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Magnetism and superconductivity of the U(Pt, Pd)$_3$ system

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Abstract

The superconducting phase diagram of UPt_3 has been studied by a variety of techniques, all leading to three different phases in the B–T plane that meet the normal phase in a tetracritical point. Superconductivity has been reported to coexist with small-moment antiferromagnetism. The effects of substitutions on either the U site or the Pt site on the superconducting transition have been addressed in several studies. Pd substitutions for Pt play a particular role since the zero-field splitting between two superconducting phases increases from about 60 mK for pure UPt_3 to about 120 mK for the 0.2 at % Pd alloy. On further increasing the Pd content, superconductivity is suppressed above 0.5 at % Pd, whereas between 2 and 10 at % Pd long-range antiferromagnetic order is observed with values of the uranium moment up to $0.6\mu_B$. The relevant questions in these Pd substitution studies are: by which mechanism is the splitting between the two zero-field superconducting phases enhanced and, secondly, in which way does the small-moment antiferromagnetism evolve into the large-moment antiferromagnetic order at higher Pd concentrations. In this contribution, the salient features are reviewed with respect to the occurrence of magnetic order and superconductivity in the pseudo-binary system or U(Pt, Pd)$_3$ alloys, with an emphasis on dilatation experiments.

1. Introduction

Experiments on the U(Pt, Pd)$_3$ system started shortly after the discovery of UPt_3 as a heavy-fermion system in 1983 [1] and were largely stimulated by the discovery of superconductivity in this system in 1984 [2]. The early experiments made it clear that by Pd substitutions for Pt, the overall behaviour of the temperature dependence of the electrical resistivity changed from a spin-fluctuation dominated curve to a typical Kondo curve for 10 at % Pd. A review of these alloying experiments has been presented by De Visser et al. in 1987 [3]. Near this Pd concentration of 10 at %, the alloys are more like the other heavy-fermion compounds as $CeCu_2Si_2$ and UBe_{13} where coherence effects govern the low-temperature behaviour of the normal state and where Kondo behaviour is observed at higher temperatures [4]. On the basis of the strongly enhanced specific heat at low temperatures, Pd substituted UPt_3 alloys have been concluded to belong to the class of heavy-fermion compounds at least up to 10 at % Pd. In between the two extreme Pd concentration of 0 and 10 at % Pd, heavy-fermion behaviour is concomittant with long-range antiferromagnetic order that seems to be best developed with magnetic moments up to $0.6\mu_B$ and Néel temperatures up to 6 K for the 5 at % Pd alloy. In fact, long-range magnetic order was claimed for the 2 and 7 at % Pd alloys as well, although the specific heat transition was broadened for these two alloys and shifted to lower temperatures. Early resistivity measurements on Pd-doped UPt_3 with doping concentrations of 0.1, 0.2 and 0.5 at % Pd demonstrated a fast suppression of superconductivity with Pd alloying with no superconductivity present above 30 mK for the 0.5 at % Pd alloy.

The interest in the superconducting properties of UPt_3 was revitalised by the discovery of the double transition in the specific heat at the superconducting transition with

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two distinct transition temperatures separated over about 60 mK [5]. This double transition has been studied in great detail by a variety of experimental techniques and has led to a unique phase diagram in the B–T plane with three different superconducting phases that meet the normal state in a tetracritical point ($T_{tet} = 389$ mk, $B_{tet} = 0.443$ T for fields in the hexagonal plane and $T_{tet} = 351$ mK, $B_{tet} = 0.948$ T for fields along the hexagonal axis) [6]. No significant anisotropy is observed for fields in the hexagonal plane, i.e. for fields parallel to the two different crystallographic directions in this plane. Group-theoretical considerations have pointed out that the double superconducting transition is only compatible with the hexagonal symmetry in the presence of a symmetry-breaking field for which either the weak antiferromagnetism or local distortions of the crystal symmetry have been invoked. Impurity studies on the double superconducting transition have subsequently been carried out by Vorenkamp and Aronson with either substitutions of Y for U or of Pd for Pt with the remarkable conclusion that the splitting between the two transitions remains virtually unchanged for Y doping on the uranium sublattice whereas the splitting is largely enhanced with Pd substitutions on the platinum sublattice [7]. For the 0.2 at % Pd alloy the splitting amounts to about 120 mK, i.e. almost double the value observed for pure UPt_3. Other substitutions for Pt (Ir, Au) and for U (Th, Gd) underline the special role of Pd since for none of them an evident increase of the splitting has been observed.

