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Magnetic properties of the $UCo_{1-x}Ni_xAl$ system

V.H. Tran[a,*], R. Troć[a], H. Noël[b]

[a] *W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 50-950, P.O. Box 937, Poland*
[b] *Laboratoire de Chimie du Solide et Inorganique Moléculaire, Université de Rennes I, Av. du Général Leclerc, 35042 Rennes, France*

Abstract

We have measured the DC- and AC-magnetic susceptibility on the pseudoternary system $UCo_{1-x}Ni_xAl$ in the composition range $0 \leq x < 1.0$. All the samples studied were single phase and crystallize in the hexagonal Fe_2P-type structure. Such behaviour can be explained assuming that the Ni-atoms first occupy the (1b)-sites up to $x \sim 0.3$ and then the (2c)-sites. Substitution of Co with small amounts of Ni in UCoAl ($x < 0.1$) leads to a disappearance of a magnetic ordering. Below 15 K these compositions exhibit a metamagnetic transition in magnetic fields. In the composition range $0.1 < x < 0.5$, there exist ferromagnetic correlations between U-moments at low temperatures, weakening with increasing x. Hence, the compositions $x = 0.5$–0.7 are paramagnetic to the lowest temperature measured (1.7 K). On the Ni-rich side of compositions ($x \geq 0.8$), the antiferromagnetic state sets in. For these alloys, the susceptibility anomaly related to the Néel temperature, increases from 3 to 23 K, being highest for UNiAl. © 1997 Elsevier Science S.A.

Keywords: Magnetic phase diagram; $UCo_{1-x}Ni_xAl$; Susceptibility; Metamagnetism; Antiferromagnetic materials

1. Introduction

In recent years, we have intensively studied two systems $UFe_{1-x}Ni_xAl$ [1] and $UFe_{1-x}Ni_xCoAl$ [2] by means of X-ray diffraction, magnetization and ^{57}Fe Mössbauer measurements. We have found that these solid solutions crystallize in the hexagonal Fe_2P-type structure and show an interesting magnetic behaviour. Within a certain concentration range of the doped content Ni or Co, a spontaneous ferromagnetism was observed. The Curie temperature and saturation moment appear to depend non-linearly on concentration x and in each case to pass through a maximum. All these findings prompted us to investigate the $UCo_{1-x}Ni_xAl$ solid solutions which should give a complementary information on the magnetic properties of the $U(T_{1-x}T'_x)Al$ systems, where T and T′ are 3d-electron transition metals.

In this paper we have investigated the last member of the above series, namely the $UCo_{1-x}Ni_xAl$ alloys, using X-ray powder diffraction, DC- and AC-magnetic measurements. Previously, some magnetization, σ, and specific heat (C/T), data were reported by Brück et al. [3], but only for several Ni-rich compositions. The most remarkable result was an increase in C/T at low temperatures with increasing concentration of the Co-content in UNiAl up to 20 mol%, while the Néel temperature diminished to a lowest value.

2. Experimental details

Approximately 14 samples from the $UCo_{1-x}Ni_xAl$ system with the compositions $0.0 < x < 1.0$ were prepared by arc-melting stoichiometric constituents under a high purity argon atmosphere. After an annealing at 650°C for 2 weeks, the samples were analyzed by X-ray diffraction technique.

The DC-magnetization was performed between 1.7 and 300 and in magnetic fields up to 5.5 T, using a

* Corresponding author.

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SQUID magnetometer (Quantum Design MPMS-5 type). The AC-magnetic susceptibility was measured with a LAKE SHORE susceptometer (series 7000) between 4.5 and 60 K and in an AC-field of 10 Oe applying a frequency of 160 Hz.

