

Influence of off-stoichiometry on the properties of the heavy fermion superconductors UNi_2Al_3 and UPd_2Al_3

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Abstract

We have investigated the influence of deviations from stoichiometry on the metallurgical, superconducting and magnetic properties of UNi_2Al_3 and UPd_2Al_3 . Deviations from stoichiometry in UNi_2Al_3 generally increase the width of the superconducting transition and can lead to a complete suppression of the anomalies related to the antiferromagnetic (AF) ordering. By contrast, in UPd_2Al_3 we have observed a reduction in the superconducting transition temperature T_c , whereas the AF transition is not affected. We discuss the implication of these results on the metallurgical phase diagram and on the nature of both the superconducting and the AF state of these compounds.

1. Introduction

The new heavy fermion (HF) superconductors UNi_2Al_3 [1] and UPd_2Al_3 [2] have attracted considerable interest owing to the coexistence of superconductivity and antiferromagnetic (AF) ordering at low temperatures with a magnetic moment unusually large for HF superconductors [3]. The investigation and interpretation of the physical properties of these compounds is hampered by metallurgical problems during the preparation of the samples leading to some irreproducibility in the superconducting and magnetic properties. In order to understand these variations and to increase the reproducibility, we have investigated how deviations from stoichiometry affect the metallurgical, superconducting and magnetic properties of UNi_2Al_3 and UPd_2Al_3 . We have prepared several polycrystalline samples of UNi_2Al_3 and UPd_2Al_3 with slight deviations (excess or deficiency of each element) from the 1–2–3 composition by a standard arc melting technique. The starting materials U (depleted, Merck), Ni (99.998%, Johnson Matthey), Pd (99.998%, Demetron) and Al (99.999%, Heraeus) have been used. The physical properties of the samples have been investigated by measurements of the resistivity $\rho(T)$, the a.c. and d.c. susceptibilities $\chi_{ac}(T)$ and $\chi_{dc}(T)$, and, in some cases, the specific heat $C(T)$ in the temperature range $0.04 \text{ K} \leq T \leq 300 \text{ K}$.

2. Results

2.1. UNi_2Al_3

X-ray (XR) powder diffraction patterns of the as-cast Ni-based samples exhibit all reflections belonging to the hexagonal PrNi_2Al_3 structure. Additional peaks with intensities lower than about 5% can be resolved in the XR patterns and identified as a foreign phase of UAl_2 . Only the sample with 1–1.95–3.05 composition contains as much as 30 at.% UAl_2 . For the sample $\text{UNi}_{2.05}\text{Al}_{2.95}$ no foreign phases are visible in the XR pattern. Further exchange of Al by Ni results in the appearance of the reflections related to UNiAl and NiAl . This strongly suggests that UNi_2Al_3 forms peritectically according to $\text{melt} + \text{UAl}_2 \rightleftharpoons \text{UNi}_2\text{Al}_3$ and that the 1–2–3 composition is the primary phase which forms out of slightly Ni-rich melts. After an annealing process at 900 °C for 120 h the amount of the UAl_2 foreign phase was reduced to 1 at.% or less, and in the case of the 1–1.95–3.05 composition to 10 at.%. In Table 1 the superconducting properties and the resistivity ratio $\text{RR}_{4.2 \text{ K}} = \rho_{300 \text{ K}}/\rho_{4.2 \text{ K}}$ of the following off-stoichiometric Ni compounds are shown: six $\text{U}_{1 \pm x}\text{Ni}_{2 \pm y}\text{Al}_{3 \pm z}$ samples with $x, y, z = 0.02$ and two $\text{UNi}_{2 \pm x}\text{Al}_{3 \mp x}$ samples with $x = 0.05$. The results are compared with those of an undoped sample. Except for three of these compositions the onset temperature T_c^{onset} of the superconducting transition is not affected with respect to the undoped sample. In the case of the compositions 1.02–2–3 and 1–1.95–3.05, T_c^{onset} is reduced to about one-half of the value for stoichiometric UNi_2Al_3 , and

