

Magnetic and electrical properties of dhcp NpPd_3 and $(\text{U}_{1-x}\text{Np}_x)\text{Pd}_3$

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We have made an extensive study of the magnetic and electrical properties of double-hexagonal close-packed NpPd_3 and a range of $(\text{U}_{1-x}\text{Np}_x)\text{Pd}_3$ compounds with $x=0.01, 0.02, 0.05,$ and 0.50 using magnetization, magnetic susceptibility, electrical resistivity, and heat capacity measurements on polycrystalline samples, performed in the temperature range $2\text{--}300$ K and in magnetic fields up to 9 T. Two transitions are observed in NpPd_3 at $T=10$ and 30 K. Dilute Np samples ($x\leq 0.05$) exhibit quadrupolar transitions, with the transition temperatures reduced from those of pure UPd_3 .

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I. INTRODUCTION

The magnetism of $4f$ (lanthanide) metallic systems has been studied extensively for several decades. The standard localized moment model of rare earth magnetism, as expounded by Jensen and Mackintosh,¹ remains the foundation for explaining the magnetic and electrical properties of almost all such materials, with the exception of cerium and its compounds where band and hybridization effects play a crucial role. In $5f$ (actinide) metallic systems, the f -electron wave functions are distinctly more extended than in the corresponding $4f$ systems, leading to a more itinerantlike nature as manifested by their magnetic and electrical behaviors. Actinide systems display a unique complexity within the Periodic Table, exhibiting a rich variety of phenomena such as heavy-fermion and non-Fermi liquid behaviors and unconventional superconductivity. Most uranium metallic compounds have the $\text{U}^{3+} 5f^3$ configuration and exhibit itinerantlike properties. In contrast, UPd_3 shows the $\text{U}^{4+} 5f^2$ configuration and is a rare example of a localized moment uranium intermetallic compound. In this context, we recall the theory of Zwicky and Fulde² for the dual nature of f electrons in uranium compounds: They interpret the behavior of $5f^3$ systems such as UPT_3 in terms of two $5f$ electrons being localized and one being itinerant.

Due to the inherent difficulties in handling neptunium, relatively few neptunium compounds have been studied. A principal motivation for the work presented in this paper has been to explore the magnetic and electrical properties of NpPd_3 with the aim of comparing them with those of UPd_3 and to examine the effect of a dilute substitution of U by Np on the unusual behavior of UPd_3 .

Numerous studies of UPd_3 , both macroscopic (heat capacity,^{3,4} susceptibility,⁵ thermal expansion,⁶ and ultrasonics⁷) and microscopic (neutron⁸ and x-ray diffraction⁹), indicate four phase transitions below $T=8$ K. These have been attributed to a series of antiferroquadrupolar (AFQ) orderings of the U $5f^2$ electrons. However, a detailed understanding of the origin of these transitions has been a challenge for many years, but a new proposed crystal field scheme⁵ has been able to explain the existence of the four

transitions and new x-ray resonant scattering experiments have revealed the order parameters of one of the AFQ phases.^{10,11} In comparison, very little has been published on the neptunium analog double-hexagonal close-packed (dhcp) NpPd_3 . Its magnetic properties were first examined 30 years ago by Nellis *et al.*,¹² but several questions remain unanswered in relation to the nature of the ordering. As far as the present authors are aware, there has been no further research until our own work, and we report here a systematic study of the magnetization, magnetic susceptibility, electrical resistivity, and heat capacity of NpPd_3 . Given the very similar lattice parameters between the isostructural U and Np compounds, we have anticipated complete solid solubility from UPd_3 to NpPd_3 , and the very small difference in ionic radii should lead to little induced strain. This has enabled us to investigate the perturbation of the quadrupolar structures of UPd_3 by substitution of Np on some U sites while looking to explain the nature of the ordering previously observed in NpPd_3 .

II. EXPERIMENTAL DETAILS

Polycrystalline samples of dhcp $(\text{U}_{1-x}\text{Np}_x)\text{Pd}_3$ with $x=0, 0.01, 0.02, 0.05, 0.50,$ and 1 were prepared at the Institute for Transuranium Elements by arc melting stoichiometric amounts of the constituent elements in a high purity argon environment on a water cooled copper hearth using a Zr getter. We used Pd of 99.99% purity, while our U and Np were of 99.9% purity. Quantitative analysis of the impurities, including the oxygen content, was not available to us. The resultant ingots were repeatedly turned and remelted, before they were annealed at 1300 °C for one week to ensure phase homogeneity. This is important as pure NpPd_3 is known to exist in two phases: dhcp and cubic with the AuCu_3 -type structure¹²; the latter allotrope orders antiferromagnetically at $T_N=50$ K. No weight losses were observed during the arc melting and annealing processes, and given the low vapor pressures of U, Np, and Pd metals, the error bars on the sample compositions are very small and correspond to the precision of the balance used in the element weighing pro-

TABLE I. The structural parameters of dhcp ($U_{1-x}Np_x$)Pd₃ compounds, where esd is the estimated standard deviation.

Compound	Unit cell dimensions (Å)		c/a	Cell volume (Å ³)	Reference
	a	c			
UPd ₃	5.765	9.545	1.656	274.7	This work
	5.775	9.654	1.672	278.8	14 ^a
	5.763	9.542	1.656	274.5	14 ^b
	5.757	9.621	1.671	276.1	15
	5.769	9.652	1.673	278.2	16
1%Np	5.769	9.635	1.670	277.7	
2%Np	5.768	9.631	1.670	277.5	
5%Np	5.766	9.623	1.669	277.1	
50%Np	5.774	9.576	1.658	276.4	
	5.765	9.545	1.656	274.7	This work
NpPd ₃	5.767	9.544	1.655	274.9	12

^aU rich.

^bPd rich.

cedure, e.g., an error of 3/1000 wt % and hence 4/1000 at. %. The phase purity of the samples was checked using room temperature x-ray powder diffraction (Cu $K\alpha$ radiation) on a Bragg-Brentano D-500 diffractometer. A Rietveld-type full refinement of the data proves that all the samples have the dhcp structure. The lattice parameters of all the compounds are given in Table I, and the cell volume and c -axis parameter of ($U_{1-x}Np_x$)Pd₃ as a function of x are plotted in Fig. 1. Interestingly, the cell volume rapidly increases with the addition of just 1% neptunium before decreasing with further neptunium doping. This is not the standard behavior and violates Vegard's law.¹³

Also given in Table I are additional values for the lattice parameters of UPd₃ from the literature, reflecting the observation of a homogeneity range around the exact UPd₃ composition, 23.3 to 24.8 at. % uranium,¹⁴ which affects the lattice parameters significantly. Based on these measurements, it could appear that our UPd₃ sample is slightly palladium rich. However, since the mixed actinide samples were synthesized using the UPd₃ and NpPd₃ samples as starting materials, in the correct stoichiometric ratios, any uranium deficiency affecting the UPd₃ lattice parameters should be preserved through the different composition samples. The sharp deviation from a linear trend at low neptunium concentrations may be possible evidence of a change in the valence state of uranium.

