

**SPECIFIC HEAT, SUSCEPTIBILITY  
AND HIGH-FIELD MAGNETISATION EXPERIMENTS  
ON HEAVY FERMION  $UPt_3$  ALLOYED WITH Pd**

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Specific heat, susceptibility and high-field magnetisation experiments have been performed on a number of pseudobinary  $U(Pt_{1-x}Pd_x)_3$  compounds with  $x \leq 0.30$ . For low Pd concentrations ( $x \leq 0.10$ ) the spin-fluctuation contribution to the specific heat is enhanced with respect to pure  $UPt_3$ . For  $x \geq 0.15$  the spin-fluctuation phenomena are lost. On alloying, the anomalies present for  $UPt_3$  in the susceptibility at 17 K and in the high-field magnetisation at 21 T (at 4.2 K), shift towards lower temperatures and fields, respectively, and have not been observed in a compound with  $x = 0.15$ . Superconductivity has not been found down to 40 mK in a  $U(Pt_{0.995}Pd_{0.005})_3$  sample.

At present the intermetallic compound  $UPt_3$  attracts a great deal of interest, owing to its classification as a heavy-fermion superconductor [1,2]. As a result a large variety of experiments have been performed in order to elucidate its unusual low-temperature properties. Surveys of these studies have recently been presented by Franse et al. [3,4]. In the normal state spin-fluctuation phenomena are believed to play a dominant role at low temperatures. Evidence for spin fluctuations mainly arises from the thermal properties: a  $T^3 \ln(T/T^*)$  contribution to the specific heat [1,2,5] and an anomalous linear thermal expansion coefficient [6]. Further support is offered by an initially quadratic field dependence of the differential susceptibility at 4.2 K [7] and by the overall temperature dependence of the electrical resistivity [8]. Recent neutron-scattering experiments [9,10] and theoretical work [11], justify the description of the low-temperature properties of  $UPt_3$  in terms of a spin-fluctuation model. However, the present spin-fluctuation models seem not capable to account for the high-field anomaly, near 21 T, that has been observed in magnetisation

and magnetoresistivity experiments [3–5,7,12]. Regarding the bulk of information available on  $UPt_3$ , we are, nevertheless, inclined to believe that the same many-body effects that cause the anomalies in the thermal properties are responsible for the anomalies in the magnetic and transport properties [4].

Superconductivity in  $UPt_3$  has been observed at 0.5 K [1,2]. The unusual coexistence of spin fluctuations and superconductivity has led Stewart et al. [1] to speculate on p-wave superconductivity, intermediated by spin-fluctuations. Although the nature of the superconducting state has been studied extensively, it is still subject to large controversies [4].

In our further investigation of the exciting low-temperature properties of  $UPt_3$  we have alloyed  $UPt_3$  by substituting Pt by isoelectronic Pd. Although the distances between neighbouring uranium atoms in hexagonal closed packed  $UPt_3$  (4.13 Å) and double hexagonal closed packed  $UPd_3$  (4.12 Å) are nearly identical, the low-temperature properties are quite different. Neutron-scattering experiments have revealed that  $UPd_3$  has well-localized f-electrons, with a  $5f^2$

Table 1

Lattice parameters ( $a$  and  $c$ ), neighbouring uranium distance ( $d_{U-U}$ ), molar volume ( $V_m$ ), susceptibility ( $\chi_{a,b}$  and  $\chi_c$ ), effective moment ( $\mu_{\text{eff}}$ ), and the electronic term in the specific heat ( $\gamma$ ), for hcp  $\text{UPt}_3$  (MgCd<sub>3</sub>-type of structure) and dhcp  $\text{UPd}_3$  (TiNi<sub>3</sub>-type of structure); data from refs. [2,7,13,15,18].