3. Results

The X-ray diffraction analysis showed that all the prepared $UCo_{1-x}Ni_xAl$ solid solutions were almost single-phase having the hexagonal Fe_2P-type structure (the presence of impurity phases was less than 5%). A quite unusual change in the lattice parameters with composition was observed (Fig. 1). The parameter c shows a minimum at $x \approx 0.3$, while the parameter a first increases with Ni-content up to $x \approx 0.3$, but then with a further increase of x it remains almost constant. Thus, the concentration dependence of the lattice parameters does not obey Vegard's law. The concentration dependence of lattice parameters with the anomalous behaviour at $x \approx 0.3$, indicates a preferential occupation of the (1b)-sites by the Ni-atoms. Similar anomalous behaviour of the lattice parameters has previously been observed for the pseudoternary systems with the same Fe_2P-type structure, namely for $UFe_{1-x}Ni_xAl$ [1], $UFe_{1-x}Co_xAl$ [2] and $URu_{1-x}Co_xSn$ [4]. This effect has been explained by preferential occupation of the 1b-site by a transition metal with less atomic volume [5]. However, in the investigated here system Ni and Co atoms do not differ so much in size. This indicates that geometrical size of transition metal atoms is not likely to be the major contributing factor. Recently, we have studied the solid solutions $URu_{1-x}Pd_xGa$ [6], where a similar development of lattice parameters was observed. Surprisingly, in this system the (1b)-sites were also found to be preferentially occupied, but by the Pd atoms, having larger atomic volume compared to that of Ru-atoms. We have proposed, therefore, that the anomaly in $a(x)$ and $c(x)$ of $URu_{1-x}Pd_xGa$ is related to the difference of d-electron numbers of the transition metal atoms, i.e. the atoms with a more filled d-electron shell are more willing to occupy the (1b)-sites. It may be reasonable to assume that the electronic mechanism is a possible reason for the anomalous lattice parameter behaviour observed in hexagonal Fe_2P-type $U(T_{1-x}T'_x)M$ solid solutions (T, T' = transition metal atoms, M = p-electron elements).

Reciprocal magnetic susceptibility as a function of temperature, $\chi^{-1}(T)$, measured for some compositions of the $UCo_{1-x}Ni_xAl$ alloys is displayed in Fig. 2. At higher temperatures, the $\chi^{-1}(T)$-functions could be analyzed by a modified Curie–Weiss law: $\chi(T) = \chi_o + C/(T - \Theta)$. Values of μ_{eff}, χ_o and Θ, as found from a least-squares procedure, are listed in Table 1. It appears that the effective magnetic moment, μ_{eff} increases steadily from approx. 1.5 μ_B for UCoAl [2,7,8] to approx. 1.7–2.7 μ_B for all the compositions with $x > 0.3$. The paramagnetic Curie temperature, Θ_p, of UCoAl is positive [2,7] becoming negative for $x = 0.02$. This temperature of the antiferromagnetic

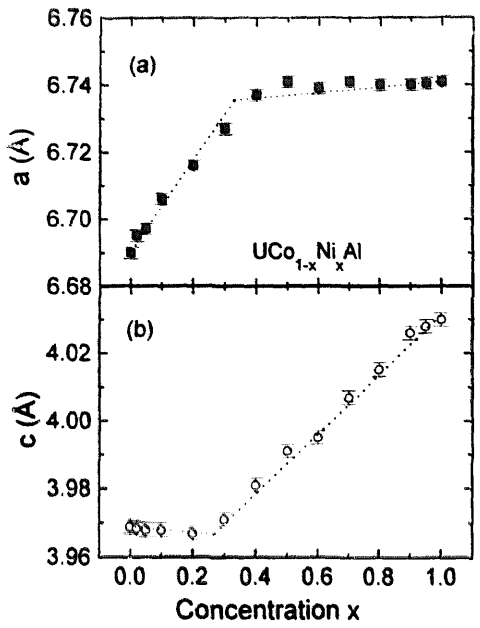

Fig. 1. Lattice parameter a (a) and parameter c (b) as a function of a Ni-concentration in the $UCo_{1-x}Ni_xAl$ solid solutions. The dotted lines are guides for the eye. The solid lines show the case of statistical occupancy of the sites by Co and Ni atoms.

Table 1
AC- and DC-magnetic susceptibility results for polycrystalline samples of the $UCo_{1-x}Ni_xAl$ solid solutions

x	$\chi_o 10^3$ (emu mol^{-1})	μ_{eff} (μ_B)	Θ_p (K)	Type of order T_t (K)
0[a]	0.8	1.51	25	F-AF/15
0.02	0.6	1.80	−15	Meta/10
0.05	0.5	2.07	−27	Meta/6
0.10	0.9	2.06	−29	P
0.20	0.5	2.11	−36	P
0.30	0.9	2.04	−78	P
0.40	0.8	2.08	−63	P
0.50	0.7	2.04	−141	P
0.60	0.9	1.64	−98	P
0.70	0.9	1.92	−58	P
0.80	0.3	2.75	−36	AF/3
0.90	0.3	2.60	−30	AF/8
0.95	0.3	2.65	−30	AF/13
1.0[b]	0.3	2.50	−21	AF/19

[a] Data from Troć et al. [2].
[b] Data from Tran et al. [1].
Notes: T_t indicates either T_M, T_C or T_N (see Figs 3 and 5).
The magnetic parameters χ_o, μ_{eff} and Θ_p are obtained by fitting the susceptibility data in the temperature range 70–300 K to a modified Curie–Weiss law.

