Tuning of the electronic properties in $PuCoGa_5$ by actinide (U, Np) and transition-metal (Fe, Rh, Ni) substitutions

P. Boulet,[1] E. Colineau,[1,*] F. Wastin,[1] J. Rebizant,[1] P. Javorský,[1,2] G. H. Lander,[1] and J. D. Thompson[3]
[1]*European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*
[2]*Charles University, Faculty of Mathematics and Physics, Department of Electronic Structures, Ke Karlovu 5, 12116 Prague 2, The Czech Republic*
[3]*Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
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The physical properties of *An*-substituted (*An*=U, Np) and *T*-substituted (*T*=Fe, Rh, Ni) $PuCoGa_5$ have been studied by magnetization, specific heat, and electrical resistivity. In all cases, the superconducting critical parameters decrease with substitution and different trends emerge. Isoelectronic substitution is the least destructive for superconductivity. On the contrary, for nonisoelectronic substitution, the T_c decrease versus c/a does not follow the trend observed in the cerium and plutonium isostructural compounds. Substituting Pu with actinides most dramatically affects the critical parameters. In particular, superconductivity is predicted to vanish in $PuCoGa_5$ with 18% Np substitution, making the coexistence of superconductivity and magnetism unlikely in a $(Pu_{1-x}Np_x)CoGa_5$ system. The electron count in $AnTGa_5$ compounds appears as a general and plausible quantity to evaluate trends in the variation of the critical (T_c, $H_{c2}(0)$) and electronic (γ) parameters.

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I. INTRODUCTION

The discovery of superconductivity at 18.5 K in $PuCoGa_5$[1] has raised a number of interesting questions pertinent to solid state physics; in particular, is the form of superconductivity unconventional or not? We have argued in a recent paper[2] that the strong correlation between the c/a ratio and T_c in both the Pu and Ce 1:1:5 structures (compounds having the tetragonal $HoCoGa_5$ structure with a symmetry of P4/mmm) points to a basic similarity between the mechanism of superconductivity in these materials. Although that mechanism is not yet established, the fact that superconductivity is found only in Ce and Pu materials with this structure, and not, for example, in other (rare earths or U and Np) isostructural compounds, strongly suggests that it is not conventional.

The compounds $UCoGa_5$ and $NpCoGa_5$ are paramagnetic[3–6] and antiferromagnetic,[7,8] respectively. In $UCoGa_5$ the susceptibility is almost independent of temperature and the specific heat[5] shows that $\gamma=21$ mJmol^{-1} K^{-2}. $NpCoGa_5$ is strongly magnetic with $T_N=47$ K, showing an ordered moment of 0.82(4) μ_B/Np, less than 0.05 μ_B on the Co site and $\gamma=64$ mJmol^{-1} K^{-2}.[7,8] In all actinide-based $AnCoGa_5$ systems, band-structure calculations[9–11] have suggested that the 5*f* electrons are itinerant, that the actinide ion is in an approximate trivalent state, and that the 3*d* states are filled and below E_F.

In this paper we continue the investigation of the superconductivity of $PuCoGa_5$ by studying the doping of the parent material $(Pu_xAn_{1-x})(Co_xT_{1-x})Ga_5$ with small amounts of actinides (*An*=U, Np) and different transition metals (*T*=Fe and Ni). These dopings affect the electronic structure, as opposed to doping Co with Rh, both of which are nominally iso-electronic with ~7 *d* electrons in the transition metal *d* shell. We present magnetic and electronic parameters but the main goal and interest of the present paper is the evolution and trends of the superconductivity parameters.