	$a$ (Å)	$c$ (Å)	$d_{U-U}$ (Å)	$V_m$ (m <sup>3</sup> /mol)	$\chi_{a,b}$ <sup>a)</sup>	$\chi_c$ <sup>a)</sup>	$\mu_{\text{eff}}$ ( $\mu_B$ )	$\gamma$ <sup>b)</sup>
$\text{UPt}_3$	5.572	4.897	4.13	$4.23 \times 10^{-5}$	107	57	2.6	422
$\text{UPd}_3$	5.770	9.631	4.11	$4.18 \times 10^{-5}$	300	160	2.8	10

a) In  $10^{-9}$  m<sup>3</sup>/mol U. b) In mJ/K<sup>2</sup> mol U.

configuration in an  $L-S$  ground-state  $^3H_4$  [13]. The low value of the coefficient of the linear term in the specific heat,  $\gamma < 10$  mJ/K<sup>2</sup> mol U [14,15], illustrates the absence of a narrow band, and contrasts with the "heavy-fermion" value of 422 mJ/K<sup>2</sup> mol U for  $\text{UPt}_3$ . In  $\text{UPd}_3$  two phase transitions have been observed, at 5 and 7 K, both non-magnetic of origin [14,16]. Evidence for crystal-field states comes from neutron-scattering experiments [13]: for both uranium sites in dhcp  $\text{UPd}_3$ , the hexagonal and the quasi-cubic sites, a singlet ground state with an energy distance to the first excited (doublet) level of 164 and 24 K, respectively, has been derived. Which energy splitting belongs to which site, however, has not firmly been established. In table 1 some crystallographic and magnetic parameters for  $\text{UPt}_3$  and  $\text{UPd}_3$  have been collected. Given the obvious differences between both compounds, large effects on the low-temperature properties of  $\text{UPt}_3$  might be expected, on alloying with Pd.

In this paper we report on specific heat measurements, in the temperature range 1.2–30 K, in zero field and in an applied field of 5 T, on a number of pseudobinary  $\text{U}(\text{Pt}_{1-x}\text{Pd}_x)_3$  compounds ( $x = 0.01, 0.02, 0.05, 0.10, 0.15, 0.20$  and  $0.30$ ). The samples with  $x = 0.02, 0.05$  and  $0.15$  have been studied in susceptibility experiments (1.4–300 K) and in high-field magnetisation experiments up to 35 T (at 4.2 K), as well. Parts of the specific heat results will be published elsewhere [4,17].

Polycrystalline compounds were prepared by arc melting the appropriate amounts of the pure elements, U (Koch Light, purity 99.8%), Pt and Pd (MRC-Marz grade), in a titanium-gettered argon atmosphere. All samples were annealed, in evacuated sealed silica tubes, at 1000°C for a period of 10 days. X-ray diffraction patterns taken on powdered samples

at room temperature confirmed the hexagonal MgCd<sub>3</sub>-type of structure. Samples with  $x \geq 0.15$  showed additional unresolved diffraction lines, pointing to at least one second phase. Small needle-like single-crystalline whiskers were obtained, for all pseudobinary compounds, from the arc melted buttons, just as for pure  $\text{UPt}_3$  [18]. Lattice parameter determinations from the X-ray diffraction patterns on the powdered samples and on the whiskers ( $x = 0.10, 0.20$  and  $0.30$ ) show that the  $a$  parameter remains constant within the experimental accuracy,  $a = 5.752(3)$  Å, on diluting. The  $c$  parameter decreases linearly with Pd concentration, from 4.897(3) Å for pure  $\text{UPt}_3$  down to 4.886(3) Å for  $x = 0.30$ .