The above mentioned phenomena provide the arguments to once more review the $U(Pt, Pd)_3$ data and to discuss experiments that could enlighten the specific role of Pd substitutions. In order to conduct these studies, a series of monocrystalline samples has been prepared for Pd concentrations on the platinum sublattice of 0.2, 1, 2, 5, 7 and 10 at %. Some of the latest results on these compounds will be mentioned as well.

2. Magnetism of the $U(Pt, Pd)_3$ compounds

Magnetic order for the 2, 5 and 7 at % Pd alloys is evident from huge anomalies in the specific heat and rather weak features in the electrical resistivity. Neutron-diffraction experiments have established the type of magnetic order and the value of $0.6\mu_B$ per uranium atom for the 5 at % Pd alloy [8]. The specific-heat anomaly is most pronounced in this series for the 5 at % Pd alloy and becomes weaker and smeared out for the other alloys. Polycrystalline samples of 1 at % Pd and lower Pd concentrations do not show any observable anomaly in the specific heat or the electrical resistivity revealing magnetic order. The same holds for the 10 at % Pd alloy. These observations do not exclude the presence of weak-moment antiferromagnetism as observed in pure UPt_3 for which no features are observed in specific heat and electrical resistivity as well. As indicated, the presence of this weak type of magnetic order has been revealed in UPt_3 in neutron-diffraction experiments [9] and could be confirmed in magnetotransport and magnetostriction studies in a rather indirect way [6]. Characteristic features of the magnetic behaviour of UPt_3 are the peak in the basal-plane susceptibility near 17 K and the meta-magnetic-like transition at 20 T in the liquid-helium temperature range. Both features shift to lower values upon Pd substitutions with the result that for the 10 at % Pd alloy the peak in the susceptibility is very close to 0 K and the metamagnetic transition very close to 0 T. Illustrative for the suppression of the meta-magnetic transition in $U(Pt, Pd)_3$ is the change in the field effect on the specific heat going from pure UPt_3 to the 10 at % Pd alloy. The low-temperature c/T values of UPt_3 increase with field up to 20 T and after reaching their maximal values at this field value start to decrease [10]. Similar behaviour has been found for $CeRu_2Si_2$ and discussed in terms of a suppression of the short-range antiferromagnetic correlations at the metamagnetic transition field and a gradual decrease of the mass enhancement consistent with a Kondo-type of mechanism for fields above the meta-magnetic transition [10]. Instead, for the 10 at % Pd alloy where the metamagnetic transition field is shifted to 0 T the field effect on the specific heat is substantial and negative. The formation of the heavy-fermion state in $U(Pt, Pd)_3$ is accompanied by large volume anomalies that have been studied in thermal expansion and volume magnetostriction measurements. The results of thermal expansion measurements in the field along the three main crystallographic directions are summarised in Figs. 1–3 for 0, 5 and 10 at % Pd alloys [11]. The expansion data can be combined with specific heat results obtained on the same samples in order to evaluate the effective Grüneisen parameter, Γ_{eff}, defined as:

$$\Gamma_{eff} = V_{mol}\,\alpha_V/(\kappa c), \tag{1}$$

where V_{mol} is the molar volume, α_V the volume expansion coefficient, $\frac{1}{3}(\alpha_a + \alpha_b + \alpha_c)$, and κ the isothermal volume compressibility. Most unusual are the large values for the electronic Grüneisen parameter that change from $+60$ to about -200 going from pure UPt_3 to the 10 at % Pd alloy [12]. Attempts have been made to evaluate the volume anomaly due to the formation of the heavy-fermion state resulting in a low-temperature volume collapse $\Delta V/V$ of 1.15×10^{-3} for UPt_3. The effect of an applied field along the a-axis on Γ_{eff} is shown in Fig. 4. On passing the meta-magnetic field of 20 T, we observe for UPt_3 a change in sign in this parameter which is

