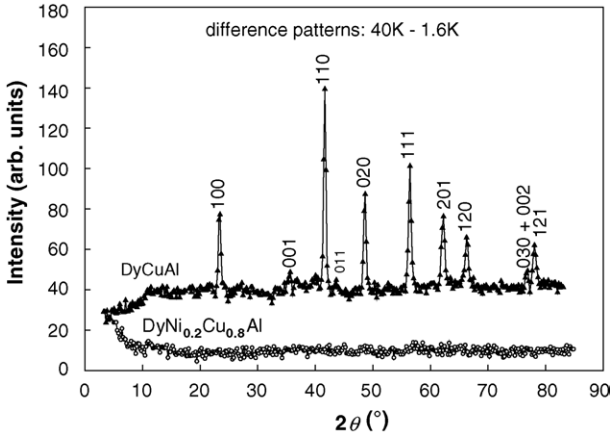

Fig. 2. The difference patterns between the lowest measured temperature 1.6 K and the paramagnetic state for compounds with $x = 0.8$ and 1.0. The data for DyCuAl are shifted for better view.

appears to be very similar both for DyNiAl and DyCuAl series, analogous evolution of magnetic structures in the two compounds can be also expected [6].

2. Crystal structure

The X-ray diffraction studies on the Er- and Dy-based series revealed an abrupt change of lattice parameters—observed for x within the intervals (0.5, 0.6) and (0.3, 0.4), respectively (Fig. 1). The step observed at room temperature (X-ray data) persists down to the lowest studied temperature (1.6 K—powder neutron diffraction experiment). The step-like changes of a and c are of opposite sign leaving the unit cell volume unaffected, following the Vegard's law. The abrupt c/a change is probably connected with different intra-plane and inter-planar chemical bonding. Comparison with crystallographic data for other isostructural RTX compounds implies an idea of a "forbidden" c/a ratio of $c/a \approx 0.56$–0.57. The $a(x)$ and $c(x)$ discontinuity is shifted to lower Cu concentrations with increasing the extent ion-radius (i.e. when spanning the rare-earth series from Er to Tb). By extrapolating the above mentioned evolution to Tb-case the possible anomaly already falls beyond $x = 0.0$, which is confirmed by experiment [3].

3. Magnetism

The magnetic phase diagrams of the $RNi_{1-x}Cu_xAl$ compounds were found to be quite complex when substituting Cu for Ni [3,4]. For the $DyNi_{1-x}Cu_xAl$ compounds, two magnetic phases – AF below T_{ord} and additional F below $T_1 < T_{ord}$ – were found for $x \leq 0.2$. An IC propagation of the AF phase was found also in this series in a narrow concentration region around $x = 0.4$. A commensurate propagation of AF order is then present again up to $x = 0.6$. Only one magnetic phase was observed for $x \geq 0.4$. For samples with $x \in (0.6; 0.9)$, signs of SRO were found with strongest suppression of magnetic ordering for $x = 0.8$ (see Fig. 2). Our powder neutron diffraction measurements showed only one ferromagnetic phase below T_{ord} down to $T = 1.6$ K for $x = 0.9$ and 1.0.

4. Discussion

The structural discontinuity seems to be rather a consequence of geometrical properties and chemical-bonding forces, since this effect is present in both—the paramagnetic and ordered state. The shift of the c/a ratio through the lanthanide period in the periodic table is systematic with respect to rare-earth atomic radius.

Evolution of magnetic behavior within the substituted series is nontrivial. The question arisen during our studies of Er- and Dy-based systems about relation of structural and magnetic anomalies can be answered now. The transition from AF to F and change of the magnetocrystalline anisotropy occur independently on structure discontinuity (the c/a step), that could have only minor influence e.g. on crystal-field parameters. Since the LRO is lost in all studied systems at the same Cu-concentration, the number of 3d electrons in the Ni, Cu sublattice seems to be the crucial parameter here, and neither the structural anomaly nor the rare-earth element species play considerable role in this effect. Already the rather low magnetic temperatures of the $RNi_{1-x}Cu_xAl$ compounds indicate that the indirect RKKY-type exchange interactions are mainly responsible for magnetic order in these materials. A question arises how the itinerant 3d electrons brought in the system by Ni enter in the exchange interaction game. One scenario proposed by Ehlers et al. [3] considers an exchange interaction mediated by the transition-metal free 3d electrons competing with the RKKY interaction [3]. Result of this competition may be the frustrated state for certain composition of the (Ni,Cu) sublattice. Another approach may be to include the itinerant 3d electrons