X-ray powder diffraction is unable, however, to show how the dopant atoms sit within the host crystal structure. We therefore do not know whether the Np atoms in ($U_{1-x}Np_x$)Pd₃ are randomly distributed over the two U sites (one locally hexagonal and the other quasicubic) or whether they are located preferentially on one of the symmetry-type sites. An x-ray absorption spectroscopy experiment is planned to look at the local configuration of the Np atoms.

Measurements were made on encapsulated samples at ITU. Magnetic studies were carried out for $T=2-300$ K and in fields up to 7 T using a superconducting quantum inter-

ference device magnetometer (Quantum Design MPMS-7). Four-point (pressure contacts) ac probe electrical resistivity measurements were made using a Quantum Design PPMS-9 for $T=2-300$ K in a range of fields up to 9 T. Additional low temperature measurements were obtained using two coupled cryopump devices (³He-⁴He). Self-heating effects make it difficult to cool samples containing neptunium below 400 mK. Heat capacity measurements were made also using the PPMS-9 via the hybrid adiabatic relaxation method on both the ($U_{1-x}Np_x$)Pd₃ samples and a sample of ThPd₃, to be used as an isostructural phonon blank. Using a ³He refrigeration insert, measurements could be made over a range of $T=0.4-400$ K in fields up to 9 T. Contributions to the measured heat capacity from the sample platform including the grease were measured separately and subtracted from the total. The heat capacity of the sample coating, Stycast 2850 FT, is well known¹⁷ and was subtracted off from the total heat capacity.

Hereafter, the solid solutions investigated in this paper will be identified, for ease and clarity, by the percentage

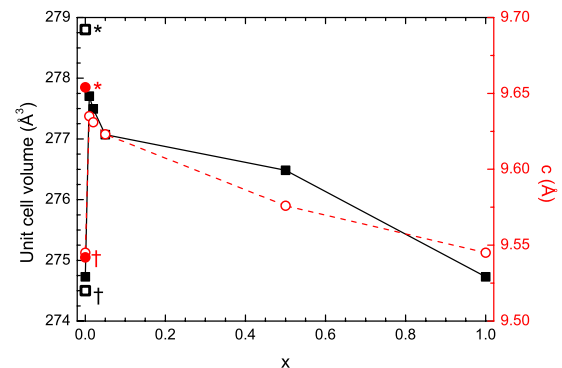


FIG. 1. (Color online) The variations of cell volume (■) and c -axis parameter (○) as a function of x in ($U_{1-x}Np_x$)Pd₃ do not obey Vegard's law. Data points taken from Ref. 14 for U rich (*) and Pd rich (†) UPd₃ samples are not included in the line guide.

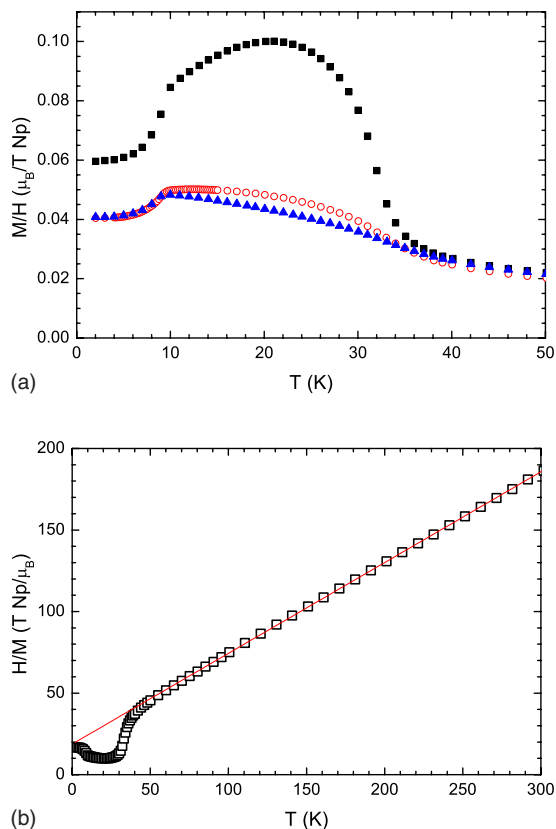


FIG. 2. (Color online) (a) $M/H(T)$ of $NpPd_3$ at $H=1.1$ T (■), 4 T (○), and 7 T (▲), showing transitions at $T=10$ and 30 K. (b) Curie-Weiss fit to $H/M(T)$ for $H=1.1$ T.

neptunium doping, for example, 25%Np would refer to $(U_{0.75}Np_{0.25})Pd_3$.

III. MAGNETIC PROPERTIES

A. $NpPd_3$

In $NpPd_3$, in low applied magnetic fields of 0.03 and 1.1 T, M/H (defined here for convenience as the magnetic susceptibility) shows a sharp increase below 35 K to a broad maximum centered at 20 K, as previously reported.¹² However, in addition, we observe a shoulder at 10 K. In higher fields of 4 and 7 T, the form of M/H changes such that the 10 K feature becomes more pronounced, see Fig. 2.

The 10 and 30 K anomalies could be attributed to two antiferromagnetic transitions; these might occur separately on the locally hexagonal and quasicubic sites, similar to the transitions observed in neodymium,¹⁸ or successively on only one of the site types, as in praseodymium.¹⁹ While an increase of M/H may be indicative of a ferromagnetic component, it is not inconsistent with the increases in M/H seen at the successive antiferroquadrupolar transitions in UPd_3 .¹¹ Interestingly, no difference was seen in the neutron diffraction patterns measured for dhcp $NpPd_3$ at $T=4.2$ and 78 K,¹² which could be consistent with the higher temperature transition being to a quadrupolar phase. This would result in a relatively high quadrupolar temperature, considerably higher

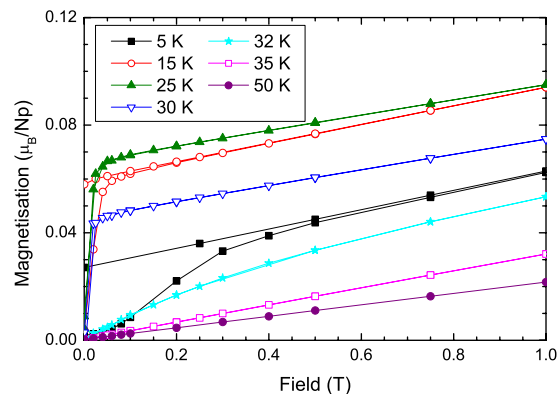


FIG. 3. (Color online) M vs H of $NpPd_3$ at a range of temperatures showing hysteresis below 30 K.

than those in UPd_3 , but comparable to that for DyB_2C_2 , $T_Q=24.7$ K,²⁰ and for NpO_2 , $T_Q=25$ K.^{21,22} However, the observed absence of magnetic Bragg peaks at 4.2 K suggested that there is no long range magnetic order, which is inconsistent with our proposed antiferromagnetic transition at 10 K.