TABLE 1. Superconducting properties (onset temperature T_c^{onset} and width ΔT_c of the superconducting transition) and resistivity ratio $\text{RR}_{4.2\text{K}} = \rho_{300\text{K}}/\rho_{4.2\text{K}}$ of off-stoichiometric $\text{U}_{1\pm x}\text{Ni}_{2\pm y}\text{Al}_{3\pm z}$ samples

Composition			T_c^{onset} (K)	ΔT_c (K) (10%–90%)	$\text{RR}_{4.2\text{K}} =$ $\rho_{300\text{K}}/\rho_{4.2\text{K}}$
U	Ni	Al			
1	2	3	1.126	0.46	23
1.02	2	3	0.510	⊕	7
0.98	2	3	1.145	⊕	9
1	2.02	3	1.140	⊕	5
1	1.98	3	1.130	⊕	4
1	2	3.02	1.135	⊕	8
1	2	2.98	1.155	⊕	11
1	2.05	2.95	⊖	⊖	3
1	1.95	3.05	0.660	⊕	7

⊕, very broad transition; ⊖, no superconductivity above $T=0.04$ K.

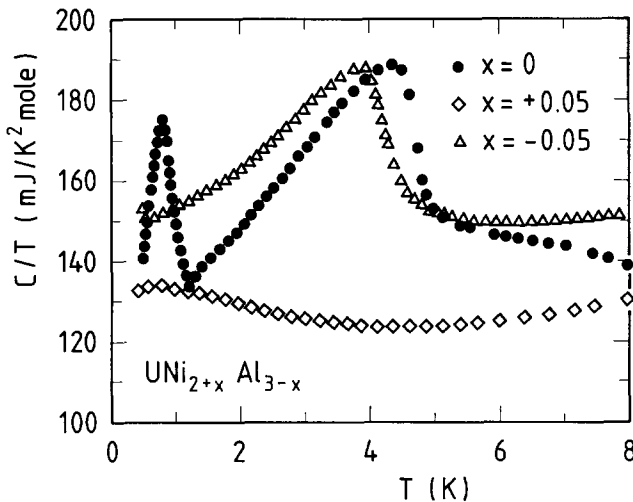


Fig. 1. Specific heat C/T vs. T of UNi_2Al_3 , $\text{UNi}_{2.05}\text{Al}_{2.95}$ and $\text{UNi}_{1.95}\text{Al}_{3.05}$.

$\text{UNi}_{2.05}\text{Al}_{2.95}$ does not exhibit superconductivity at all above $T=40$ mK. Another parameter characterizing superconductivity is the width ΔT_c of the superconducting transition, deduced from 10% to 90% of the jump height in $\rho(T_c)$ and $\chi(T_c)$. Whereas the width of the superconducting transition of undoped UNi_2Al_3 is already quite big ($\Delta T_c \approx 0.46$ K), ΔT_c of all off-stoichiometric samples cannot be determined, since the superconducting transition is not completed down to the lowest temperatures measured: $\rho(T=40 \text{ mK}) > 0$, $\chi(T=40 \text{ mK}) > -1$. The resistivity ratio of the off-stoichiometric Ni compounds is strongly decreased compared with undoped UNi_2Al_3 . However, no systematic trend can be stated between the kind of excess-deficiency element and $\text{RR}_{4.2\text{K}}$.

In Fig. 1 the specific heat C/T vs. T of $\text{UNi}_{2.05}\text{Al}_{2.95}$, $\text{UNi}_{1.95}\text{Al}_{3.05}$ and UNi_2Al_3 is shown. Both antiferro-

magnetic ordering at T_N and superconductivity at T_c are indicated by anomalies in the specific heat. Whereas these anomalies occur at $T_N=4.7$ K and $T_c=1$ K in the undoped sample, in the $\text{UNi}_{1.95}\text{Al}_{3.05}$ compound T_N is slightly reduced to 4.3 K, and the onset of the superconducting transition is about to appear as indicated by an upturn in $C(T)/T$ at the lowest temperature measured, $T=0.6$ K. (It should be noted that $T_c^{\text{onset}}=0.66$ K according to a.c. susceptibility measurements.) In the case of $\text{UNi}_{2.05}\text{Al}_{2.95}$, both the superconducting and the AF transition appear to be completely suppressed.