An adiabatic method served to obtain specific heat data on the polycrystalline samples (mass 3–4 g). Data were taken in zero and in a 5 T applied field, see figs. 1 and 2, respectively. On alloying  $\text{UPt}_3$ , two remarkable features can be observed: (1) for  $x \leq 0.10$  the  $\gamma$  value increases with respect to pure  $\text{UPt}_3$ , and (2) an anomaly develops at low temperatures for the 2% and 5% buttons. The former observation points to an enhancement of the many-body effects at low temperatures. Although the extrapolation of the linear term in the specific heat to zero K is not unambiguously,  $\gamma$  might easily amount to 600 or 700 mJ/K<sup>2</sup> mol U for the 5% and 10% compounds. This signifies a surprisingly large increase of the  $\gamma$  value with respect to pure  $\text{UPt}_3$  with almost 50%. In a magnetic field of 5 T the  $\gamma$  values are only slightly modified, as indicated by the  $c/T$  values at 1.4 K in fig. 3. The entropy difference, in the temperature interval 1.2–20 K, between the curve for pure  $\text{UPt}_3$  and the curve for  $\text{U}(\text{Pt}_{0.80}\text{Pd}_{0.20})_3$  equals 2.4 J/K mol U. On diluting by Pd, the corresponding entropy differences with the 20% compound remain 2.4 J/K mol U, for  $x \leq 0.05$ . The entropy difference between the curves for  $x = 0.20$  and  $x = 0.30$  amounts to 1.0 J/K mol U.

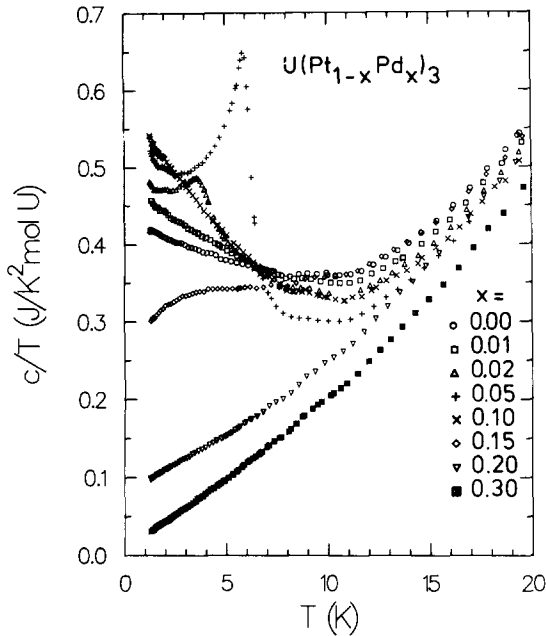


Fig. 1. Specific heat data for  $U(Pt_{1-x}Pd_x)_3$  compounds in a plot of  $c/T$  versus  $T$ , for  $x \leq 0.30$ .

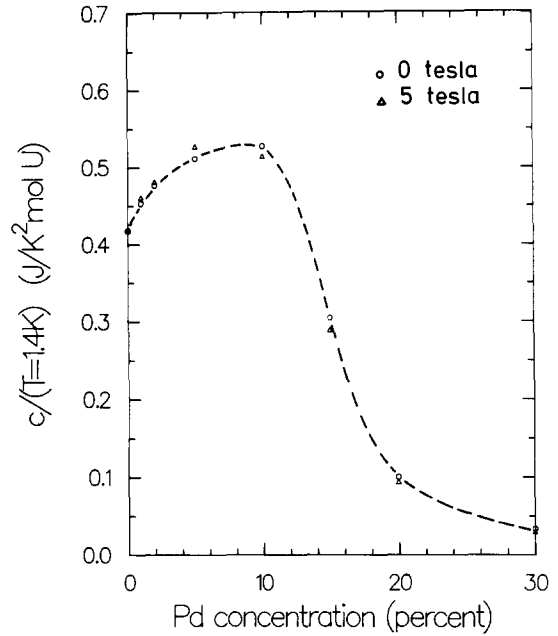


Fig. 3.  $c/T$  values at  $T = 1.4$  K versus Pd concentration for  $U(Pt_{1-x}Pd_x)_3$  compounds ( $x \leq 0.30$ ) in a magnetic field of 5 T ( $\Delta$ ) and at zero field ( $\circ$ ). The broken line serves as a guide to the eye.