The transition at 30 K is seen more clearly in the inverse susceptibility, see Fig. 2(b). Above 50 K, the inverse susceptibility follows a Curie-Weiss law, with an effective magnetic moment of $2.83 \pm 0.05 \mu_B/Np$ atom deduced from a series of measurements made in 1.1 and 4 T. This suggests that Np is trivalent in this compound, since in the Russell-Saunders coupling scheme, the moment value one would expect for a $5f^4$ electron configuration is $2.68 \mu_B$, whereas if Np was tetravalent, as U is in UPd_3 , the expected moment would be $3.62 \mu_B$. Within the intermediate coupling scheme, which given the high atomic mass of the neptunium may be more appropriate, the expected moment for trivalent Np is $2.755 \mu_B/Np$ ion, and tetravalent Np is $3.682 \mu_B/Np$ ion,²³ which again supports our conclusion that Np is trivalent in $NpPd_3$.

The isothermal magnetization, Fig. 3, measured after cooling the sample in zero field, below 30 K increases rapidly in low fields before increasing more slowly and linearly. On reducing the field, hysteresis is observed below 0.1 T, with a maximum residual ferromagnetic moment of $0.06 \mu_B/Np$ atom at $T=15$ K. Below the 10 K transition, hysteresis is observed up to 0.5 T but with a reduced residual ferromagnetic moment. At 7 T, the maximum moment was $0.30 \mu_B/Np$ atom. The absence of saturation in 7 T and the low remanent magnetization, if intrinsic properties, may indicate that the structure below 30 K contains a small ferromagnetic moment. An alternative explanation is the presence of some ferromagnetic impurity phase, but the measurements made in constant applied magnetic field appear to rule out either carbides or nitrides, commonly occurring ferromagnetic impurities in other systems, and the x-ray powder diffraction data show the high purity of the sample phase. Nevertheless, a 2% impurity of an unidentified neptunium compound with a moment of $3 \mu_B/Np$ would produce such a residual moment, and our x-ray powder diffraction measurements cannot preclude such a possibility. However, we note

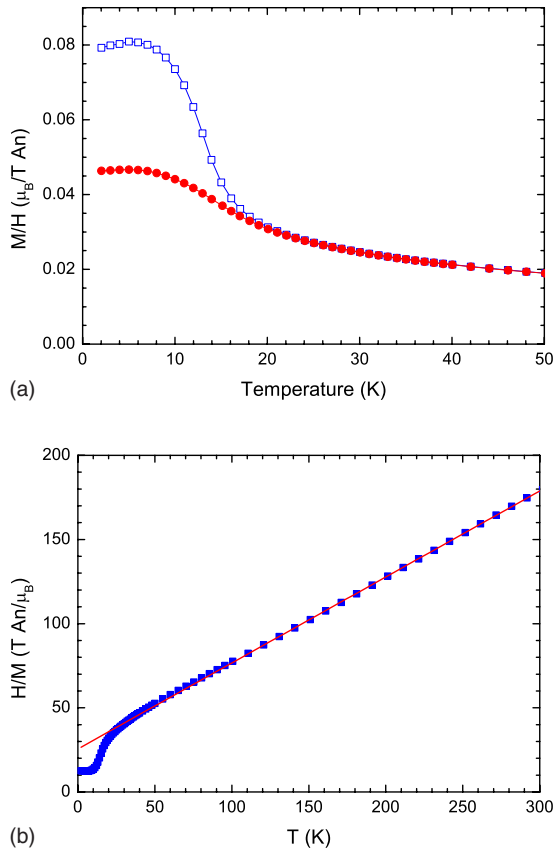


FIG. 4. (Color online) (a) $M/H(T)$ of $(U_{0.5}Np_{0.5})Pd_3$ at $H = 1.1$ T (\square) and 4 T (\bullet), showing a transition at $T \sim 12$ K. (b) Curie-Weiss fit to $H/M(T)$ for $H = 1.1$ T, giving an effective moment of $2.956 \pm 0.003 \mu_B/\text{An}$.

that no other Np-Pd binary compound has yet been reported.

Since neptunium is Mössbauer active, one might envisage measuring the Mössbauer spectra to learn more about the magnetic properties of $NpPd_3$. However, the data from previous experiments^{12,24} have proven difficult to interpret. Although paramagnetic line broadening was observed below the 30 K transition, at 4.2 K, the data could not be fitted, even using two hyperfine patterns taking into account the two inequivalent neptunium sites.

B. $(U_{0.5}Np_{0.5})Pd_3$

The 50%Np M/H data, Fig. 4(a), qualitatively resembles that for pure $NpPd_3$ shifted down in temperature, such that there is a sharp rise below 15 K to a broad maximum centered at 5 K. In the H/M data, the transition is seen clearly at 15 K, while above the transition, the data are linear exhibiting Curie-Weiss behavior, Fig. 4(b). Curie-Weiss fits to a series of data sets measured in 1.1 and 4 T give an effective paramagnetic moment of $2.96 \pm 0.01 \mu_B$ per actinide ion. Hysteresis is observed in magnetization measurements as a function of applied magnetic field while saturation is absent. Below 15 K, the field below which hysteresis is observed increases with decreasing temperature to 1 T at 2 K. The maximum residual ferromagnetic moment is $0.05 \mu_B/\text{An}$.

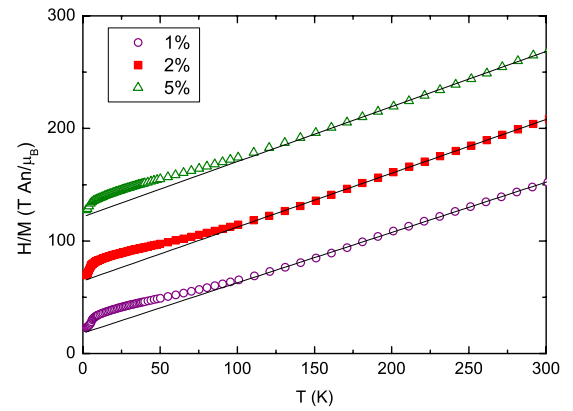


FIG. 5. (Color online) H/M measurements on dilute Np doped samples for $H = 1.1$ T with Curie-Weiss fits at high temperature. The data sets have been displaced vertically by 50 and 100 units for clarity.