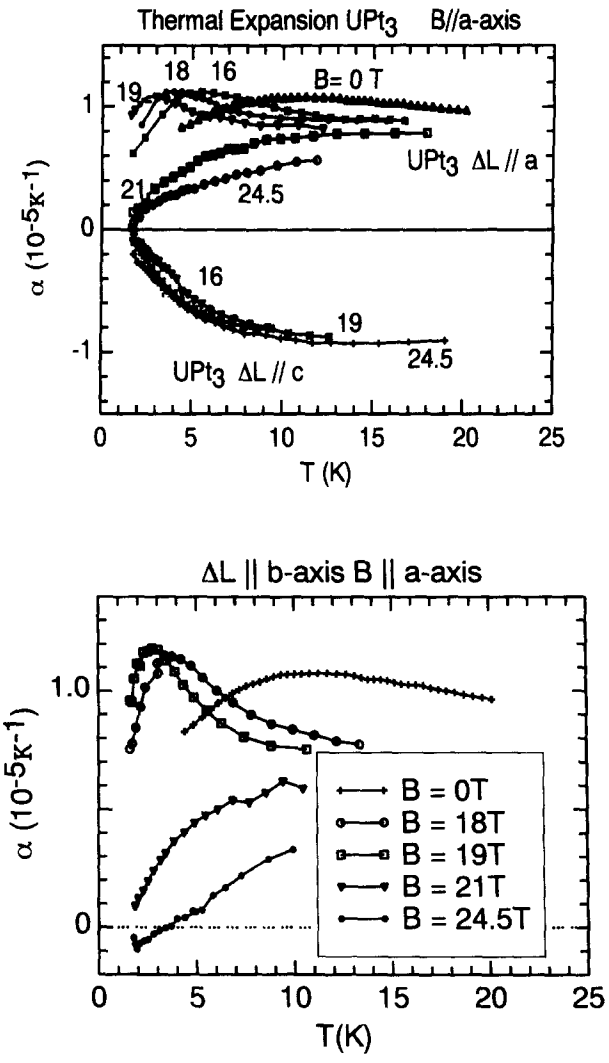

Fig. 1. Thermal expansion data of UPt_3 along the three main crystallographic directions for the applied field parallel to the *a*-axis in the hexagonal plane and for field values below and above the meta-magnetic field of 20 T [11].

consistent with the negative sign of Γ_{eff} for the 10 at % Pd alloy where the meta-magnetic transition field is close to 0 T. This change in sign suggests two different regimes in which different interactions dominate. For the long-range ordered 5 at % Pd alloy, the field effect on the expansion in the hexagonal plane has been studied below and above the magnetic ordering temperature. In a plot of the hexagonal-plane expansion versus the reduced temperature (Fig. 5) we note that below T_N the curves at different field values coincide, except for a small anomaly in the 0.5 T curve which is ascribed to magnetic domain effects. Above T_N, where short-range correlations still exist, the field effect is very pronounced.

