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Double superconducting transition in the specific heat of non-stoichiometric UPt_{3+x}

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We have studied the double superconducting transition of polycrystalline UPt_{3+x} prepared from a non-stoichiometric melt ($-0.06 < x < 0.06$). Samples prepared with a Pt deficit show the sharpest double transition, suggesting the binding of oxygen by excess uranium. However, microprobe investigations reveal that impurity phases (UPt_2 and UPt_5) are formed and that the actual deviation from stoichiometry ($-0.01 < x < 0.01$) is much smaller than the nominal value.

The heavy-fermion superconductor UPt_3 attracts much attention because of the double step-structure at the superconducting transition, first observed in the specific heat [1]. Two distinct anomalies appear, 60 mK apart, at $T_c^+ = 490$ mK and $T_c^- = 430$ mK. An appealing explanation for the double transition is inferred from group theoretical work [2]: the superconducting transition is split due to the lifting of the degeneracy of the superconducting (vector) order parameter by a symmetry breaking field. The symmetry breaking field is possibly provided by the antiferromagnetic order, with an extremely small moment ($|\mu| = (0.02 \pm 0.01)\mu_B$/f-atom), detected below $T_N = 5$ K by neutron-diffraction experiments [3]. However, the appearance of such a tiny moment is not easily reconciled within the current models and, therefore, the question rises whether residual defects and/or strain-fields are at its origin.

The sharpest double superconducting transition obtained thus far, is observed on samples prepared under ultrahigh vacuum [1]. Unfortunately, the double superconducting transition is not equally pronounced in all the samples [1,4], indicating that metallurgical aspects play a major role. In our investigation of such effects we have also started a number of impurity studies, with rather surprising results. The addition of small amounts of boron enhances T_c: for single-crystalline $UPt_3B_{0.11}$ (nominal boron concentration) $T_c^+ = 532$ mK and $T_c^- = 478$ mK [4]. Although the enhancement of T_c is partly related to a volume increase, the main effect is likely due to the purifying effect of boron addition (oxygen binding). Substitution of Pd on the Pt sites has been studied for polycrystalline samples (for Pd concentrations up to 0.2 at%) [5]. Both T_c^+ and T_c are suppressed, but remarkably, T_c^- is suppressed more rapidly and thus an increase of the splitting with Pd contents results. Substitution of Y on the U sites reveal that T_c^+ and T_c^- are suppressed at an equal rate. It is tempting to ascribe this distinctly different effect to an increase of the (induced) magnetic moment on the uranium site and thus to a stronger symmetry breaking field, in case of Pd doping, in contrast to the purely pairbreaking effect for Y doping. Further careful studies will be needed to verify this hypothesis.

Obviously, the influence of minor amounts of impurities is enormous. Therefore, it is of large interest to study the effects of non-stoichiometry on the double superconducting transition as well. Previous resistive studies [6] on polycrystalline samples revealed that for small deviations from stoichiometry T_c remained quite large ($T_c = 540$ mK). In this paper we investigate the double superconducting transition of these non-stoichiometric samples by means of a specific-heat study. Metallurgical aspects are detailed by a microprobe analysis.

Polycrystalline samples UPt_{3+x} ($x = -0.06$, -0.03, 0.00, 0.03 and 0.06) were prepared in an arc-furnace from a non-stoichiometric melt. The as-cast samples were wrapped in tantalum and annealed at 900°C for one week in an evacuated quartz tube, together with a piece of uranium metal that served as getter. Details of the sample preparation method are described in ref. [6]. A microprobe study revealed that the off-stoichiometric samples contained an impurity phase, UPt_2 in the case of Pt deficit, and UPt_5 in the case of Pt excess. The actual deviation from stoichiometry in the UPt_{3+x} phase cannot be determined, due to the limited accuracy of the microprobe analysis, but the upperbound amounts to 0.33% ($x = \pm 0.01$). The uranium-platinum phase diagram has thus a very limited homogeneity region for the UPt_3 phase. The sample with $x = 0.00$ did not contain an impurity phase. We estimate that the nominal sample $UPt_{2.94}$ contains almost 6% of UPt_2, whereas $UPt_{3.06}$ contains about 3% of UPt_5. The impurity phases were not identified from the Debye–Scherrer pictures, although additional lines were observed for the Pt-rich samples [6]. These lines are probably related with superstructures, due to stacking faults. Possible impurity uranium-oxide phases were not detected by the microprobe analysis.

