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Published in:
Physics Letters A

DOI:
[10.1016/0375-9601\(86\)90127-1](https://doi.org/10.1016/0375-9601(86)90127-1)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
1986

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Visser, A. D., Klaasse, J. C. P., Sprang, M. V., Franse, J. J. M., Menovsky, A., Palstra, T. T. M., & Dirkmaat, A. J. (1986). Specific Heat, Susceptibility and High-Field Magnetisation Experiments on Heavy Fermion UPT3 Alloyed with Pd. *Physics Letters A*, 113(9). [https://doi.org/10.1016/0375-9601\(86\)90127-1](https://doi.org/10.1016/0375-9601(86)90127-1)

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

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Received 6 August 1985; accepted for publication 13 November 1985

Specific heat, susceptibility and high-field magnetisation experiments have been performed on a number of pseudobinary $\text{U}(\text{Pt}_{1-x}\text{Pd}_x)_3$ 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 $\text{U}(\text{Pt}_{0.995}\text{Pd}_{0.005})_3$ 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 χ_c), effective moment (μ_{eff}), and the electronic term in the specific heat (γ), for hcp UPt_3 (MgCd₃-type of structure) and dhcp UPd_3 (TiNi₃-type of structure); data from refs. [2,7,13,15,18].

	a (Å)	c (Å)	d_{U-U} (Å)	V_m (m ³ /mol)	$\chi_{a,b}$ ^{a)}	χ_c ^{a)}	μ_{eff} (μ_B)	γ ^{b)}
UPt_3	5.572	4.897	4.13	4.23×10^{-5}	107	57	2.6	422
UPd_3	5.770	9.631	4.11	4.18×10^{-5}	300	160	2.8	10

a) In 10^{-9} m³/mol U. b) In mJ/K² 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/K² mol U [14,15], illustrates the absence of a narrow band, and contrasts with the "heavy-fermion" value of 422 mJ/K² mol U for UPt_3 . In 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 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 UPt_3 and UPd_3 have been collected. Given the obvious differences between both compounds, large effects on the low-temperature properties of 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 MgCd₃-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 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 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 UPt_3 , two remarkable features can be observed: (1) for $x \leq 0.10$ the γ value increases with respect to pure 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, γ might easily amount to 600 or 700 mJ/K² mol U for the 5% and 10% compounds. This signifies a surprisingly large increase of the γ value with respect to pure UPt_3 with almost 50%. In a magnetic field of 5 T the γ 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 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. 2. c/T versus T for $U(Pt_{1-x}Pd_x)_3$ compounds for $x = 0.00$ ($\circ$) and ($\square$), $x = 0.02$ ($\triangle$) and (∇), $x = 0.05$ ($+$) and ($\diamond$), and $x = 0.30$ ($\otimes$) and ($\times$), at zero field and an applied field of 5 T, respectively.

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 ($\triangle$) and at zero field ($\circ$). The broken line serves as a guide to the eye.

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 pseudo-binary 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 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 ≈ 0.3 g). Since preferred orientations were found to be present in these samples, and since the susceptibility of 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 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 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 ($\mu_{\text{eff}} = 2.6 \pm 0.1 \mu_B$). The paramagnetic Curie–Weiss temperature increases from $-80(\pm 10)$ K, for pure UPt_3 , up to $-50(\pm 10)$ K for $\text{U}(\text{Pt}_{0.85}\text{Pd}_{0.15})_3$. In the case of UPd_3 a value for μ_{eff} of $2.8 \mu_B$ 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 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 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 $\text{U(Pt}_{1-x}\text{Pd}_x)_3$ compounds. The absolute values at 35 T amount to 0.806, 0.782, 0.882 and 0.832 μ_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 γ 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 $\text{U(Pt}_{0.99}\text{Pd}_{0.01})_3$ 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 $\text{U(Pt}_{0.995}\text{Pd}_{0.005})_3$ 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 $\text{U(Pt}_{1-x}\text{Pd}_x)_3$ 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 $\text{U(Pt}_{0.98}\text{Pd}_{0.02})_3$ 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.

It is a pleasure to thank A.C. Moleman and P.H.M. van Berge Henegouwen for the X-ray analysis of the samples. This work is part of the research pro-

gram of the Dutch Stichting FOM (Foundation for Fundamental Research of Matter).

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