The picture we are left with on the basis of these studies on the $U(Pt, Pd)_3$ system is that due to Pd substitutions on the one hand the antiferromagnetic correlations are stabilised resulting in long-range antiferromagnetic order that is best developed for the 5 at % Pd alloy, but on the other hand the antiferromagnetic interactions are weakened resulting in a steady decrease of the meta-magnetic transition field with increasing Pd concentration. The stabilisation of the antiferromagnetic correlations is a gradual process and leads to a rather broad anomaly in the specific heat for the 2 at % Pd alloy near 3.5 K before reaching a sharp peak for the 5 at % Pd alloy. Upon further increasing the Pd concentration, the

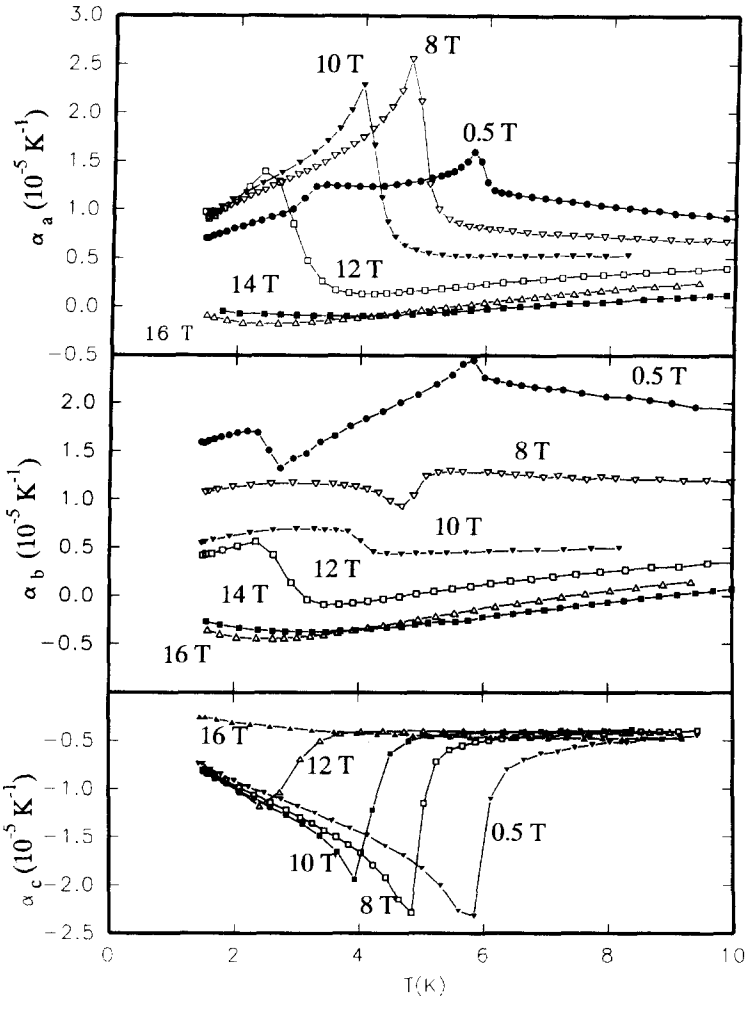

Fig. 2. Thermal expansion data of $U(Pt_{0.95}\ Pd_{0.05})_3$ along the three main crystallographic directions for the applied field parallel to the a-axis in the hexagonal plane and for field values below and above the meta-magnetic field of approximately 12 T [11].

uranium ions apparently loose their moments probably due to a Kondo-type of screening and no long-range magnetic order is observable any more for the 10 at % Pd alloy. The development of the uranium moment, in particular, the transition from a weak moment of the order of $0.01\mu_B$ to values of $0.6\mu_B$ as well as the coexistence of short-range antiferromagnetic correlations and long-range antiferromagnetic order and the type of magnetic order are now under investigation in neutron-diffraction experiments on a series of monocrystalline samples.