2.2. UPd_2Al_3

XR powder diffraction on all Pd-based samples reveals reflections only of the hexagonal PrNi_2Al_3 structure before as well as after heat treatment (900 °C for 120 h): within the instrumental resolution there are no secondary phases. In Table 2 the same parameters as in Table 1 are shown for seven $\text{U}_{1\pm x}\text{Pd}_{2\pm y}\text{Al}_{3\pm z}$ samples (it should be noted that here the midpoint temperature T_c^{mid} of the superconducting transition is given instead of T_c^{onset}). In addition, the AF ordering temperature T_N is listed. Whereas the magnetic properties do not seem to be affected by off-stoichiometry, both T_c^{mid} and $\text{RR}_{4.2\text{K}}$ are strongly reduced for some compositions. Remarkably enough, in these very samples the superconducting transition width is still of the same size as in the undoped sample. Since we have already observed a similar correlation between a decreasing resistivity ratio $\text{RR}_{4.2\text{K}}$ and a decreasing T_c in doped UPd_2Al_3 [4], we wished to learn whether such a relation is already obeyed in nominally pure compounds, where small (uncontrolled) changes of stoichiometry and defects lead to a scatter of T_c around 1.8 K. In Fig. 2 we have plotted T_c vs. $1/\text{RR}_{4.2\text{K}}$ for undoped, nominally stoichiometric samples, both polycrystalline as well as single-crystal material (grown by the Czochralski method

TABLE 2. Superconducting properties (midpoint temperature T_c^{mid} and width ΔT_c of the superconducting transition), antiferromagnetic ordering temperature T_N and resistivity ratio $\text{RR}_{4.2\text{K}} = \rho_{300\text{K}}/\rho_{4.2\text{K}}$ of off-stoichiometric $\text{U}_{1\pm x}\text{Pd}_{2\pm y}\text{Al}_{3\pm z}$ samples

Composition			T_c^{mid} (K)	ΔT_c (K) (10%–90%)	T_N (K)	$\text{RR}_{4.2\text{K}} =$ $\rho_{300\text{K}}/\rho_{4.2\text{K}}$
U	Pd	Al				
1	2	3	2.0	0.20	14.5	25
1.01	2	3	1.88	0.14	14.7	17
0.99	2	3	1.94	0.07	14.8	15
1	2.02	3	0.83	0.25	14.9	4
1	1.98	3	1.20	0.23	14.9	3
1	2	3.03	0.61	0.19	14.8	5
1	2	2.97	⊖	⊖	14.5	3

⊖, no superconductivity above $T=0.04$ K.

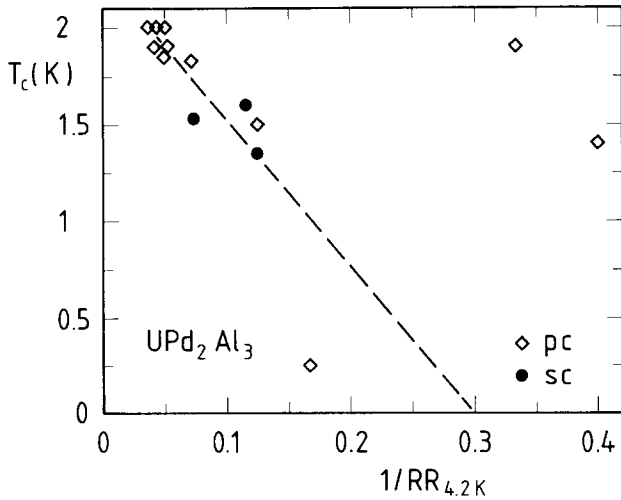


Fig. 2. Superconducting transition temperature T_c vs. $1/RR_{4.2\text{K}}$ (resistivity ratio $RR_{4.2\text{K}} = \rho_{300\text{K}}/\rho_{4.2\text{K}}$) for several nominally stoichiometric UPd_2Al_3 samples (polycrystalline as well as single-crystal material). The straight line is intended as a guide to the eye.