Low-temperature ($0.3 < T < 0.6$ K) specific-heat measurements were performed on the samples prepared with $x = -0.06$, 0.00 and 0.06 (we used pieces of the samples resistively studied in ref. [6]). The specific

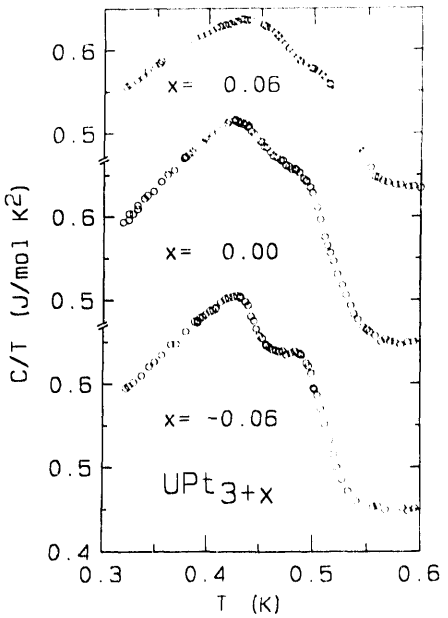

Fig. 1. c/T versus T for UPt_{3+x} prepared from a non-stoichiometric melt with $x = -0.06$, 0.00 and 0.06 (nominal x value).

heat was measured with a relaxation technique in a single-shot ^{3}He cryostat. The samples were fixed with silver paint on a sapphire plate, equipped with a RuO_2 thermometer and a heater. The experimental results are shown in fig. 1, in a plot of c/T versus T. The c/T-values have been corrected for the estimated amounts of impurity phases. The sample prepared with a Pt deficit clearly shows the sharpest double superconducting transition. With increasing x the transition broadens and a higher onset temperature (T_{onset}) results. Values for T_c^+, T_c^- and $\Delta = T_c^+ - T_c^-$ are collected in table 1, where we have also listed the residual resistance values [6]. In order to determine T_c^+ and T_c^- we used an entropy conserving construction [1]. Note that the entropy under the c/T versus T curve ($0.3 < T < T_{onset}$) for $x = 0.06$ is somewhat smaller than for the other two samples. The superconducting transition temperatures as determined resistively [6] are in agreement with the onset temperatures found in the specific heat experiments. An interesting trend follows from the data in fig. 1 and table 1. As fore-mentioned, the sharpest transitions occur for $x = -0.06$, the sample with the lowest residual resistance value ($\rho_0 = 0.94$ $\mu\Omega$ cm). In seeming contrast to this, the samples with $x = 0.00$ and 0.06 yield increasingly higher values for T_c^+ and T_c^-. As the samples have been prepared and heat-treated in exactly the same way, this trend is likely related to the actual deviations from stoichiometry ($-0.01 \leq x \leq 0.01$), and might thus be related to vacances on the Pt or U lattice, or site inversion. The broadening of a superconducting transition (as observed for increasing x) is normally ascribed to stress fields induced by impurities or defects. However, it is remarkable that the largest amount of an impurity phase, namely 6% UPt_2, is present in the sample with the sharpest transitions. This suggests that the impurity phases UPt_2 and UPt_5 play only a minor role. Probably, for the Pt poor samples binding of oxygen by the excess uranium leads to an overall smaller residual stress. For further investigations of this intriguing problem, detailed metallurgical studies are indispensable.

Table 1
Some characteristic parameters of UPt_{3+x} (nominal x-value). The residual resistance ρ_0 [6], the upper and lower superconducting transition temperature, T_c^+ and T_c^-, and the splitting (Δ)

x	ρ_0 ($\mu\Omega$ cm)	T_c^+ (mK)	T_c^- (mK)	Δ (mK)
−0.06	0.94	507	441	66
0.00	1.09	510	445	65
0.06	1.19	531	460	71

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References

[1] R.A. Fisher, S. Kim, B.F. Woodfield, N.E. Philips, L. Taillefer, K. Hasselbach, J. Flouquet, A.L. Giorgi and J.L. Smith, Phys. Rev. Lett. 62 (1989) 1411.
[2] See e.g.: K. Machida, M. Ozaki and T. Ohmi, J. Phys. Soc. Jpn. 58 (1989) 4116.
[3] G. Aeppli, E. Bucher, C. Broholm, J.K. Kjems, J. Baumann and J. Hufnagl, Phys. Rev. Lett. 60 (1988) 615.
[4] T. Vorenkamp, Z. Tarnawski, H.P. van der Meulen, K. Kadowaki, V.J.M. Meulenbroek, A.A. Menovsky and J.J.M. Franse, Physica B 163 (1990) 564.
[5] M.C. Aronson, T. Vorenkamp, Z. Koziol, A. de Visser, K. Bakker, K. Kadowaki, A.A. Menovsky, J.J.M. Franse and J.L. Smith, J. Appl. Phys. 69 (1991) 5487.
[6] M. van Sprang, J.Q.A. Koster, A.A. Menovsky and J.J.M. Franse, J. de Phys. 49-C8 (1988) 765.