3. Superconductivity of the $U(Pt, Pd)_3$ system

As mentioned in the introduction, the effects of Pd doping on the superconducting phase diagram are exceptional compared to other substitutions. A detailed analysis of these impurity studies has been performed by Vorenkamp et al. [7]. These studies have recently been extended to Gd and Ni substitutions on the uranium and platinum sublattice, respectively [13]. Characteristics results for these substitutions are the identical effects that are measured for magnetic (Gd) and non-magnetic (Y and Th) impurities on the uranium sublattice. All substitutions on the uranium sublattice induce an increase of the residual resistivity with 12 μΩ cm/at% impurity and a decrease of the superconducting transition temperature with a rate of 0.6 K/at % impurity. Doping of the platinum sublattice by Ni, Ir, Pd and Au reveals a more complex picture. For all substitutions on the platinum sublattice, the superconducting transition temperature fastly decreases. It turns out that in the Ni-substituted

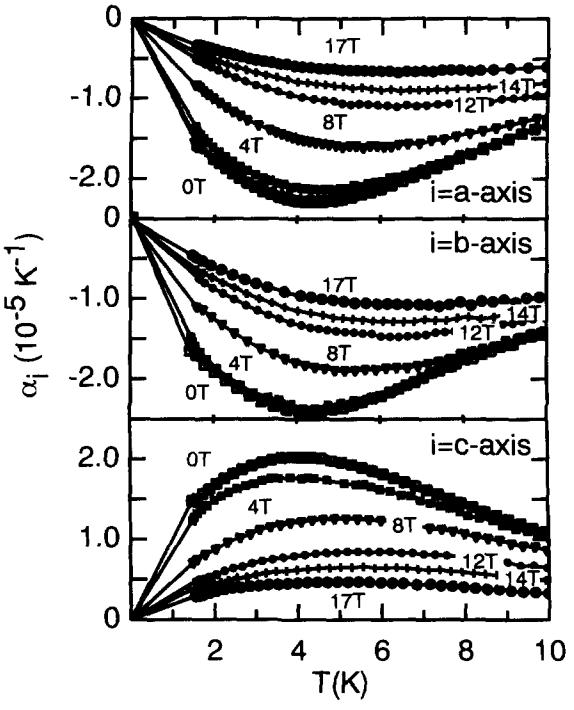

Fig. 3. Thermal expansion data of $U(Pt_{0.90}\ Pd_{0.10})_3$ along the three main crystallographic directions for the applied field parallel to the a-axis in the hexagonal plane [11].

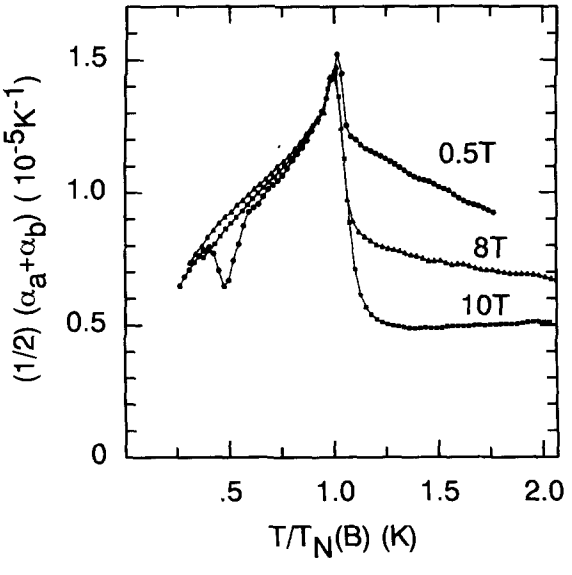

Fig. 4. The effective Grüneisen parameter, Γ_{eff}, for UPt_3 as a function of temperature for different field values applied along the a-axis in the hexagonal plane [11].