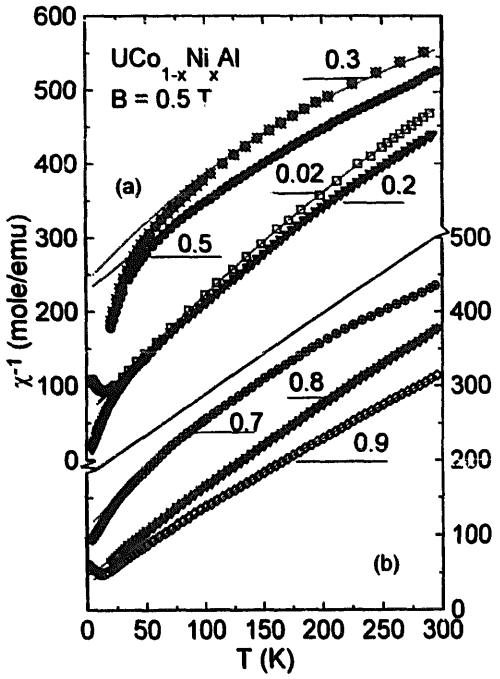

Fig. 2. Reciprocal magnetic susceptibility as a function of temperature for the $UCo_{1-x}Ni_xAl$ samples for $0.02 \leq x \leq 0.5$ (a) and $0.7 \leq x \leq 0.9$ (b). The solid lines are the fit of the experimental data to the modified Curie–Weiss law.

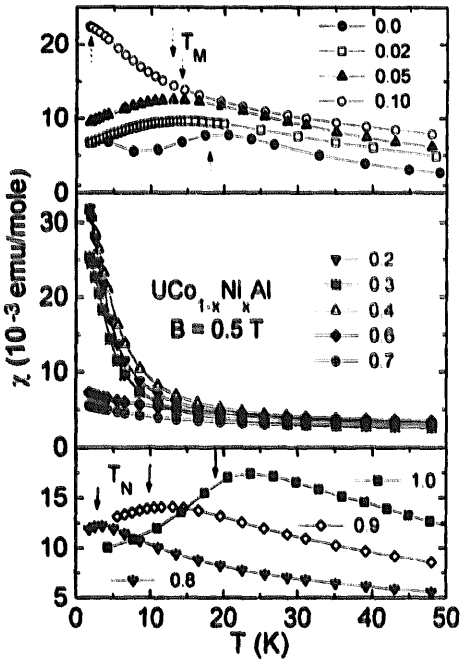

Fig. 3. Temperature dependence of the susceptibility of the solid solutions $UCo_{1-x}Ni_xAl$. The temperature T_m denotes the temperature, below which the metamagnetic state is observed. T_N indicates the Néel temperature.

UNiAl is close to the Néel temperature (~21 K). The temperature-independent susceptibility, χ_o, across the series lies in the range of $0.3–0.9 \times 10^{-3}$ emu mol^{-1}.

The low temperature susceptibility, $\chi(T)$, of the $UCo_{1-x}Ni_xAl$ alloys is shown in Fig. 3. $\chi(T)$ of

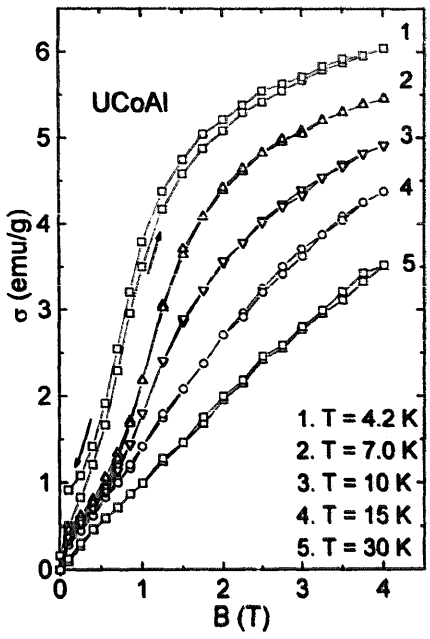

Fig. 4. Magnetization at various temperatures as a function of applied magnetic field for UCoAl.