II. EXPERIMENTAL

Polycrystalline ingots were synthesized by arc melting stoichiometric amounts of the constituent elements under an atmosphere of high purity argon on a water-cooled copper hearth, using a Zr getter. To ensure homogeneity, the arc-melted buttons were turned over and remelted three times. Weight losses were checked during the synthesis process and found to remain below 0.5%. For further heat treatment, the pellets were wrapped in tantalum foil, and annealed at 850 °C for one week under very high vacuum. The crystal structure and the purity of the polycrystalline samples obtained were then checked from x-ray powder diffraction data (Cu $K\alpha$ radiation) collected on a Bragg-Brentano D500 diffractometer. A significant amount of neighboring phases (An_2TGa_8 and an unidentified hexagonal phase) were found in the sample with 10%Np substitution and also seen as traces in 10%Ni, 20%Fe, and 50% Rh samples. However, most of these 2:1:8 phases have been investigated separately and none were found to exhibit either superconductivity or magnetic order. The possible, but limited, impact of these impurity phases on the physical measurements is taken into account by the large error bars given for the parameters listed in Table I. Note that the values of the most important parameters like the critical temperature or field are not affected by small amounts of impurity phases. The lattice parameters of all compounds (at room temperature) are given in Table I.

All measurements were made on encapsulated polycrystalline samples, as described elsewhere.[12] DC-magnetization measurements were performed on a commercial SQUID magnetometer from 2 to 300 K in magnetic fields up to 7 T.

TABLE I. Structural parameters (x-rays), critical parameters (magnetoresistance), effective moment μ_{eff} and paramagnetic Curie temperature θ_p (magnetization) and Sommerfeld coefficient γ (specific heat) of $AnTGa_5$ systems. The values of the γ coefficient should be taken with care as linear extrapolations to $T=0$ K from the normal state are difficult due to the high critical temperatures (see text).

Compound	Unit cell dimensions in (Å) (with esd <0.001)			T_c(K) ±0.2	$\mu_0 H_{c2}(0)$(T) ±5	$\mu_{eff}(\mu_B)$ ±0.20	θ_p(K) ±5	γ(mJmol^{-1} K^{-2}) ±20
	a	c	c/a					
$PuCoGa_5$ (Refs. 1 and 14)	4.235	6.795	1.604	18.5	72	0.75	−40	80
10% U	4.228	6.778	1.603	8.4	8.7[a]	0.63	−17	-
$UCoGa_5$ (Ref. 5)	4.244	6.741	1.588	-	-	-	-	21
10% Np	4.229	6.776	1.602	7.2	3.4[a]	0.76	−25	120[b]
$NpCoGa_5$ (Ref. 7)	4.237	6.787	1.601	T_N=47	-	1.45	42	64
50% Rh	4.261	6.818	1.600	15.5	70	0.77	−32	190
90% Rh	4.293	6.849	1.595	10.2	28	0.66	−40	120
$PuRhGa_5$	4.301	6.857	1.594	8.9	22	0.56	−36	150
10% Fe	4.230	6.780	1.602	13.5	64	0.86	−53	80
20% Fe	4.232	6.780	1.601	10.0	40	?	?	130[b]
$PuFeGa_5$	4.263	6.768	1.587	-	-	-	-	-
10% Ni	4.229	6.779	1.602	16.6	69	0.66	−24	142[b]
$PuNiGa_5$	4.245	6.796	1.600	-	-	0.74	−44	195

[a] $\mu_0 H_c$ values, obtained from magnetization measurements.
[b] Values with higher uncertainties (±30).

The specific heat and electrical resistivity were measured on a commercial PPMS instrument within the temperature range 1.8–300 K and in magnetic fields up to 9 T.

All solid solutions investigated in this paper being based on $PuCoGa_5$, they will, for convenience and clarity, be simply identified by the percentage of doping element, e.g., "10% Np" will refer to $(Pu_{0.9}Np_{0.1})CoGa_5$, 20%Fe to $Pu(Co_{0.8}Fe_{0.2})Ga_5$, etc.