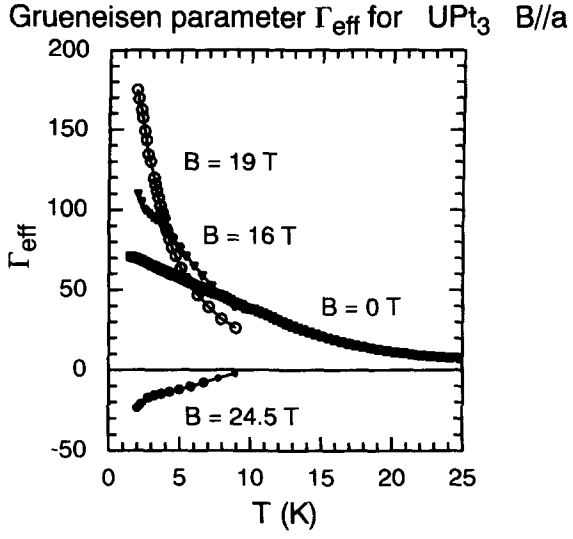

Fig. 5. Thermal expansion within the hexagonal plane of $U(Pt_{0.95}Pd_{0.05})_3$ for different field values applied along the a-axis in the hexagonal plane, plotted as a function of the reduced temperature $T/T_N(B)$, where $T_N(B)$ is the temperature at which the peak in the thermal expansion is observed [11].

alloys, the prepared samples are not in their equilibrium condition and part of the nickel atoms reside in a non-equilibrium state in the UPt_3 matrix and another part on the grain boundaries where a non-superconducting phase has been identified, probably of the $U_2Pt_5Ni_3$ type. Due to the application of a standard heat treatment which is always followed for the UPt_3 compounds, a certain fraction of the starting nickel concentration remains dissolved in the matrix, causing a decrease of T_c nearly proportional to the nominal composition but with a non-zero resistivity level within the superconducting state which is proportional to the nominal composition as well. Evidence for this picture is found in the electron-microprobe analysis and from an inspection of the sample surface by optical means. The grain size drops with increasing nickel content whereas the amount of a second phase in the grain boundaries increases. Gold substitutions for platinum generate another problem for the interpretation due to the more than linear increase of the residual resistivity with increasing Au content [14]. Other substitutions like iridium and palladium have a more regular behaviour with respect to the increase of the residual resistivity. We will focus our discussion on the effects of substitutions in the platinum sublattice on the superconducting properties of these two elements. It turns out that iridium impurities suppress T_c faster than palladium impurities. For the 0.2 at % nominal substitution, for instance, T_c decreases from 0.55 K for pure UPt_3

to 0.22 K for iridium and to 0.41 K for palladium. Specific-heat experiments on both diluted alloy systems show that the double transition to the superconducting state can be observed for both substitutions with the remarkable result that for iridium the separation between the two transition temperatures remains virtually the same whereas for palladium it increase from 60 mK to almost 120 mK for the 0.2 at % Pd alloy. This increased splitting of the two superconducting states can at least partly explain the much faster decrease of the superconducting ordering temperature in case of iridium. On the other hand, palladium substitutions and the concomittant changes in the superconducting phase diagram provide an interesting opportunity in the search for the origin of the symmetry-breaking field that is behind the multiple phase diagram of UPt_3. In case the weak staggered moment of $0.02\mu_B$ in UPt_3 is at the origin of the symmetry-breaking field, one is able, in principle, to deduce an increase in the uranium moment (μ_U) at palladium substitutions according to the relation [7]:

$$\Delta T_c = k\mu_U^2, \tag{2}$$

where ΔT_c is the difference in temperature between the two superconducting transitions as measured in specific-heat experiments and k is a constant of proper dimension. Taking an increase of ΔT_c by a factor of two for the 0.2 at % Pd alloy, one expects the uranium moment to be increased by a factor $\sqrt{2}$. Given the uncertainty in the determination of the absolute value of the weak uranium moment in the neutron experiments on UPt_3, it will not be an easy task to verify this factor $\sqrt{2}$ in a neutron experiment on the 0.2 at % Pd alloy. Nevertheless, it is of crucial importance to better study the development of the uranium moment in the $U(Pt, Pd)_3$ system at low palladium concentration. For this purpose a new set of samples has been prepared which is at present under study in neutron diffraction experiments. To this set belongs a monocrystalline sample with nominal composition $U(Pt_{0.998}\ Pd_{0.002})_3$ that will be employed for a study of the superconducting phase diagram, provided the specific-heat and thermal expansion anomalies at the phase boundaries are well developed [15]. The superconducting phase diagram of UPt_3 as studied by thermal expansion and magnetostriction measurements is shown in Fig. 6, demonstrating that dilation measurements provide a useful tool for this type of investigations.

