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Alexander Krimmel, Alois Loidl, C. Geibel, Frank Steglich, G. J. McIntyre

Angaben zur Veröffentlichung / Publication details:

Krimmel, Alexander, Alois Loidl, C. Geibel, Frank Steglich, and G. J. McIntyre. 1992. "Neutron diffraction experiments on UCu4+xAl8−x." Journal of Magnetism and Magnetic Materials 103 (1-2): 73–77. https://doi.org/10.1016/0304-8853(92)90238-j.

Neutron diffraction experiments on $UCu_{4+x}Al_{8-x}$

A. Krimmel, A. Loidl

Institut für Physik, Universität Mainz, 6500 Mainz, Germany

C. Geibel, F. Steglich

Institut für Festkörperphysik, T.H. Darmstadt, 6100 Darmstadt, Germany

and

G.J. McIntyre

Institut Laue-Langevin, 156X, 38042 Grenoble, France

Neutron diffraction experiments are reported on $UCu_{4+x}Al_{8-x}$ for concentrations $0.1 \leq x \leq 1.9$ and temperatures 1.6 K $\leq T \leq$ 300 K. For $x \leq 1$ these compounds undergo antiferromagnetic phase transitions into a collinear AF I-type structure, with the magnetic moments aligned along the tetragonal c-axis and alternating order within the $a-b$ planes. With increasing concentration the ordering temperatures decrease and moment compensation due to a Kondo-type interaction develops for $x > 1$.

1. Introduction

$UCu_{4+x}Al_{8-x}$ crystallizes in the $ThMn_{12}$-structure [1–3] with a homogeneity range from $0.1 \leq x \leq 1.95$ [3]. These compounds reveal an alloying-induced transition from local moment magnetism ($x \approx 0.1$) to a heavy-fermion liquid state ($x \approx 1.95$) [3]. Magnetic susceptibility, heat capacity and electrical resistivity measurements have been reported previously [3,4] and revealed antiferromagnetic (AF) order for $x \leq 1.25$ and a Fermi liquid state for $x \geq 1.5$. At low temperatures the Sommerfeld coefficient γ reaches 100 mJ/mol K^2 in the magnetically ordered states and approximately 800 mJ/mol K^2 in the non-magnetic compounds [3,4]. A neutron diffraction study for $x = 0.5$ indicated AF order with the magnetic moments localized at the uranium positions and pointing along the tetragonal c-axis [2]. At 4.2 K the magnitude of the ordered uranium moments μ_S was estimated to be $(1.3 \pm 0.5)\mu_B$. The aim of the present neutron diffraction study was to explore the transition from local moment magnetism (LMM) ($x \approx 0.1$) to a Fermi-liquid state of heavy quasiparticles ($x \approx 1.9$) in detail. Traditionally, this transition has been understood in the framework of Doniach's [5] phase diagram. However, new theoretical concepts [6] have predicted the occurrence of heavy fermion band magnetism (HFBM) which is supported by some experimental evidence [7]: upon increasing hybridization of the localized 4f(5f)-states with conduction electrons the compensation of local moments, involving antiferromagnetic correlations, becomes almost complete. In this regime, HFBM may result from an ordering process of small renormalized magnetic moments which are tied to heavy-fermion quasiparticles.

2. Experimental results and discussion

The samples were melted in an arc furnace and subsequently annealed for five days at 750 °C. $UCu_{4+x}Al_{8-x}$ forms peritectically and hence, the annealing procedure is essential to get single phase material. Polycrystalline samples with x = 0.25, 0.75, 1, 1.25, 1.5 and 1.9, approximately 40 g each, were prepared as described in ref. [3], grounded to fine powders and loaded into vanadium cans. The neutron diffraction experiments were performed on the multidetector diffractometer D1B located on a thermal neutron guide at the high flux reactor at the Institut Laue–Langevin in Grenoble, France. A neutron wavelength of 2.52 Å was selected by a pyrolytic graphite (002) monochromator. The powder diffraction pattern, recorded for $x = 1$ at 1.6 K, is shown in the upper frame of fig. 1. The lower part of fig. 1 shows the difference pattern: here the intensities as recorded in the paramagnetic phase have been subtracted from the pattern observed at 1.6 K. Already a brief inspection of the pure magnetic structure reveals a simple type of antiferromagnetic spin arrangement.