III. RESULTS

A. Doping on actinide site, *An*

A sharp decrease to negative values of the zero-field-cooled magnetic susceptibility indicates the occurrence of superconductivity in the 10% U and Np compounds below $T_c \approx 8.4$ K and $T_c \approx 7.2$ K, respectively (Fig. 1). In a first approximation, the 10% U doped material is close to a perfect diamagnetism, whereas the susceptibility of the 10% Np reaches only ~5% of the "ideal" value of $-\frac{1}{4}\pi$. This suggests that the 10% Np sample may contain nonsuperconducting phases. Indeed, the x-ray diffraction patterns show that the 10% U sample displays pure 1:1:5 phase, whereas the 10% Np sample contains non-negligible (roughly estimated around 30%) amounts of the 2:1:8 phase (Ho_2CoGa_8 type see, e.g., Ref. 13) and another, so far undetermined, phase.

The magnetization versus magnetic field (Fig. 2) shows a typical "butterfly" shape indicative of type-II superconductivity with pinning centers that trap the magnetic field vortices and allow superconductivity to survive in high magnetic fields, as observed in the pure $PuCoGa_5$[1] and $PuRhGa_5$[14] compounds. In both the 10% U and 10% Np compounds the fields H_c required to close the "butterfly" at $T=5$ K are close to $\mu_0 H_c \approx 7$ T and ≈ 1 T, respectively. Using the slope of $H_c(T)$ near T_c and the WHH approximation for the upper critical field at $T=0$, $H_{c2}(0) = -0.69\ T_c \partial H_{c2}/\partial T$,[15] we extrapolate $\mu_0 H_c(0) \approx 8.7$ T and $\mu_0 H_c(0) \approx 3.4$ T, respectively. This may be compared to the $\mu_0 H_{c2}(0) \approx 74$ T inferred for $PuCoGa_5$ using resistivity measurements,[1] or rather to $\mu_0 H_c(0) \approx 31$ T similarly inferred from magnetization loops. The critical field H_c measured by SQUID actually corresponds more closely to the irreversible field H_{irr}, which may be significantly lower than H_{c2}. It should also be mentionned that in favorable geometry, surface superconductivity may

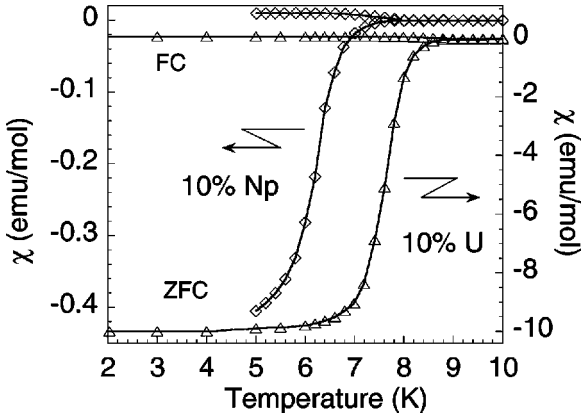

FIG. 1. Zero-Field Cooled (ZFC) and Field-Cooled (FC) magnetic susceptibility of 10%U (△) and 10%Np (◇), measured at $\mu_0 H = 0.001$ T and $\mu_0 H = 0.01$ T, respectively.

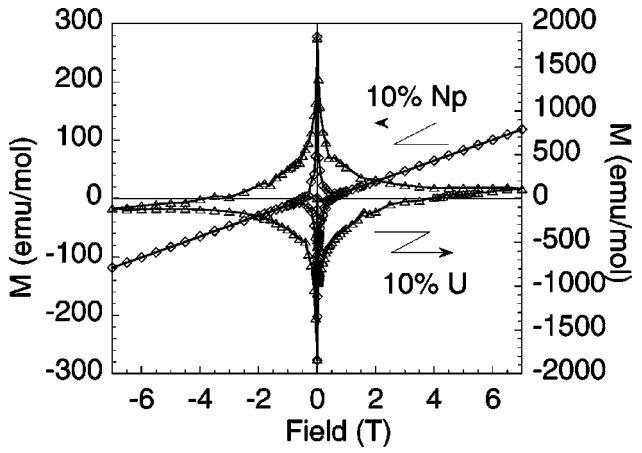

FIG. 2. Magnetization of 10%U (△) and 10%Np(◇), measured at $T=5$ K.

survive once the bulk superconductivity is destroyed and magnetoresistance may observe a surface nucleation field $H_{c3} \approx 1.67\ H_{c2}$.[16]