Again, we have not been able to distinguish whether it is an intrinsic ferrimagnetic effect or if it is due to a very small quantity of an impurity phase with a large ferromagnetic moment. However, if it is assumed that the residual ferromagnetic moment measured from the $NpPd_3$ sample was the result of a 2% unidentified magnetic impurity phase, in this 50%Np sample, which was produced using the $NpPd_3$ sample, the impurity phase should only make up 1% of the total mass, and therefore one would have expected the residual ferromagnetic moment to have halved, instead of only being reduced by a sixth.

C. Dilute Np samples, $x = 0.01, 0.02, 0.05$

The 5%, 2%, and 1%Np magnetic measurements show no clear evidence of a magnetic transition, and there is no evidence of hysteresis in the isothermal magnetization data. Above 100 K, H/M follows a modified Curie-Weiss law for the 5%Np sample, possibly indicative of a singlet ground state with a large energy gap to the first excited state, giving an effective paramagnetic moment of $3.02 \pm 0.02 \mu_B$ per actinide ion. Fits to a Curie-Weiss law for the 2% and 1%Np samples above 100 and 150 K give effective paramagnetic moments of 3.07 ± 0.01 and $3.16 \pm 0.01 \mu_B$ per actinide ion, respectively, and are shown in Fig. 5.

Plotting the M/H data for all the different samples, $NpPd_3$, 50%Np, 5%Np, 2%Np, and 1%Np, as a function of temperature on a logarithmic plot, Fig. 6, shows that the 5%Np data approximately follow a negative logarithmic trend. This can be characteristic of non-Fermi liquid behavior. It is also interesting to note that the value of M/H at $T = 2$ K is a minimum for $x = 0.05$, with the value increasing as a function of x moving away from this composition toward both the more dilute and more concentrated regions of the phase diagram.

Figure 7 shows how the Curie-Weiss temperature θ_p , obtained from Curie-Weiss fits to the high temperature H/M data and tabulated in Table II, varies as a function of the neptunium concentration in $(U_{1-x}Np_x)Pd_3$. The data point for $x = 0$ was obtained from an appropriate average $(\frac{1}{3}\theta_p^{(c)})$

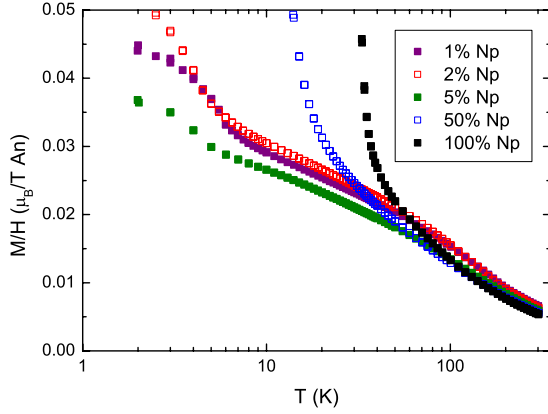


FIG. 6. (Color online) M/H of pure NpPd_3 and mixed $(\text{U},\text{Np})\text{Pd}_3$ at $H=1.1$ T plotted vs $\log T$. $(\text{U}_{0.95}\text{Np}_{0.05})\text{Pd}_3$ shows a near negative logarithmic trend, possibly indicative of a non-Fermi liquid.

$+\frac{2}{3}\theta_P^{(a)})$ of the single crystal data.⁵ The sharp change in θ_P with low neptunium doping is very unusual. The behavior may be associated with the dramatic change in the lattice parameters, Fig. 1. One possibility is that the addition of a small quantity of Np leads to a sharp change in the cohesive energy, and hence the lattice constants, and the exchange interaction, which is dependent on the conduction electrons, may be very sensitive to the lattice spacing due to changing bands near the Fermi level.

IV. ELECTRICAL RESISTIVITY

A. NpPd_3

In NpPd_3 in zero field, the electrical resistivity shows two anomalies, at $T=10$ and 30 K, corresponding to the transitions seen in the magnetization data. Below 300 K, the resistivity increases with decreasing temperature, see Fig. 8(a), following a Kondo-like behavior,

$$\rho = \rho_0 + cT - \rho_S \ln(T), \quad (1)$$

until 30 K, when it drops dramatically with the onset of coherent scattering. In heavy-fermion materials, Kondo behav-

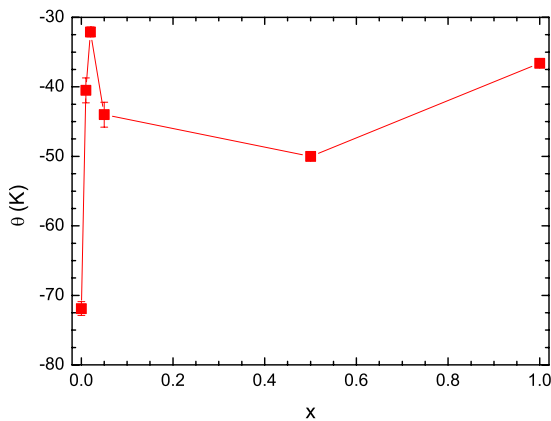
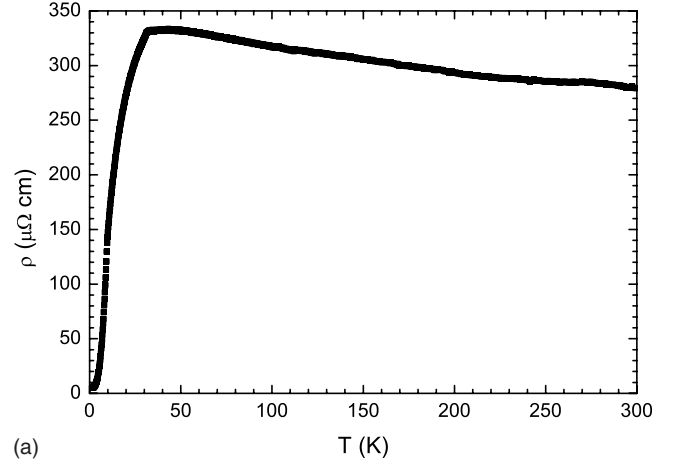
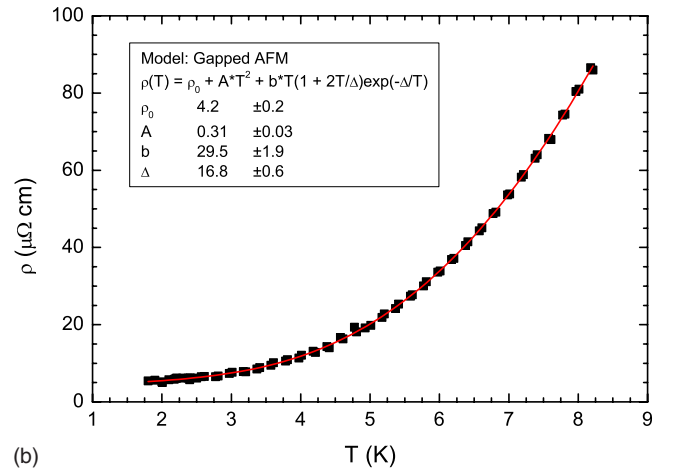


FIG. 7. (Color online) The Curie-Weiss temperature θ_P as a function of x in $(\text{U}_{1-x}\text{Np}_x)\text{Pd}_3$.