[5]). $1/RR_{4.2\text{K}}$ is roughly proportional to the resistivity at $T = 4.2\text{K}$ which is dominated by the residual resistivity ρ_0 . Most of the data suggest a linear relationship between T_c and $1/RR_{4.2\text{K}}$ and thus, ρ_0 . An extrapolation of this correlation leads to $T_c = 0\text{K}$ at $(1/RR_{4.2\text{K}})_0 \approx 0.3$. This is consistent with $(1/RR_{4.2\text{K}})_0 \approx 0.15\text{--}0.3$ previously obtained for doped samples [4], which generally exhibit lower T_c and higher $1/RR_{4.2\text{K}}$ values. Thus, it seems that this relation between increasing residual resistivity and decreasing T_c holds also for a small reduction of T_c and $RR_{4.2\text{K}}$.

3. Discussion

Our results show that UNi_2Al_3 and UPd_2Al_3 behave quite differently on changes in stoichiometry. The AF transition remains completely unaffected in the Pd compound, but reacts quite sensitively in the Ni compound. This remarkable difference supports different types of AF ordering in these two compounds, *i.e.* being of localized character in UPd_2Al_3 , but of a more itinerant kind in UNi_2Al_3 . Recent neutron scattering experiments on UNi_2Al_3 [6] have revealed an incommensurate AF structure while resistivity measurements [7] suggest a spin-density wave type of transition. Further evidence for the weakness of the AF state in UNi_2Al_3 compared with that in UPd_2Al_3 is given by doping experiments recently performed on both compounds [4, 5]. Those results show that T_N is only weakly reduced by doping with 10 at.% Gd, Pr, Y or Th on the U site in UPd_2Al_3 , while already 1 at.% Gd doping in UNi_2Al_3 results in a complete suppression of T_N .

The difference in the superconducting properties between UNi_2Al_3 and UPd_2Al_3 can be attributed to their different metallurgical properties: slight deviations from stoichiometry leave the superconducting transition temperature T_c^{onset} unchanged in the Ni compound (except for $\text{U}_{1.02}\text{Ni}_2\text{Al}_3$), whereas they strongly reduce T_c^{mid} in the Pd compound. On the contrary, the transition width ΔT_c becomes too broad to be accurately determined in the former, but remains unchanged in the latter compound. In the case of UNi_2Al_3 , our observations can be explained by a broad homogeneity range between Al and Ni. Therefore, slightly off-stoichiometric samples exhibit a wide distribution of T_c values; in particular, they contain some parts with that composition corresponding to the highest T_c . Only larger changes in stoichiometry will eventually lead to a suppression of superconductivity. Regarding the 1.02–2–3 composition, whose superconducting transition temperature is reduced to less than half the value of the stoichiometric compound, we note that because of the size mismatch an excess of U cannot be put on Ni or Al sites in the lattice. Our results also suggest that the optimal T_c corresponds to a composition in the middle of the homogeneity range (in contrast to, for example, CeCu_2Si_2 , where T_c corresponds to a composition at the Cu-rich boundary [8]). This explains the difficulties in preparing UNi_2Al_3 samples with a sharp specific heat anomaly at T_c . In the case of off-stoichiometric UPd_2Al_3 , on the contrary, the strongly reduced, but still sharp, superconducting phase transition is attributed to a narrow Pd–Al homogeneity range. Concerning $\text{UPd}_2\text{Al}_{2.97}$, the disappearance of superconductivity is attributed to the deficiency of Al. Measurements of the resistivity on UPd_2Al_3 single crystals grown by the Czochralski method [5, 9] have revealed the samples grown from a melt with a slight Al excess (of 0.3–1 at.%) to exhibit a higher T_c and a sharper phase transition compared with those grown from a stoichiometric melt. This effect has been ascribed to the partial evaporation of Al during the growing process. In this sense, if one starts with a deficiency of Al, superconductivity cannot be expected in $\text{UPd}_2\text{Al}_{2.97}$.

In conclusion, our investigations on the influence of off-stoichiometric UNi_2Al_3 and UPd_2Al_3 have revealed quite different superconducting and magnetic properties. The AF ordering is of localized character in the Pd compound, but of a more itinerant kind in the Ni compound. The broad homogeneity range between Al and Ni in UNi_2Al_3 leads to a broad superconducting transition width, whereas the strongly reduced superconducting transition temperature at a still sharp phase transition of slightly off-stoichiometric UPd_2Al_3 is attributed to a narrow Al–Pd homogeneity range.

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