To analyse the neutron diffraction patterns in detail, standard Rietveld analyses have been performed for both the nuclear as well as the magnetic structures. The parameters fitted include lattice constants, atomic coordinates, temperature factors and magnetic moments. The most relevant parameters resulting from the best fits are listed in table 1. The $ThMn_{12}$-structure has two free positional parameters, which are the x-coordinates of the aluminum ions at sites i and j. The x-coordinates, derived from the best fits, are also included in table 1. A representative result of the quality of the fits is shown as solid line in the 1.6 K pattern of fig. 1 (upper frame).

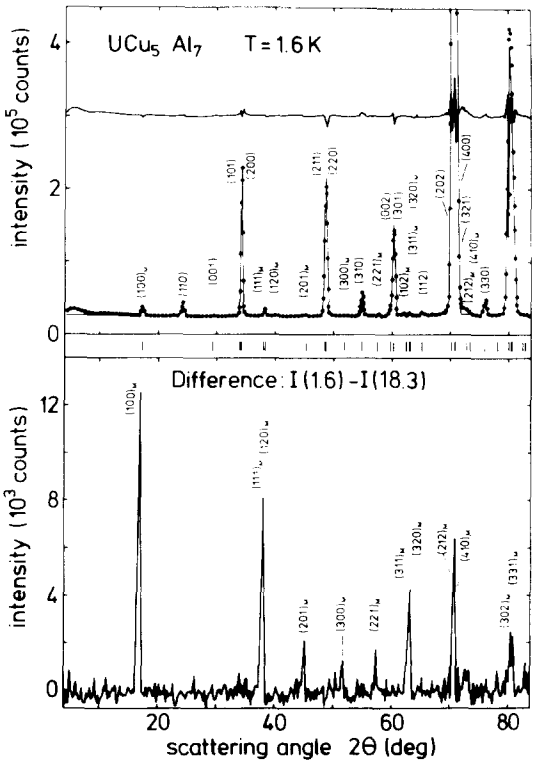

Fig. 1. Upper frame: observed diffraction pattern for the nuclear and magnetic Bragg reflections of UCu_5Al_7 at 1.6 K. The solid line through the experimental points is the result of a Rietveld fit to the nuclear and the magnetic Bragg reflections. The difference counts between calculated and observed intensities are indicated (note that the zero-line has been shifted to 3×10^5 counts. Lower frame: difference pattern for UCu_5Al_7 [I(1.6 K)–I(18.3 K)], yielding the magnetic Bragg reflections, only.

Table 1
Lattice constants a and c, x-coordinates of the aluminum ions at 8i (x_i,0,0) and at 8j (x_j,0.5,0) and ordered moments μ_S in $UCu_{4+x}Al_{8-x}$ at 1.6 K. R_B-factors for the nuclear and magnetic structure: $R_{Bragg} = 100\sigma_i|I_i(obs)-I_i(calc)|/\sigma_i I_i(obs)$. Antiferromagnetic ordering temperature T_N as determined from $\mu_S(x)$ (see fig. 4)

x	a (Å)	b (Å)	x_i	x_j	μ_S (μ_B)	R_B	T_N (K)
0.25	8.746 (1)	5.096 (1)	0.351 (2)	0.282 (3)	1.6 (1)	6.83	37 (1)
0.5	8.725 (2)	5.090 (2)	0.351 (3)	0.283 (3)	1.65 (10)	4.66	35 (1)
0.75	8.707 (1)	5.083 (2)	0.353 (4)	0.284 (4)	1.6 (1)	4.42	27 (1)
1	8.698 (3)	5.081 (2)	0.354 (3)	0.282 (3)	1.2 (1)	4.16	18 (2)
1.25	8.682 (3)	5.071 (2)	0.353 (4)	0.280 (4)	< 0.23	5.94	10 (ref. [3])
1.5	8.680 (3)	5.062 (3)	0.350 (4)	0.268 (5)	–	7.49	–
1.9	8.680 (3)	5.058 (3)	0.356 (5)	0.237 (7)	–	10.40	–