(a)



(b)

FIG. 8. (Color online) (a) $\rho(T)$ of NpPd_3 at $H=0$ T for $T=2-300$ K, showing a marked change in the gradient at $T=30$ K. Below 30 K, the resistivity decreases with decreasing temperature as for a normal metal, but above 30 K, $d\rho/dT$ is negative. The 30 K transition appears to coincide with the onset of coherence. (b) At low temperatures, $\rho(T)$ is not proportional to T^2 . Instead, it can be modeled using an antiferromagnetic ground state with an energy gap $\Delta=17$ K (Ref. 27).

our is commonly observed in the form of a maximum in the resistivity at a temperature T_M , which is a function of the Kondo temperature T_K and the mean Ruderman-Kittel-Kasuya-Yosida interaction strength between the magnetic ions,²⁵ rather than as a low temperature resistivity minimum. For example, the resistivity of NpRu_2Si_2 is similar to that of NpPd_3 displaying a logarithmic variation with T above the ordering temperature, 27.5 K, and a precipitous drop below T_M understood as a huge magnetic contribution of an energy gap antiferromagnet.²⁶ It is interesting that the higher temperature transition observed in magnetization measurements should coincide with T_M .

The low temperature resistivity below 10 K does not vary as a simple Fermi liquid $\rho(T) \propto T^2$, but instead behaves as an antiferromagnet with an energy gap Δ :

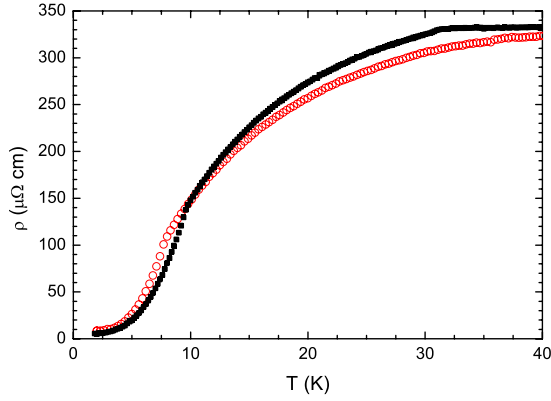


FIG. 9. (Color online) $\rho(T)$ for NpPd_3 in $H=0$ T (■) and 9 T (○). In zero field, the two transitions at 10 and 30 K can be seen clearly. At 9 T, the upper transition is smoothed away, while the lower transition is shifted down in temperature.

$$\rho(T) = \rho_0 + AT^2 + bT(1 + 2T/\Delta)\exp(-\Delta/T), \quad (2)$$

see Fig. 8(b). The fit to the $H=0$ T data indicates $\Delta=17$ K. The residual resistivity ratio given by $\rho(T=0 \text{ K})/\rho(T=300 \text{ K})$ is 85, showing the high quality of the sample.

When a 9 T field is applied, the feature associated with the higher temperature transition is smoothed away, while that of the lower transition becomes more pronounced and shifts down in temperature, consistent with an antiferromagnetic transition, see Fig. 9. Below the transition, the 9 T data still behave as a gapped antiferromagnet but the parameters given by the fit are modified to $A=0.14\pm 0.04 \mu\Omega \text{ cm/K}^2$ and $\Delta=15.7\pm 0.5$ K.

B. $(\text{U}_{0.5}\text{Np}_{0.5})\text{Pd}_3$

Again, for the 50%Np sample, the high temperature resistance has a negative gradient, displaying a Kondo-like behavior, Fig. 10(a). However, the onset of coherence is not so sharp, varying over a broader range of temperatures, and is not associated with a transition temperature deduced from the magnetic measurements. The low temperature resistivity

TABLE II. Magnetic property parameters of dhcp $(\text{U}_{1-x}\text{Np}_x)\text{Pd}_3$ compounds. Temperatures quoted in parentheses correspond to transitions which may be of quadrupolar origin. The effective magnetic moments quoted are the statistical averages from Curie-Weiss fits to repeated inverse susceptibility data fits with their associated errors.

Compound	Magnetic ordering temperatures (K)	μ_{eff} ($\mu_B/\text{An ion}$)	θ_p (K)
UPd_3		3.24 ± 0.01	-72 ± 1
1%Np		3.16 ± 0.01	-40 ± 2
2%Np		3.06 ± 0.01	-32 ± 1
5%Np		3.02 ± 0.02	-44 ± 2
50%Np	(12)	2.96 ± 0.01	-50 ± 1
NpPd_3	10 (30)	2.83 ± 0.05	-35 ± 1

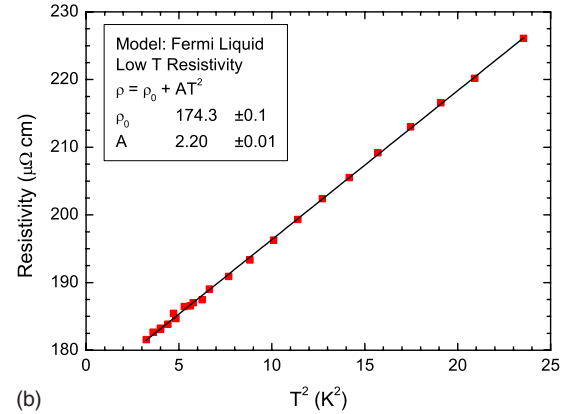
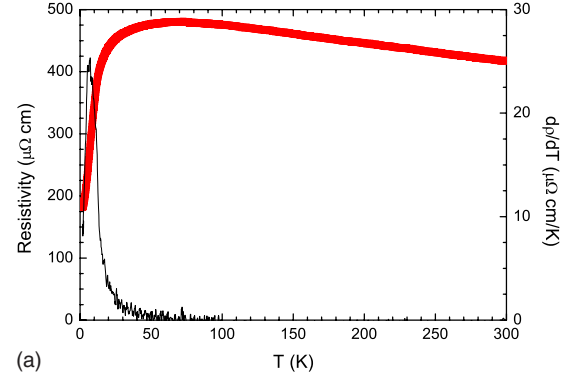


FIG. 10. (Color online) (a) $\rho(T)$ of $(\text{U}_{0.5}\text{Np}_{0.5})\text{Pd}_3$ at $H=0$ T (■) for $T=2-300$ K, showing a smooth change from a positive to a negative gradient at $T\sim 50$ K. The transition observed in the magnetization measurements is seen more clearly in the temperature derivative (black line). (b) Below 5 K, the resistivity varies as T^2 , in very good agreement with the Fermi liquid theory.

varies as T^2 , with a residual resistivity of $174 \mu\Omega \text{ cm}$, Fig. 10(b). This is some 2 orders of magnitude larger than in pure NpPd_3 , which we attribute to the statistical disorder introduced with the uranium atoms. As shown in Fig. 11, a kink is observed in the zero field resistivity at $T=12$ K, which is smoothed away in a 9 T field.