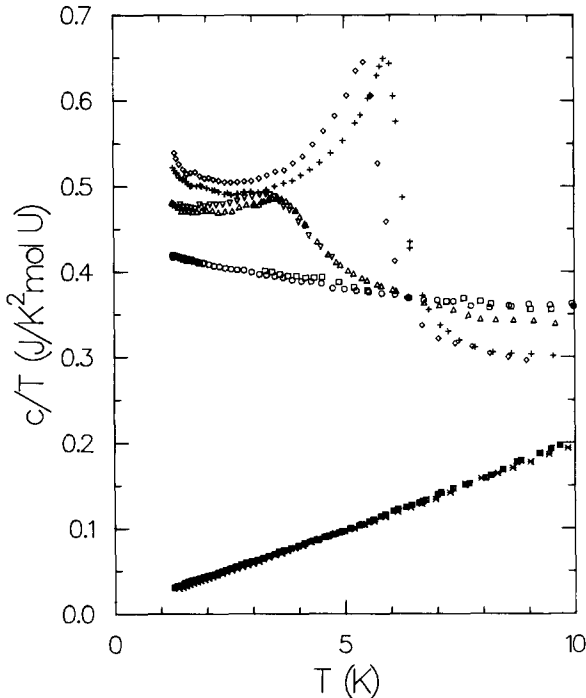


Fig. 2.  $c/T$  versus  $T$  for  $U(Pt_{1-x}Pd_x)_3$  compounds for  $x = 0.00$  ( $\circ$ ) and ( $\square$ ),  $x = 0.02$  ( $\Delta$ ) and ( $\nabla$ ),  $x = 0.05$  ( $+$ ) and ( $\diamond$ ), and  $x = 0.30$  ( $\boxtimes$ ) and ( $\times$ ), at zero field and an applied field of 5 T, respectively.

The nature of the anomalies in the specific heat data for the 5% and 2% compounds is not clear. In a magnetic field of 5 T the temperature at which the maximum in  $c/T$  is observed shifts from 5.8 to 5.4 K (5% Pd), and from 3.6 to 3.3 K (2% Pd), but the shape of both peaks remains essentially unchanged (fig. 2). These anomalies remind one of the phase transitions in  $UPd_3$  at 5 and 7 K [14,16]. From entropy considerations it follows that the anomalies in these pseudobinary compounds cannot be due to a second phase of  $UPd_3$  (that might be overlooked in the X-ray patterns). For  $UPd_3$  the excess entropy up to 15 K equals 3 J/K mol U [14], whereas the entropy involved in the peaks of the 5% and 2% samples amounts to 0.8 J/K mol U and 0.2 J/K mol U, respectively. Moreover the field effect on the specific heat anomaly for  $UPd_3$  has the opposite sign [15].

The specific heat data of  $UPt_3$  have been analysed with a  $T^3 \ln(T/T^*)$  contribution, characteristic for spin-fluctuation effects [1,2]. A computer fit to the data, in the temperature interval 1.2–10 K, including such a term, reveals a reduction of the characteristic

temperature,  $T^*$ , from 29 K (pure  $\text{UPt}_3$ ) to 22 K (1% Pd) and 19 K (10% Pd). For  $x \geq 0.15$  the spin-fluctuation properties are rapidly lost, consistent with recent specific heat data of Stewart and Giorgi [19] taken on a  $\text{U}(\text{Pt}_{0.80}\text{Pd}_{0.20})_3$  sample.

The results of the susceptibility and high-field magnetisation experiments are shown in figs. 4 and 5, respectively. The susceptibility data have been calculated from the slopes of the linear magnetisation curves (field region 0.6–1.3 T), that were obtained with a standard pendulum magnetometer. The high-field magnetisation experiments have been performed in the Amsterdam High Field Installation [20], at 4.2 K. Both experiments have been performed on cylindrical samples, with a diameter of 1.5 mm and a length of 5 mm (mass  $\approx 0.3$  g). Since preferred orientations were found to be present in these samples, and since the susceptibility of  $\text{UPt}_3$  is strongly anisotropic (table 1), not too much value should be attached to the absolute values in fig. 4.