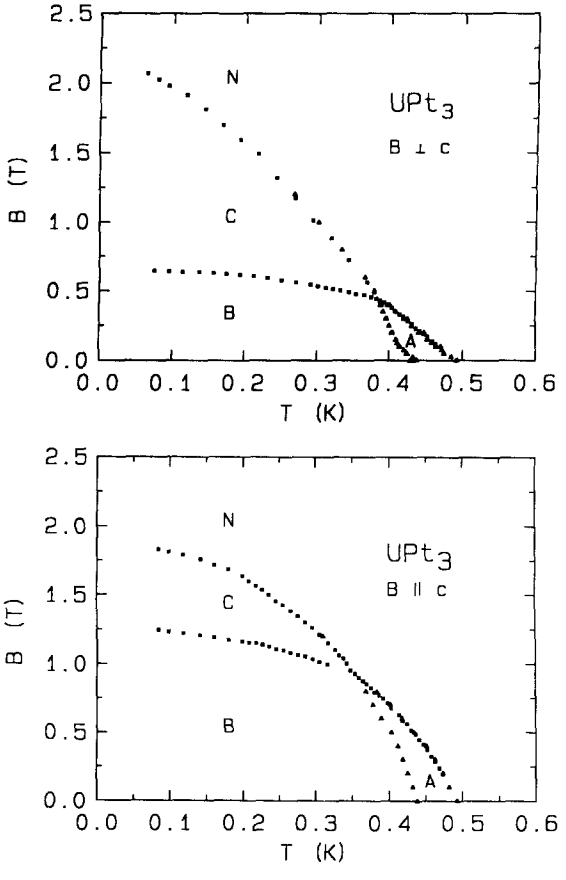

Fig. 6. The superconducting phase diagram of UPt_3 for fields applied perpendicular and parallel to the hexagonal axis, as studied by thermal expansion and forced magnetostriction measurements [6].

4. Summary

Magnetism and superconductivity have been reviewed for the $U(Pt_{1-x}Pd_x)_3$ system for x-values up to 0.1. Recent experiments on monocrystalline samples confirm results previously obtained on polycrystalline samples. In particular, the magnetic order of the 2 at % Pd alloy below 3.2 K and the meta-magnetic transition field in the liquid-helium temperature range at 18.5 T are in close agreement with the old results. The presence of magnetic order is evident from an (rather weak) anomaly in the resistivity and from an anomalous contribution to the magnetoresistivity below 11 T at 1.5 K for magnetic fields applied in the hexagonal plane. By following the weak anomaly in the resistance curve as a function of applied field, the magnetic phase diagram for the $U(Pt, Pd)_3$ system has been further completed. It is shown once again that long-range antiferromagnetic order and short-range antiferromagnetic correlations are distinct phenomena that react differently on the Pd concentration. Long-range antiferromagnetism is induced by Pd substitutions and arrives at its maximal T_N value of 6 K for the 5 at % Pd alloy whereas the meta-magnetic transition field that reflects the strength of the short-range intersite

correlations exhibits a continuous decrease with increasing Pd content from 20 T for UPt_3 down to almost zero field for the 10 at % Pd–Kondo-alloy. Superconductivity in $U(Pt, Pd)_3$ remains an intriguing phenomenon which, so far, has not been studied in great depth for the Pd-substituted alloys. The effect of Pd doping on the difference in temperature between the two superconducting transitions might provide a clue for better understanding the physics behind the multiple phase diagram of UPt_3. For this purpose, detailed studies of, on the one hand, the superconducting phase diagram of Pd substituted alloys, and, at the other hand, the development of the uranium moment in the $U(Pt, Pd)_3$ system are proposed.

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