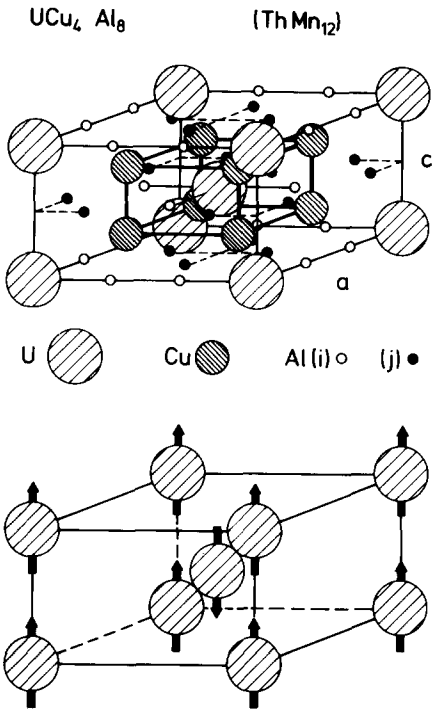

Fig. 2. Upper frame: tetragonal unit cell of UCu_4Al_8 ($ThMn_{12}$-structure). Atomic coordinates: 2 U at 2a: U (0,0,0); 8 Cu at 8f: Cu (0.25, 0.25, 0.25); 8 Al at 8i: Al(i) (x_i, 0, 0) and 8 Al at 8j: Al(j) (x_j, 0.5, 0). Lower frame: magnetic structure for $T \leq T_N$; only the U atoms are shown.

The difference between the calculated and the observed profile is also indicated.

All samples investigated revealed the tetragonal $ThMn_{12}$-structure (space group I4/mmm) with two inequivalent Al sites (i) and (j) (see fig. 2a). From the Rietveld analysis we conclude that for concentrations $0.25 < x < 1.5$ the excess Cu is substituted on the j-sites only. For $x = 1.9$, a refinement with the Cu atoms substituted randomly on the i- and j-sites yielded significantly better fits. At intermediate concentrations ($x \approx 1$) small extra reflections show up in the nuclear diffraction pattern and provide some evidence for the appearance of a superstructure. Further analysis is in progress to clarify this point. From preliminary X-ray diffraction studies and from the analysis of the concentration dependence of the residual resistivity it was concluded that the excess Cu is substituted at random on the two inequivalent Al sites [3,4].

Substitution of the Al atoms (0.143 nm) by the smaller Cu atoms (0.128 nm) results in a compression of the a and c lattice parameters by approximately 1% in the concentration range investigated (see table 1 and fig. 3). Figure 3 shows the concentration dependence of the lattice constants a and c and the concentration dependence of the volume V at room temperature (295 K) and at 1.6 K. The room temperature values of the lattice constants have been determined by X-ray diffraction and the compression of the lattice parameters evolves rather smoothly. However, at low temperatures the lattice constant a exhibits a significant deviation from a linear concentration dependence close to $x \approx 1.1$ (fig. 3) which marks the borderline from magnetic order to heavy-fermion behavior. To check whether this anomalous concentration dependence originates from magneto-elastic couplings, the temperature dependence of a and c has been determined across the magnetic phase transition temperatures. For