C. $(\text{U}_{0.95}\text{Np}_{0.05})\text{Pd}_3$

The electrical resistivity of the 5%Np sample is markedly different from the 50% and 100%Np samples showing no Kondo-like behavior at high temperatures, Fig. 12(a). This raises the possibility that the degree of electron localization is varying as we move across the phase diagram as a function of neptunium concentration. Application of a 9 T field has little effect on the resistivity. Initial resistivity measurements performed down to 2 K suggested a linear temperature dependence for $2\leq T\leq 10$ K. However, when we extended these measurements to lower temperatures using the coupled cryopump system, a fit to the data indicated that below 1.6 K, the resistivity is quadratic in temperature, Fig. 12(b), indicating that at the lowest temperatures $(\text{U}_{0.95}\text{Np}_{0.05})\text{Pd}_3$ is a Fermi liquid.

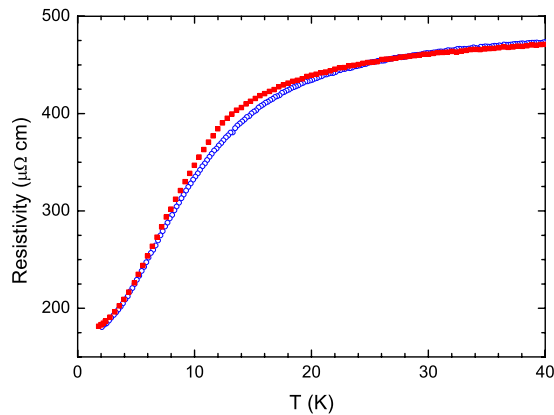


FIG. 11. (Color online) $\rho(T)$ for $(U_{0.5}Np_{0.5})Pd_3$ in $H=0$ (■) and 9 (○) T. In zero field, a transition can be seen at 12 K. At 9 T, the transition is smoothed away.

V. HEAT CAPACITY

A. NpPd₃

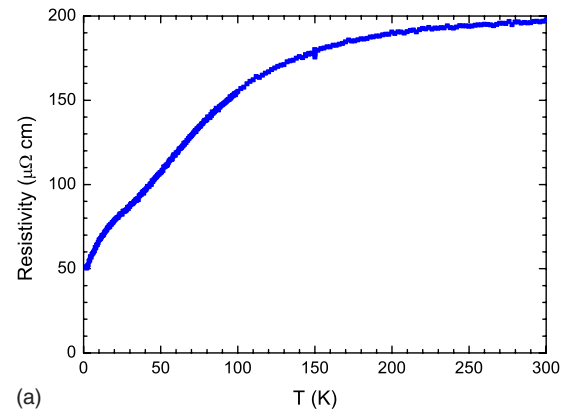
In zero field, heat capacity measurements of NpPd₃ reveal two clear lambda anomalies at $T=10$ and 30 K, Fig. 13. Making a fit to the low temperature data gives the electronic heat capacity, $\gamma=78\pm 4$ mJ K⁻² mol⁻¹, and hence a Kadowaki-Woods ratio of $A/\gamma^2=(5.2\pm 0.8)\times 10^{-5}$ $\mu\Omega$ cm(mol K/mJ)², indicating that NpPd₃ is possibly a moderately heavy-fermion material. However, estimating γ is complicated by the significant curvature due to the lambda feature at 10 K, such that this value for the electronic heat capacity corresponds to a fit, $C=\gamma T+\beta T^3$, which gives a value for β such that the Debye temperature would be 61 K, which is clearly too low.

In increasing applied magnetic fields, the anomaly associated with the 10 K transition shifts down in temperature, in agreement with the behavior expected from an antiferromagnetic transition. The feature also decreases in size until $H=7$ T after which it sharpens and increases in magnitude, a behavior which is as yet not explained. The application of a 1 T field broadens the higher temperature transition feature and shifts it up in temperature by 2 K, while in fields greater than 4 T, the feature has been smoothed away. These are not the characteristics of an antiferromagnetic phase transition; however, this could be consistent with a quadrupolar transition.

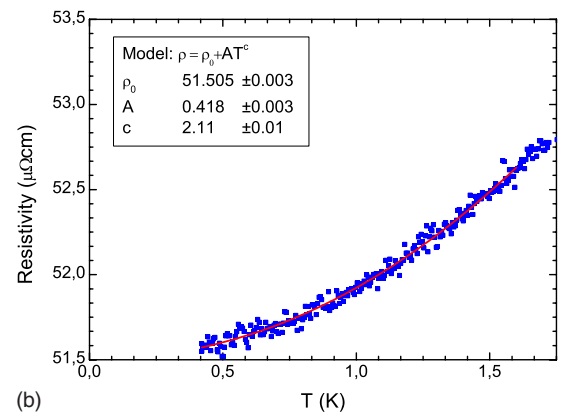
We have measured the heat capacity of ThPd₃ under identical experimental conditions. Using this isostructural non-magnetic compound as a phonon blank, the magnetic entropy of NpPd₃ has been calculated. It reaches $R \ln 4$ at 40 K, which suggests low lying excited doublet crystal field states above ground state doublets on both the locally hexagonal and quasicubic sites.

B. (U_{0.5}Np_{0.5})Pd₃

The heat capacity data for 50%Np show no lambda-like anomalies. Instead, inspection of Fig. 14 reveals a shoulder/kink at 12 K in zero field in C_p/T , corresponding to the temperature at which features are observed in the magneti-



(a)



(b)

FIG. 12. (Color online) (a) $\rho(T)$ of $(U_{0.95}Np_{0.05})Pd_3$ at $H=0$ T for $T=2-300$ K, showing a standard metallic behavior at high temperatures. (b) $\rho(T)$ at $H=0$ T for $T=0.4-1.75$ K. A fit to $\rho=\rho_0+AT^c$ for $T\leq 1.6$ K indicates that this composition is a Fermi liquid.

zation and resistivity measurements, and a broad peak centered on 5 K. No features are seen at 5 K in the susceptibility or resistivity measurements in this composition. This may be the Schottky peak arising from the splitting of the ground state doublet in the molecular field below the 12 K ordering temperature. Application of a 2 T field smoothes away the 12 K feature, while fields up to 9 T make the 5 K peak

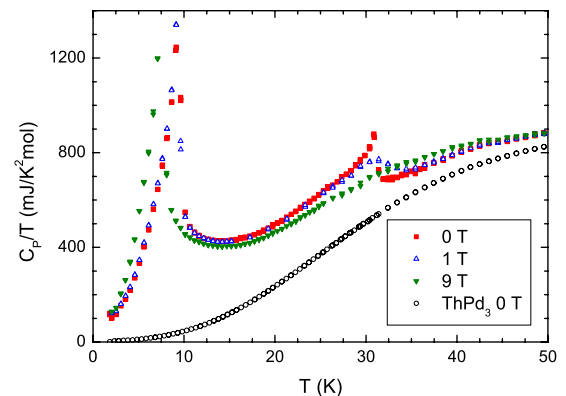


FIG. 13. (Color online) C_p/T vs T of NpPd₃, showing peak features at $T=10$ K and $T=30$ K in zero field and their evolution in different fields. Zero field results for ThPd₃ are also shown.