Obviously, the most interesting result of alloying  $\text{UPt}_3$  with Pd on the susceptibility and magnetisation is the reduction of the characteristic temperature and field at which the anomalies are observed. The maximum in the susceptibility, at approximately 17 K for pure  $\text{UPt}_3$  [5,21], shifts towards lower temperatures (11 and 7 K for the 2% and 5% sample, respectively),

and becomes more pronounced. It is not observed on a sample with  $x = 0.15$  down to 1.4 K. From a Curie–Weiss analysis of the data in the temperature range 50–300 K, it follows that the effective moment remains constant on alloying ( $\mu_{\text{eff}} = 2.6 \pm 0.1 \mu_{\text{B}}$ ). The paramagnetic Curie–Weiss temperature increases from  $-80(\pm 10)$  K, for pure  $\text{UPt}_3$ , up to  $-50(\pm 10)$  K for  $\text{U}(\text{Pt}_{0.85}\text{Pd}_{0.15})_3$ . In the case of  $\text{UPd}_3$  a value for  $\mu_{\text{eff}}$  of  $2.8 \mu_{\text{B}}$  has been reported in the temperature interval 70–300 K [15]. The anomaly in the high-field magnetisation curve at 4.2 K, i.e. a maximum in the differential susceptibility at 21 T, for pure  $\text{UPt}_3$ , shifts towards lower fields (approximately 16 and 11 T for the 2% and 5% sample, respectively). Again, it has not been observed on a sample with  $x = 0.15$ , at this temperature.

Summarizing the specific heat, susceptibility and high-field magnetisation experiments, we conclude that a close connection between the thermal and magnetic properties exists. As has been discussed in the first paragraph: the characteristic temperature as derived from the specific heat ( $T^* \approx 29$  K), the temperature at which the maximum in the susceptibility occurs ( $T_{\text{max}} \approx 17$  K), and the field at which the maximum in the differential susceptibility is found ( $B_{\text{max}} \approx 21$  T), all reduce on alloying  $\text{UPt}_3$  with Pd. It shows that the anomalies in the susceptibility and magnetisation

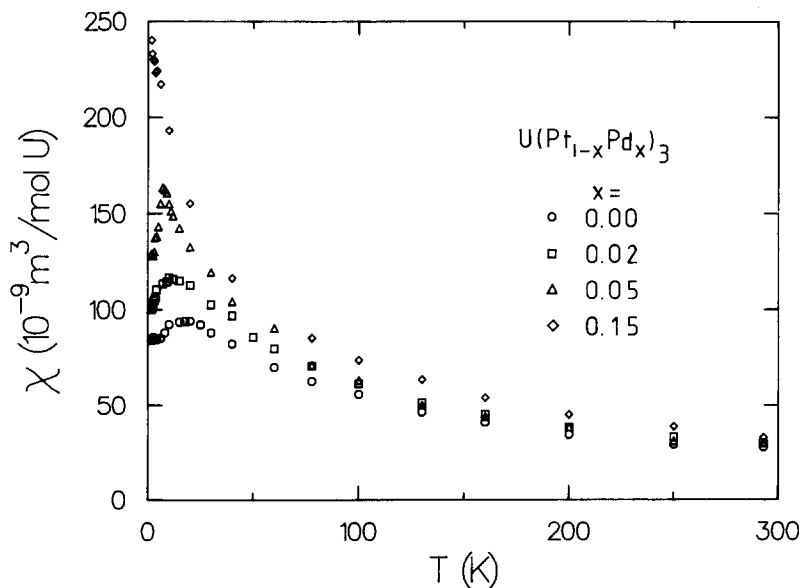


Fig. 4. Magnetic susceptibility versus temperature for polycrystalline  $\text{U}(\text{Pt}_{1-x}\text{Pd}_x)_3$  compounds ( $x = 0.00, 0.02, 0.05$  and  $0.15$ ).