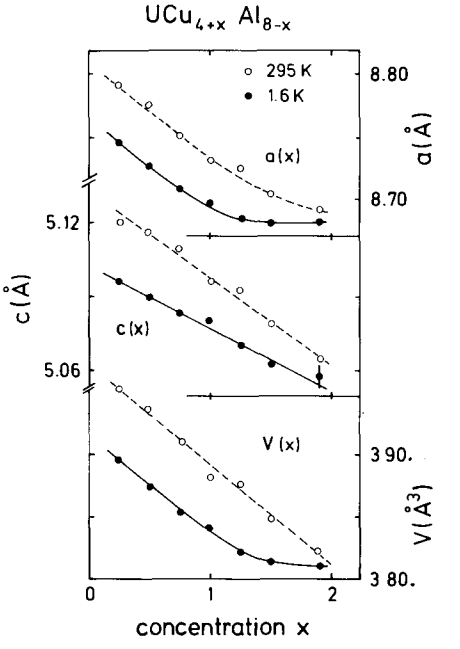

Fig. 3. Lattice constants a and c and unit cell volume V in $UCu_{4+x}Al_{8-x}$ vs. concentration x: full circles (●): neutron results at 1.6 K; empty circles (○): X-ray results at room temperature. The estimated errors in a and c are indicated, or are well within the extent of the plot symbols. The lines are drawn to guide the eye.

all compounds investigated effects, of magnetostriction are almost negligible. Hence we conclude that the change of slope in $a(x)$ is driven by the Kondo-type interactions.

Using the Rietveld refinement, the magnetic Bragg reflections for all concentrations could be consistently explained by assuming a simple collinear AF I-type structure, with the magnetic moments aligned along the c-axis and alternating ferromagnetic order within the a–b planes (see fig. 2b). At 1.6 K magnetic Bragg reflections were detected for $x = 0.25, 0.5, 0.75$ and 1. For $x \leq 0.75$ the ordered moment $\mu_S = (1.6 \pm 0.1)\mu_B$, in agreement with, but more precise, than the earlier neutron study [2]. For $x = 1$ the ordered moment is $1.2\mu_B$ and is significantly reduced by hydridization effects. In these powder diffraction experiments no long-range magnetic order could be detected for $x = 1.25$. However, magnetic susceptibility measurements [3,4] have indicated AF order below 10 K and from the apparent absence of any magnetic Bragg peaks we estimate that the ordered moment μ_S is less than $0.23\mu_B$.

The temperature dependence of the ordered moments, as determined from a complete Rietveld analysis of the diffraction patterns at different temperatures, is shown in fig. 4. $\mu_S(x)$ is of the order of $1.6\mu_B$ and almost concentration independent for $x < 0.75$. However, in the same concentration regime the AF ordering temperature T_N has been reduced by approximately 25%. For $x = 1$, T_N is reduced by a factor of two and moment compensation effects have reduced the ordered moment to $1.2\mu_B$. Finally, for $x = 1.25$, $T_N = 10$ K, as determined from susceptibility measurements and our neutron data yield an upper limit of the ordered moment, namely $\mu_S < 0.23\mu_B$.

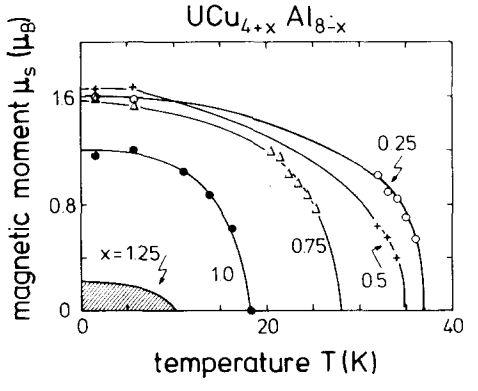

Fig. 4. Temperature dependence of the ordered magnetic moments of $UCu_{4+x}Al_{8-x}$ for $x = 0.25, 0.5, 0.75$ and 1.0. For $x = 1.25$ the upper limit of the ordered moment ($\mu_s < 0.23\mu_B$) is indicated.

3. Summary and conclusions

Neutron diffraction studies have been performed on $UCu_{4+x}Al_{8-x}$ for concentrations $x = 0.25, 0.5, 0.75, 1, 1.25, 1.5$ and 1.9. The nuclear and the magnetic structures have been determined using Rietveld analysis. As an important structural detail we found that for concentrations $0.25 \leq x \leq 1.5$ the excess Cu is substituted at the aluminum j-sites, only. The symmetry of the i- and the j-sites is the same. Thus, the most plausible reason for this preferred substitution may well be found in steric constraints: the distance Al(j)–U is about 10% larger than the distance Al(i)–U.