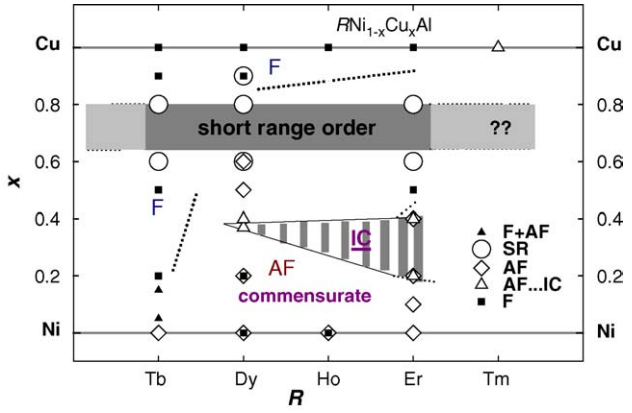

Fig. 3. The enhanced tendency to incommensurate propagation with decreasing free f-electron states. Data for another than Dy-based series were taken from refs. [3]—Tb, [5,6]—Ho, [4]—Er, [7]—Tm. The remarks have following meaning: AF, antiferromagnetic order; AF. . .IC, antiferromagnetic with incommensurate propagation; F + AF, coexistence of AF and F in sense of different parts of sample; SR, signs of short-range order; F, ferromagnetic order. If there are two marks on one position – e.g. for F and AF in $DyNi_{0.8}Cu_{0.2}Al$ sample – there are two coexisting components of the ordered moment (different from F + AF!).

to the overall balance of conduction electrons mediating the R–R exchange interaction (in fact the RKKY-type).

There is one more aspect of evolution of magnetic order with varying the composition of the (Ni,Cu) sublattice. The incommensurate (IC) propagation in Er-based system was found in range of $x \in (0.2; 0.4)$. In the Dy-based series, we found it in a quite narrower region and in the Tb-based compounds already no incommensurate propagation at all has been observed [3]. On the other hand, there is IC propagation in TmCuAl [7]. The IC propagation was also reported for compounds from the opposite end of the lanthanide group, PrNiAl and NdNiAl [5]. One can see the tendency when spanning the lanthanide group in the periodic table of elements shown in Fig. 3 suggesting that the IC propagation is connected with the occupancy of the 4f-electron shell, i.e. compounds having R-element with either almost empty or almost full f-electron shell.

Acknowledgments

This work is a part of the research program MSM 0021620834 financed by the Ministry of Education of the Czech Republic. The work has been also supported by the Higher Education Development Fund (FRVŠ, Grant #1842) and the Grant Agency of the Charles University (Grant #282/2004/B-FYZ/MFF). Partial support from the Grant ME512 of the Ministry of Education of the Czech Republic is also acknowledged.

References

[1] O. Garlea, E. Morosan, S.L. Bud'ko, J.L. Zarestky, P.C. Canfield, C. Stassis, J. Appl. Phys. 95 (2004) 6921.
[2] Ł. Gondek, A. Szytuła, J. Hernandez-Velasco, A. Zygmunt, J. Magn. Magn. Mater. 262 (2003) 177.
[3] G. Ehlers, D. Ahlert, C. Ritter, W. Miekeley, H. Maletta, Europhys. Lett. 37 (1997) 269.
[4] J. Prchal, P. Javorský, V. Sechovský, M. Dopita, O. Isnard, K. Jurek, J. Magn. Magn. Mater. 283 (2004) 34.
[5] G. Ehlers, H. Maletta, Z. Phys. B 101 (1996) 317 (G. Ehlers, Thesis, Berlin 1996).
[6] P. Javorský, L. Havela, V. Sechovský, H. Michor, K. Jurek, J. Alloys Compd. 264 (1998) 38.
[7] P. Javorský, P.C.M. Gubbens, A.M. Mulders, K. Prokeš, N. Stüsser, T.J. Gortenmulder, R.W.A. Hendrikx, J. Magn. Magn. Mater. 251 (2002) 123.