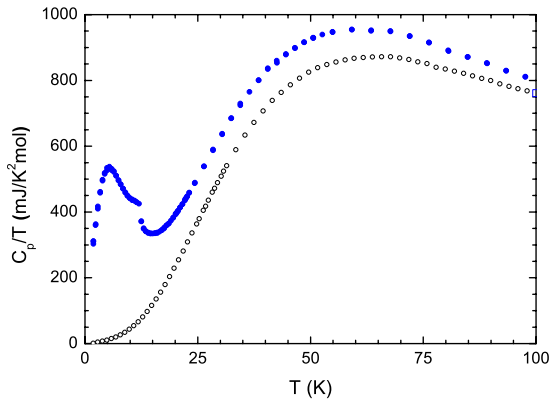


FIG. 14. (Color online) C_p/T for $(U_{0.5}Np_{0.5})Pd_3$ (\bullet) and $ThPd_3$ (\square) at $H=0$ T for $T=2-100$ K.

slightly narrower, but it does not change in magnitude.

The curvature of C_p/T down to 2 K is such that it is very difficult to make an estimate for the electronic heat capacity. It is quite possible that there is another transition below 2 K, but neglecting this possibility and extrapolating the data down to zero temperature suggest that γ is in the region of $150-250$ $mJ K^{-2} mol^{-1}$, considerably larger than that for $NpPd_3$ or UPd_3 . This results in a value of $A/\gamma^2 = (5.5 \pm 2.8) \times 10^{-5} \mu\Omega cm(mol K/mJ)^2$, which may indicate that 50% Np is another heavy-fermion material. A possible explanation is that the Np doping induces a valence change on the U ions leading to a lowering of the Fermi energy closer to the f bands, resulting in a greater deal of hybridization and hence heavy-fermion behavior. Without an accurate estimate for γ , it is not possible to calculate accurately the magnetic entropy of the sample.

C. $(U_{0.95}Np_{0.05})Pd_3$

Initial C_p/T measurements of 5%Np in zero field showed a broad rounded peak centered on 3.5 K with a value of 400 $mJ K^{-2} mol^{-1}$ at 2 K. The significant curvature at this temperature made extrapolating C_p/T back to $T=0$ K very difficult. So, to determine whether there are additional transitions which lead to a reduced estimate for γ , or whether this is another heavy fermion, as might be associated with proximity to a quantum critical point due to the suppression of a quadrupolar transition to zero temperature, additional measurements were performed using a 3He insert. These revealed the existence of more features in the data at 2.5 and 1.5 K, which may be associated with further transitions, see Fig. 15. The presence of the transitions at such low temperatures makes estimating γ very difficult, but assuming that there are no further transitions and continuing the trend in C_p/T give an estimate of $\gamma = 125 \pm 25$ $mJ/K^2 mol$. This results in a Kadowaki-Woods ratio of $(2.7 \pm 1.1) \times 10^{-5} \mu\Omega cm(mol K/mJ)^2$, indicating that the compound may also be a heavy fermion. Application of increasing magnetic fields results in the features shifting up in temperature. Such behavior is either indicative of ferromagnetic transitions, in which field reinforces the magnetic structure, or quadrupolar transitions. Since no hysteresis is seen in the

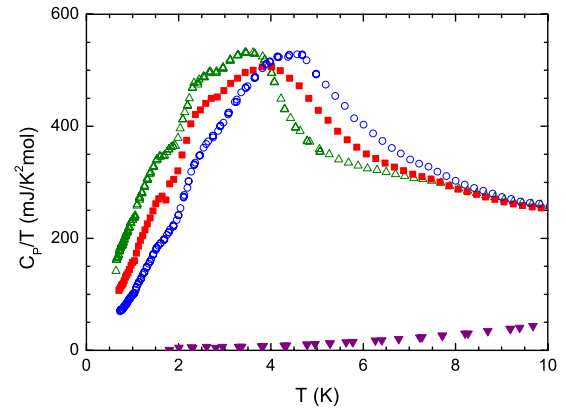


FIG. 15. (Color online) C_p/T in $(U_{0.95}Np_{0.05})Pd_3$ for $H=0$ T (\triangle), $H=5$ T (\blacksquare), and $H=9$ T (\circ) and in $ThPd_3$ (\blacktriangledown).

magnetization down to 2 K, ferromagnetism has been excluded as a possible explanation.

D. $(U_{1-x}Np_x)Pd_3$, $x=0.01, 0.02$

As one can see in Fig. 16, the heat capacity of 2%Np and 1%Np shows strong similarities to the data for UPd_3 .¹⁰ This observation is difficult to reconcile with the hypothesis that the uranium valence is changing with low neptunium doping, as postulated from the anomalous behavior of the lattice parameters as shown in Fig. 1 and discussed in Sec. II. It is also clear that the heat capacity of $ThPd_3$ below 10 K is much less than in the $5f$ analogs. The 2%Np C_p/T data have a peak at $T=4.2$ K and a shoulder at 7 K, features qualitatively similar to those at 6.5 and 7.8 K in polycrystalline UPd_3 , though the peak is approximately half the size in 2%Np. When a field is applied, the features relating to the transitions shift up in temperature, such that in $H=9$ T the peak is at 5.5 K. In addition, the shoulder becomes more pronounced with increasing field. The 1%Np C_p/T data, including additional measurements made using a 3He insert, are shown in more detail in Fig. 17, revealing transitions at 4, 6, and

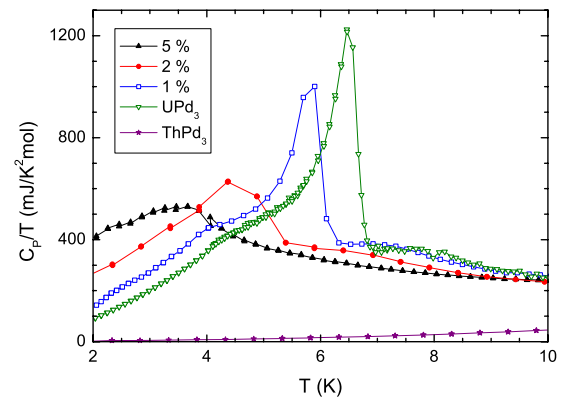


FIG. 16. (Color online) C_p/T of $(U_{1-x}Np_x)Pd_3$, with $x=0, 0.01, 0.02, 0.05$, and $ThPd_3$ in zero applied magnetic field, showing the suppression of the quadrupolar transition temperatures with increasing Np concentration.