In the normal state, the magnetic susceptibilities of 10% U and Np are intermediate between those of $PuCoGa_5$, $UCoGa_5$, and $NpCoGa_5$ (Fig. 3) and can be accounted for by a modified Curie-Weiss law:

$$\chi = \chi_0 + C/(T-\theta_p)$$

The Curie constants thus obtained were renormalized according to the formula:[17]

$$C_{\text{renorm.}} = (C-\theta_p\chi_0)^2/C$$

from which the effective moments were inferred. Doping with U makes the effective moment slightly decrease (Table I), whereas doping with Np barely raises it. These tendencies make sense as $UCoGa_5$ has no effective moment and $NpCoGa_5$ carries a twice higher effective moment than $PuCoGa_5$.

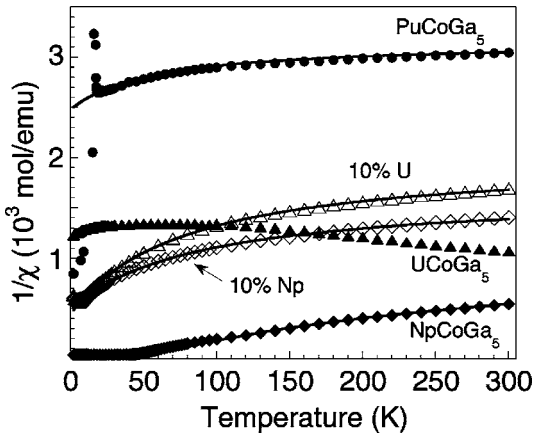

FIG. 3. Inverse magnetic susceptibility (symbols) and modified Curie-Weiss fit (full lines) of 10% U (△) and 10% Np (◇) measured at $\mu_0 H=7$ T. Pure $PuCoGa_5$ (●), $UCoGa_5$ (▲) and $NpCoGa_5$ (◆) are shown for comparison.

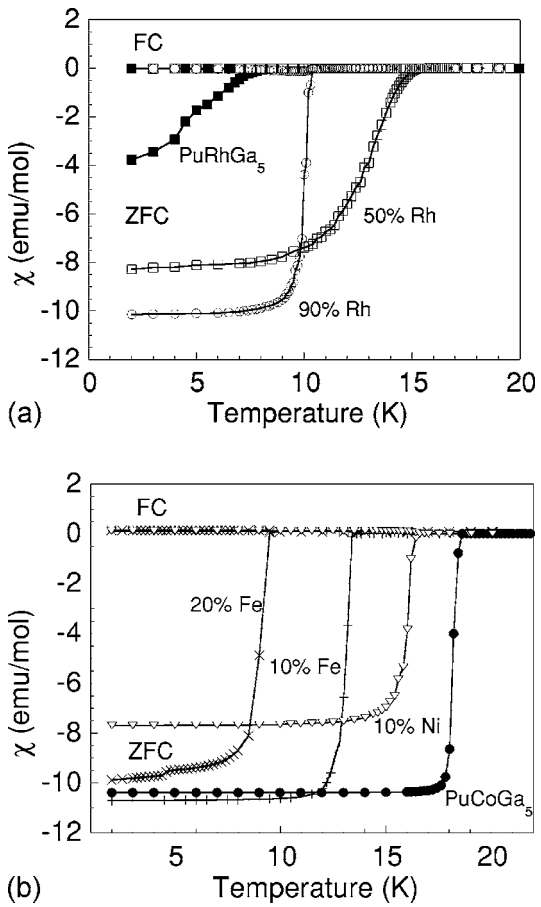

FIG. 4. (a) Zero-Field Cooled (ZFC) and Field-Cooled (FC) magnetic susceptibility measured at $\mu_0 H=0.05$ T for pure $PuRhGa_5$ (■), $\mu_0 H=0.03$ T for 50% Rh (□), and $\mu_0 H=0.001$ T for 90% Rh (○). (b) Zero-Field Cooled (ZFC) and Field-Cooled (FC) magnetic susceptibility measured at $\mu_0 B=0.001$ T for pure $PuCoGa_5$ (●), 10% Fe (+), 20% Fe (×) and 10% Ni (▽).