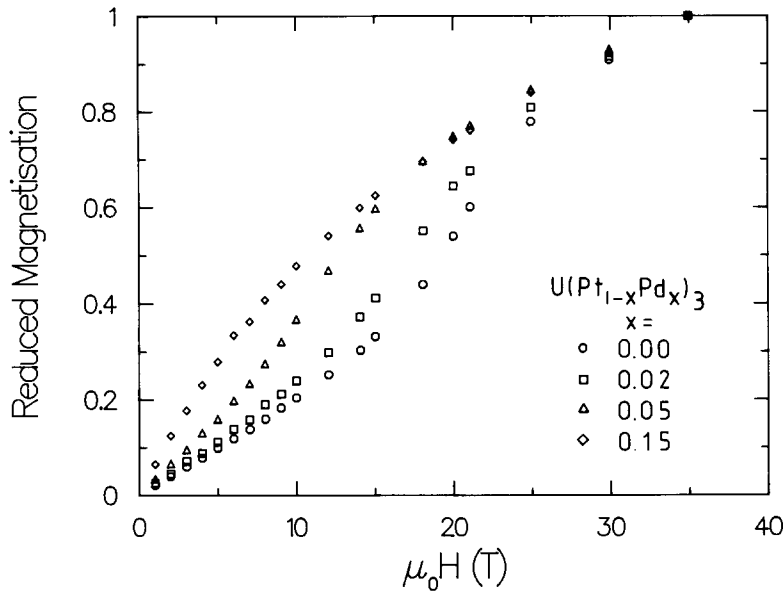


Fig. 5. High-field magnetisation in reduced units for polycrystalline  $U(Pt_{1-x}Pd_x)_3$  compounds. The absolute values at 35 T amount to 0.806, 0.782, 0.882 and 0.832  $\mu_B$  per U atom, for compounds with  $x = 0.00, 0.02, 0.05$  and  $0.10$ , respectively.

curves must be ascribed to the same many-body effects that are responsible for the anomaly in the specific heat, i.e. spin-fluctuation phenomena. For  $x \geq 0.15$  the spin-fluctuation phenomena are lost.

As has been shown above, the spin-fluctuation temperature decreases with Pd concentration, which leads to an enhancement of the spin-fluctuation effects at low temperatures (the  $\gamma$  value increases). It is an intriguing question whether superconductivity in  $UPt_3$  is closely related to the spin-fluctuation effects. Assuming that such a close relation exists, one would not expect a large change in the superconducting transition temperature for samples with small amounts of Pt substituted by Pd ( $x \leq 0.01$ ), since the spin-fluctuation effects do not change drastically for such low Pd concentrations. However, no superconductivity has been observed in a  $U(Pt_{0.99}Pd_{0.01})_3$  sample as has been concluded from an ac-susceptibility experiment down to 40 mK. Chemical analysis of the pure U and the low-field magnetisation experiments on these pseudobinary compounds, prove that magnetic impurities (probably Fe) have a maximum concentration of 600 ppm, which is approximately a factor of 10 less than the amount of Pd in this 1% sample. An annealed single-crystalline  $UPt_3$  sample, grown from this batch of U, was found to be superconducting at 0.48 K. A sub-

sequent unannealed  $U(Pt_{0.995}Pd_{0.005})_3$  sample, made of a purer batch of uranium, was not superconducting either, whereas an unannealed polycrystalline  $UPt_3$  sample made from the same uranium, became superconducting at 0.38 K. Hence, the absence of superconductivity in these pseudobinary  $U(Pt_{1-x}Pd_x)_3$  compounds is inherent to the Pd concentration, and thus a destructive influence from alloying  $UPt_3$  by Pd on the superconducting properties must be concluded. These results do not point to a close relation between superconductivity and spin fluctuations, and were taken as evidence for conventional superconductivity in  $UPt_3$  by Oguchi et al. [22]. Preliminary resistivity measurements on a  $U(Pt_{0.98}Pd_{0.02})_3$  whisker indicate that the residual resistivity ratio rapidly increases on alloying:  $\rho(300\text{ K})/\rho_0 = 3.1$ , with  $\rho_0 = 25\ \mu\Omega\text{ cm}$ . Besides, the quadratic temperature dependence of the resistivity, observed for pure  $UPt_3$  [8], has changed to a term linear in T. This confirms the strong influence of alloying  $UPt_3$  by Pd on the electronic transport properties and could be the main reason for a destruction of superconductivity in the  $U(Pt, Pd)_3$  alloys.

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