At low temperatures the lattice constant a reveals a significant deviation from a linear x-dependence. We suggest that this anomaly in the concentration dependence of the lattice constants $a(x)$ is due to hybridization effects of the localized 5f electrons with the band states. In $UCu_{4+x}Al_{8-x}$ the uranium–uranium distance d_{U-U} approximately is 0.51 nm which is well beyond Hill's limit [8] (≈ 0.36 nm for uranium) and direct f-atom interactions can be disregarded. Thus, the heavy-fermion behavior which is found for $x > 1$ develops via a strong hybridization of the 5f-electrons with the neighbouring non-f electron atoms [9]. Obviously, in $UCu_{4+x}Al_{8-x}$ the substitution of Cu for Al at the j-sites is responsible for the strong increase of the delocalization by f-ligand hybridization ($d_{U-Al(j)} \approx 0.32$ nm) Similar anomalies in the concentration dependence of the lattice constants have been found in pseudoternary solid solutions of $Ce(Cu_{1-x}Ni_x)_2Si_2$ [10]. In this system the evolution of strong mixed valency in $CeNi_2Si_2$ from the heavy-fermion behavior of $CeCu_2Si_2$ is accompa-

nied by an anomalous increase of the Ce-ligand distances [10].

The powder diffraction profiles reveal AFM order for concentrations $0.1 < x < 1$. We propose that this regime can be characterized as LMM: with increasing concentration, the transition temperatures gradually decrease and a significant compensation of the ordered moments develops for $x > 0.75$. However, the ordered moment is always less than the effective moment derived from the high-temperature Curie-type susceptibility: Geibel et al. [3] found an effective moment varying from $2.6\mu_B$ for $x = 0.5$ to $2.8\mu_B$ for $x = 1.5$. HFBM may appear for $x \approx 1.25$, however, single-crystal work is needed to identify the magnetic structure, the ordered moment and the nature of the magnetic order.

It is interesting to compare our results for $UCu_{4+x}Al_{8-x}$ with the neutron diffraction results for the heavy-fermion compound U_2Zn_{17} [11]. Both compounds have have an extremely low density of uranium atoms in common: the U density amounts one U atom per 151 Å^3 in U_2Zn_{17} and one per 193 Å^3 in UCu_4Al_8. In U_2Zn_{17} the linear term of the specific heat γ is 1070 mJ/mol K^2 (535 mJ/mol K^2 per uranium atom) in the paramagnetic state and extrapolates to 395 mJ/mol K^2 (198 mJ/mol K^2 per uranium atom) at $T = 0$ K, below the AF phase transition temperature $T_N = 9.7$ K [12]. From the high-temperature, Curie-type susceptibility, an effective moment of $2.25\mu_B$ was derived, while the ordered moment amounts $0.8\mu_B$ [11]. Despite a relatively high value of the ordered moment, U_2Zn_{17} has been interpreted as an itinerant antiferromagnet where a gap develops only over a small fraction of the Fermi surface [11].

In conclusion, the analysis of the powder diffraction pattern presented in this paper provide experimental evidence that strong hybridization effects of the 5f-electrons with the electrons of the Cu atoms, which have been substituted on the Al j-sites, are responsible for the formation of the heavy fermion state in $UCu_{4+x}Al_{8-x}$ for $x > 1$. In addition, our data suggest that a LMM to HFBM transition, so far only established for the $Ce(Cu_{1-x}Ni_x)_2Ge_2$ system [4,7], also occurs in the uranium-based heavy fermion compound $UCu_{4+x}Al_{8-x}$ close to $x = 1.25$.

Acknowledgements

This work was supported by the Sonderforschungsbereich 252 (Darmstadt/Frankfurt/Mainz/Stuttgart) and by the Bundesministerium für Forschung und Technologie under the contract number 03-LO1MAI (C4-57).

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