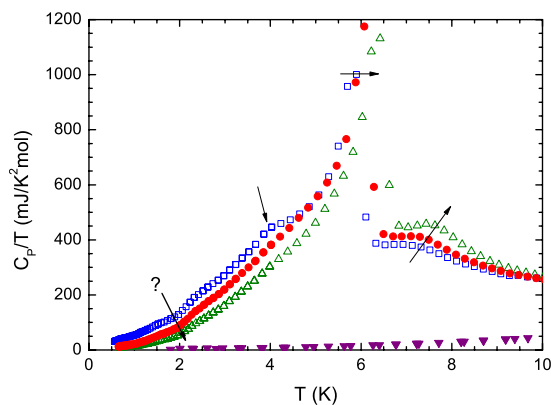


FIG. 17. (Color online) C_p/T of $(U_{0.99}Np_{0.01})Pd_3$ for $H=0$ T (\square), $H=5$ T (\bullet), and $H=9$ T (\triangle) and in $ThPd_3$ (\blacktriangledown). The general shape is very reminiscent of that for pure UPd_3 . The arrows show how the features associated with transitions evolve as a function of the applied field. The feature labeled with a question marked arrow may not be due to an intrinsic property of the system.

7.3 K, which may be labeled as T_0 , T_{-1} , and T_2 using the nomenclature for UPd_3 .¹⁰ There is another feature in the data at 2 K, which remains almost unchanged with increasing applied magnetic field. The origin of this feature is as yet unresolved. As for the 5%Np sample, the positive shift of features in temperature with field for 1% and 2%Np samples without hysteresis observed in magnetization measurements, in combination with their qualitative resemblance to those in UPd_3 , leads us to believe that these are transitions to quadrupolar phases.

VI. CONCLUSIONS

In conclusion, magnetization, electrical resistivity, and heat capacity measurements reveal two transitions in dhcp $NpPd_3$ at $T_2=10$ K and $T_1=30$ K. The in-field behavior of the features associated with the T_2 transition in different measurements indicates that it is most probably an antiferromagnetic transition. The T_1 transition is that which was observed in the previous experiments by Nellis *et al.*,¹² but unattributed. It has proven more difficult using the current polycrystalline bulk property experimental data to assign the nature of this transition. Initially, based on the magnetization data, T_1 was also assessed as being an antiferromagnetic transition;²⁸ however, the in-field behavior seen in resistivity and heat capacity results is inconsistent with such a conclusion. The smoothing away of the features with increasing field is more reminiscent of a quadrupolar transition. Interestingly, the T_1 transition is at T_M in the resistivity data, which shows high temperature Kondo behavior.

We plan to use neutron scattering to try to determine the nature of the two transitions. The previous diffraction experiment¹² observed no additional peaks at 4.2 K. However, the experiment was performed on a very small quantity of polycrystalline $NpPd_3$ with poor instrumental flux and resolution. With the immense improvements in neutron sources and instrumentation that have taken place over the past 30 years, we are confident that new diffraction data be-

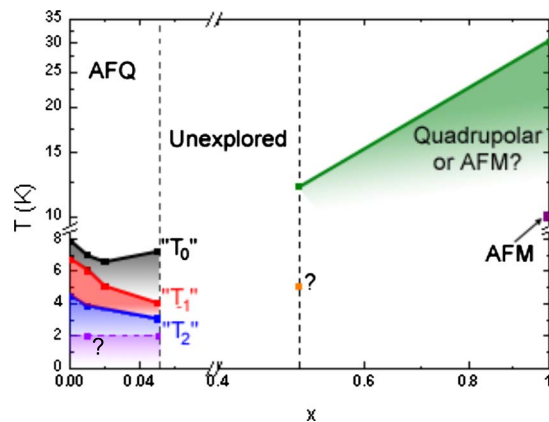


FIG. 18. (Color online) Temperature T versus neptunium concentration x phase diagram for $(U_{1-x}Np_x)Pd_3$ obtained from bulk property measurements. Points marked with “?” are from features in the heat capacity data, which either have yet to be assigned to a transition or are considered dubious. AFQ, antiferroquadrupolar; AFM, antiferromagnet.

low 10 K will provide information about the ordering vector of the antiferromagnetic phase. Measurements in the phase between the two transitions at $T=10$ and 30 K will be particularly interesting, since the absence of magnetic Bragg peaks would point to a nonmagnetic origin for the transition at 30 K. Neutrons do not couple directly to quadrupole moments, but instead we may observe a lattice modulation vector associated with an induced lattice distortion as is seen in UPd_3 . Polarized neutron diffraction techniques may be used to follow the individual susceptibilities of the hexagonal and quasicubic sites to distinguish between magnetic moments ordering on the different site types successively or simultaneously.

Our magnetic susceptibility measurements have demonstrated that neptunium is trivalent in $NpPd_3$ in contrast to uranium, which is tetravalent in UPd_3 , indicating a valence transition moving across the phase diagram. This underlines the unusual properties of UPd_3 since uranium is most commonly trivalent and raises the possibility of a tendency toward a valence instability, such that a critical percentage neptunium doping could induce a valence change on the uranium ion.

The results relating to all the different measurements performed on polycrystalline samples of $(U_{1-x}Np_x)Pd_3$ can be summarized in the phase diagram in Fig. 18. In the dilute Np region of the phase diagram, quadrupolar order is observed. The dominant feature in the heat capacity of UPd_3 is the lambda anomaly at T_{-1} , and so the evolution of this feature is the easiest to follow with increasing Np doping. The “ T_{-1} ” feature moves to lower temperatures as x is increased to 0.05, suggesting the possibility that at some critical doping concentration, this transition may be suppressed to zero temperature leading to a quantum critical point of quadrupolar origin.

Proximity to a quantum critical point at $x=0.05$ could be consistent with the apparent heavy fermion and possible non-Fermi liquid behaviors at this composition observed in the bulk thermodynamic measurements. It would be very inter-

esting to discover a quantum critical point due to the suppression of quadrupolar order, but one has to query the nature of any critical fluctuations with which it would be associated. The possibility of E/T scaling in samples close to criticality may be investigated using inelastic neutron scattering.

Further investigation of the location of the dopant Np ions in dilute $(U_{1-x}Np_x)Pd_3$ is desirable to determine whether or not they are distributed randomly over the two sites of the dhcp structure.

The results presented in this paper provide an extensive survey of the bulk magnetic and electrical properties of dhcp $NpPd_3$ and a preliminary characterization of the new and interesting mixed actinide system $(U,Np)Pd_3$. Clearly, there is considerable scope for further experimental investigation.

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