B. Doping on transition-metal site, *T*

Previous substitutions of the cobalt site in $PuCoGa_5$ have been performed only with the iso-electronic element Rh by mixing $PuCoGa_5$ and $PuRhGa_5$, both superconductors. The 50% Rh and 90% Rh show the onset of superconductivity at 15.5 and 10.2 K, respectively [Fig. 4(a)]. We have extended the study to nonisoelectronic elements by doping $PuCoGa_5$ with the two nearest neighbors of cobalt ($3d^7$), i.e., Fe($3d^6$) and Ni($3d^8$). The magnetic susceptibility of these new compounds are displayed in Fig. 4(b), showing the onset of superconductivity at 13.5, 10.0, 16.4 K, for 10% and 20% Fe and 10% Ni, respectively.

The resulting values of the susceptibilities below T_c are all rather close to perfect diamagnetism as shown in Figs. 4(a) and 4(b). The weaker susceptibility of $PuRhGa_5$ and 50%Rh can be explained by the measurement fields, 0.05 and 0.03 T, respectively, which are slightly above the critical field H_{c1}. The 10%Ni, although measured at 0.001 T, also exhibits a slightly weaker susceptibility that may be indicative of a small amount of a nonsuperconducting impurity in the bulk.

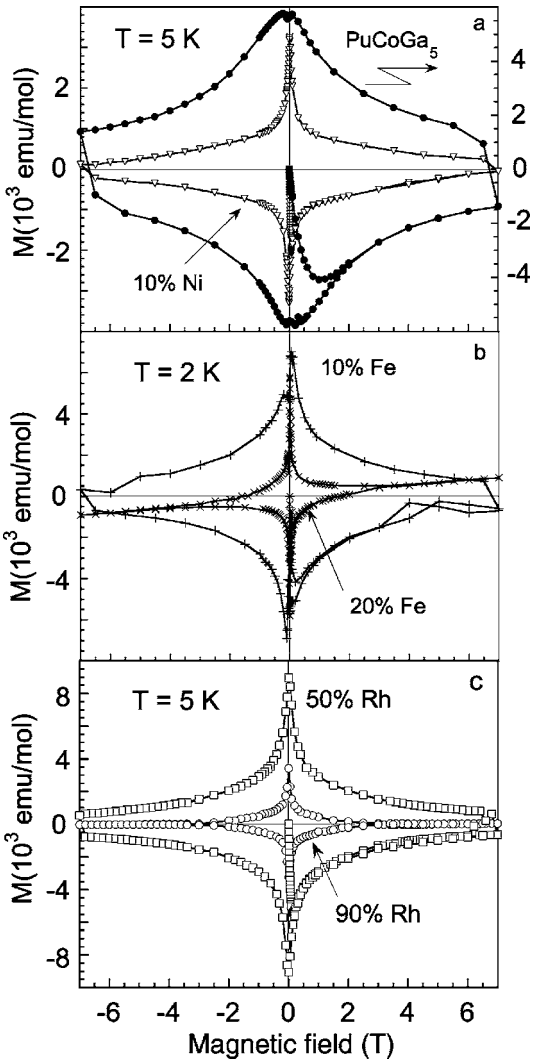

FIG. 5. (a) Magnetization of 10% Ni (▽), measured at $T=5$ K. Pure $PuCoGa_5$ (●) is shown for comparison. (b) Magnetization of 10% Fe (+) and 20% Fe (×, intensity multiplied by 4, for clarity), measured at $T=2$ K. (c) Magnetization of 50% Rh (□) and 90% Rh (○), measured at $T=5$ K.