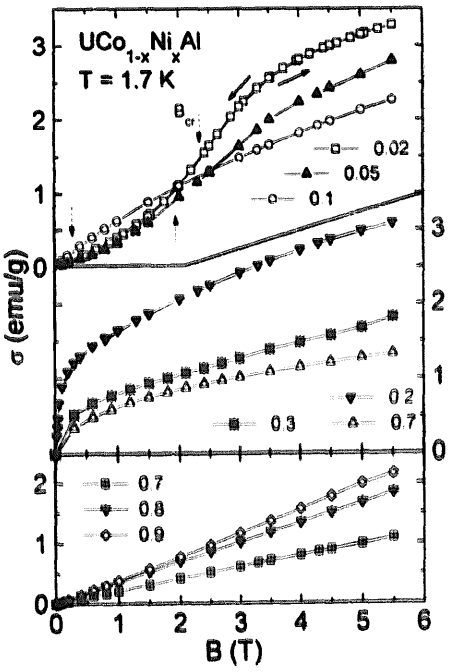

Fig. 5. Magnetization measured in magnetic fields up to 5.5 T and at 1.7 K for various $UCo_{1-x}Ni_xAl$ alloys with $0 < x < 1$. B_{cr} indicates the inflection point in the magnetization curves.

UCoAl measured at $B = 0.5$ T displays a cusp at $T_M = 17$ K and an upturn below 10 K. As discussed earlier [2], this behaviour reflects a coexistence of both the ferromagnetic and antiferromagnetic correlations in this compound. The susceptibility of the Ni-substituted alloys shows a number of remarkable features. First of all, this substitution shifts the position of χ-maximum towards lower temperatures, i.e.

to 15 K for $x = 0.02$ and to 12 K for $x = 0.05$, and finally this maximum is not observed for $x = 0.1$. At the same time, for the two former samples no upturn is observed in $\chi(T)$-curves at low temperatures. This result can be interpreted in terms of weakening of both ferro- and antiferromagnetic correlations in these compounds owing to the Ni-substitution. An essential difference between UCoAl and the Ni-doped alloys can be seen in the magnetization behaviour at 4.2 K. Unlike UCoAl, where a distinct hysteresis and remanence of the magnetization indicate the existence of the ferromagnetic content (Fig. 4), for the $x = 0.02$ and 0.05 samples we find no such feature.

The magnetization of these latter compositions exhibit a reversed S-shape with an inflection point at approx. $B_{cr} = 2.0$–2.5 T (see Fig. 5).

Further increase of the Ni content, i.e. above $x = 0.1$, leads to a recovery of the upturn in $\chi(T)$-curves at low temperatures, causing that the χ-value at 1.7 K continuously increases with increasing composition up to $x = 0.5$, reaching a huge value of approx. 35×10^{-3} emu mol^{-1}, i.e. approx. 10 times larger than the χ-value at room temperature. This increase one can interpret as being due to the presence of a weak ferromagnetism originating from the U–U correlations, which still exist in these alloys. The possibility of having a ferromagnetic impurity rather should be excluded, since we have not observed any hysteresis or any remanence (see Fig. 5) characteristic of a ferromagnetic material. With further increase of the Ni-content in the alloys the situation changes rapidly. For example, the two compositions with $x = 0.6$ and 0.7 behave as a weak temperature-dependent paramagnet down to 1.7 K.

Furthermore, the susceptibility of $x = 0.8$ shows a small maximum at $T = 3.0$ K, due to an antiferromagnetic ordering setting up in this composition. With increasing Ni-concentration, this maximum occurs at higher temperatures, i.e. at 8, 13 and 23 K for $x = 0.9$, 0.95 and 1.00, respectively (Fig. 3). Hence, we believe that starting from $x = 0.8$ a long-range antiferromagnetic ordering is formed at low temperatures in these alloys. These findings are corroborated by the specific heat measurements by Brück et al. [3], who have measured temperature dependence of specific heat for compositions from $x = 0.6$ to $x = 1.0$. The authors have argued that the λ-anomaly related to T_N disappears just between $x = 0.8$ and $x = 0.9$.

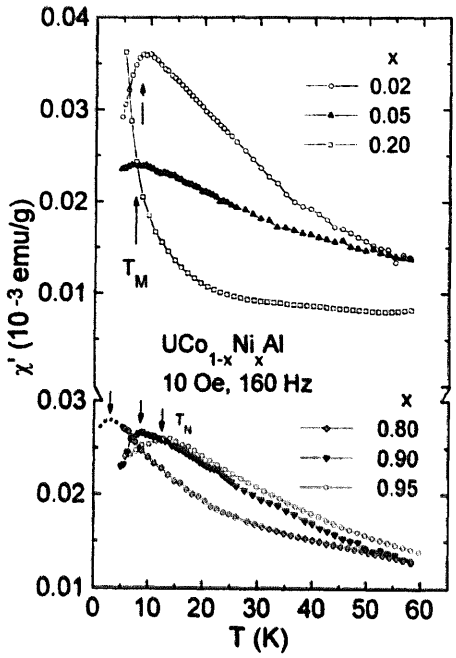

Fig. 6. Temperature dependence of the real part of AC-magnetic susceptibility, $\chi'(T)$, measured at frequency 160 Hz and in magnetic AC-field of 10 Oe for some compositions of the $UCo_{1-x}Ni_xAl$ solid solutions. The temperatures T_m and T_N are defined in Fig. 3.