Figure 5 shows the magnetization loops of the transition-metal doped $PuCoGa_5$ samples. The "butterfly" shape is clearly observed in all compounds, indicative of a type-II superconductivity with pinning centers. Except for pure $PuCoGa_5$, the magnetization maximum at low fields (when decreasing the field) is very sharp. However, the maximum magnetization M_{max} (at $H=0$) and area within the butterfly are much weaker than in pure $PuCoGa_5$: Substituting 10% of Ni or Fe decreases M_{max} by one order of magnitude. This indicates that flux pinning of $PuCoGa_5$ in the mixed state is much larger than in $Pu(Co_{1-x}T_x)Ga_5$ solid solutions. It is interesting that doping with a transition metal appears to suppress flux pinning so strongly, as pinning is thought to arise from defects created by Pu decay[1] that is independent of the transition metal.

In the normal state, similar to the $(Pu_{1-x}An_x)CoGa_5$ compounds, the magnetic susceptibility of all $Pu(Co_{1-x}T_x)Ga_5$ compounds, except 20%Fe, obey a modified Curie-Weiss

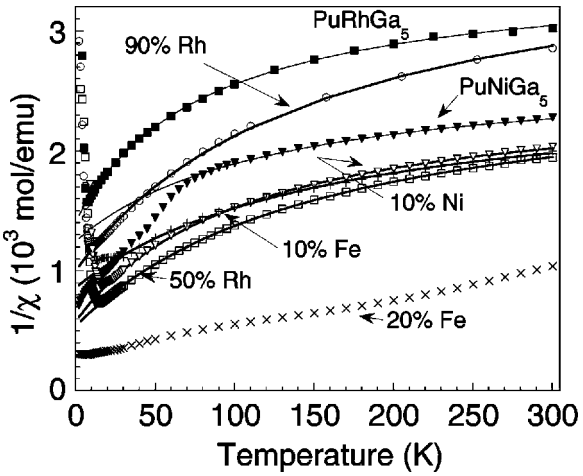

FIG. 6. Inverse magnetic susceptibility (symbols) and modified Curie-Weiss fit (full lines) of 10% Fe (+), 20% Fe (×), 50% Rh (□), 90% Rh (○), 10% Ni (▽), and $PuNiGa_5$ (▼) measured at $\mu_0 H=7$ T. Pure $PuRhGa_5$ (■) is shown for comparison.

law (Fig. 6). The values of the effective moment are listed in Table I. Rh and Ni substitution tend to decrease the effective moment, whereas Fe substitution increases it.

The specific heat (Cp) data confirm the occurrence of bulk superconductivity, with critical temperatures in good agreement with those inferred from magnetic susceptibility, in all $Pu(Co_{1-x}T_x)Ga_5$ compounds (Figs. 7 and 8). The values of specific heat (Sommerfeld coefficient) γ were estimated by the linear extrapolation of $C_p/T=\gamma+\beta T^2$ from the normal state to $T=0$ K. However, this simple law is valid at low temperatures ($T \ll \theta_D$). Such a fit becomes questionable for temperatures above ~10 K. Nevertheless, it seems that substituting Co by Fe, Ni, or Rh generally increases the γ value compared to pure $PuCoGa_5$ (Table I).

Finally, the resistivity measurements also confirm the occurrence of superconductivity in all $Pu(Co_{1-x}T_x)Ga_5$ compounds and allow a higher accuracy in the determination of

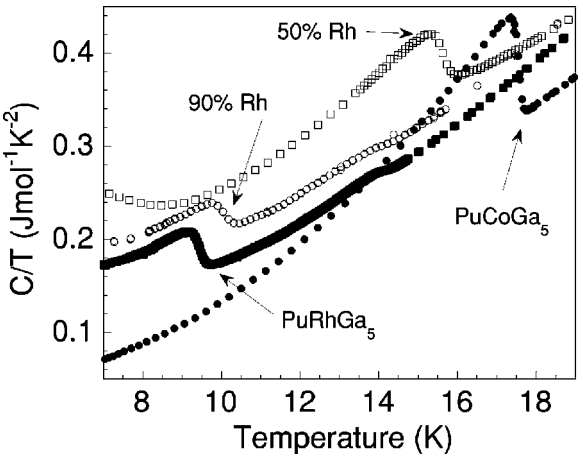

FIG. 7. Specific heat of 50% Rh (□) and 90% Rh (○). $PuCoGa_5$ (●) and $PuRhGa_5$ (■) are shown for comparison.