Consistent with the DC-susceptibility, the zero-field AC-susceptibility data exhibit pronounced maxima in the AC-susceptibility curves, but at somewhat lower temperatures, i.e. approx. 10 and 6 K, for $x = 0.02$ and 0.05, respectively (Fig. 6). For these samples, similar

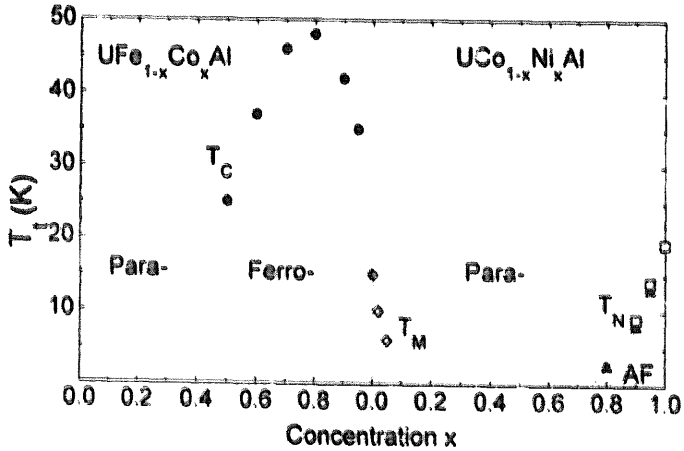

Fig. 7. Joined magnetic phase diagrams of $UFe_{1-x}Co_xAl$ [2] and $UCo_{1-x}Ni_xAl$. The open squares are the data from Brück et al. [3]. The lines are guides to the eye.

maxima are observed also in the imaginary component (not shown here). However, none maxima are observed in samples with $0.1 < x \leq 0.8$ down to 4.2 K. For Ni-rich side ($x = 0.90$ and 0.95), the maxima in $\chi_{ac}(T)$-curves are again observed. The lack of any anomaly in the imaginary part of AC-susceptibility additionaily gives evidence that these materials are typical antiferromagnets.

4. Discussion and conclusions

The data presented above are summarized in the phase diagram displayed in Fig. 7. This figure includes the data taken for the $UFe_{1-x}Co_xAl$ system from Tran et al. [2]. In general, this joined figure resembles very well the magnetic phase diagram of $UFe_{1-x}Ni_xAl$ given in Troć et al. [1]. In the previous studies on $UFe_{1-x}Co_xAl$ [2], we have shown that the substitution of Co for Fe atoms in UFeAl (Co introduces one electron more) enhances strongly the magnetism, and in a consequence leads to the appearance of long-range ordering for $x > 0.45$. This ferromagnetic state remains practically to the end alloy, i.e. UCoAl, though the final magnetic structure of this alloy is still unknown. The problem in determination of this structure arises due to the fact that the ferromagnetic interactions in the $UFe_{1-x}Co_xAl$ system are considerably reduced on the account of a gradual increase in the antiferromagnetic interactions. Hence, we have suggested that in UCoAl both the ferromagnetic and antiferromagnetic interactions are almost equally important, what can lead to form a large frustration in magnetic order. Therefore, it is not surprising that the ground state in UCoAl is extremely sensitive to a deviation from the stoichiometry or to the alloying with other 3d-electron element, differing in the number of conduction electrons.

The magnetic diagram of $UCo_{1-x}Ni_xAl$ implies three different magnetic concentration regions: (a) $x < 0.1$; (b) $0.1 \leq x \leq 0.7$; and (c) $x > 0.8$. The alloys falling into the first region show a metamagnetic-like behaviour in an applied magnetic field. This region becomes a continuous part for the magnetic phase diagram resulting from $UFe_{1-x}Co_xAl$ (see Fig. 7). The alloys belonging to the second region are paramagnetic down to 1.7 K. These with a smaller Co content are characterized by an upturn of susceptibility below 5 K, but those with a higher Co content exhibit only a weakly temperature dependent paramagnetism. Finally, the $x \geq 0.8$ samples order antiferromagnetically at low temperatures. This antiferromagnetic ground state is formed for $x = 0.9$ and 0.95 in accordance with the specific heat results reported by Brück et al. [3].

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