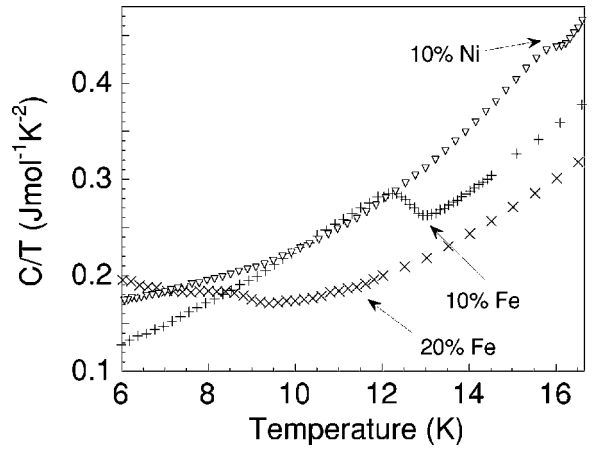

FIG. 8. Specific heat of 10% Fe (+), 20% Fe (×), and 10% Ni (▽).

the critical parameters T_c and H_{c2} (Fig. 9). The values thus obtained are listed in Table I and discussed below. As mentioned in the previous section, the extrapolated $H_{c2}(0)$ values (from the WHH approximation) inferred from resistivity are significantly higher than the values of H_c inferred from magnetization: $\mu_0 H_{c2}(0) \approx 70$ T ($\mu_0 H_c(0) \approx 21$ T from magnetization), 28 T (6.8 T), 22 T (9.1 T), 64 T (15.4 T), 40 T (4.8 T), 69 T (11.5 T) for 50% and 90% Rh, 10% and 20% Fe, and 10% Ni, respectively.

IV. DISCUSSION

From the crystal-chemistry point of view, one can already observe that solid solutions can be prepared by diluting on the actinide site as well as on the transition metal site. This behavior is significant on the stability of this crystal structure. However, when looking at the lattice parameter variation versus concentration, in all these solid solutions, Vegard's law is not fulfilled. This observation indicates that steric effects are not the only parameters involved in the stability of this crystal structure, but electronic structure influences the bonding.

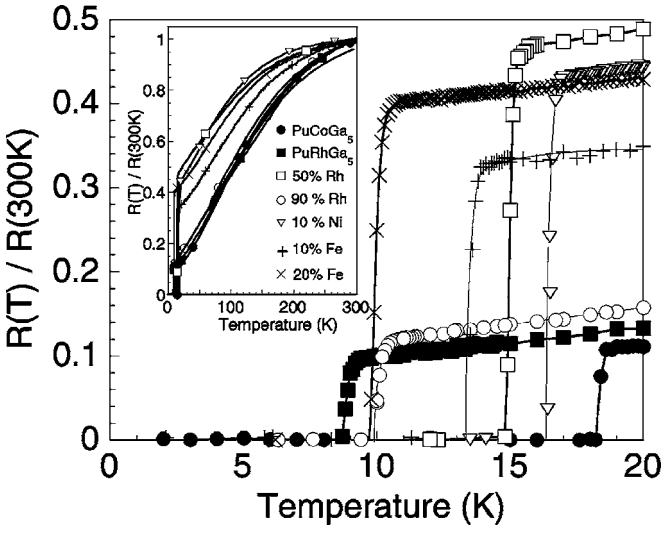

FIG. 9. Electrical resistance of 50% Rh (□), 90% Rh (○), 10% Ni (▽), 10% Fe (+), 20% Fe (×) in zero field. $PuCoGa_5$ (●) and $PuRhGa_5$ (■) are shown for comparison. The insert shows the whole temperature range. In the normal state, the magnetic field does not affect the curve significantly.

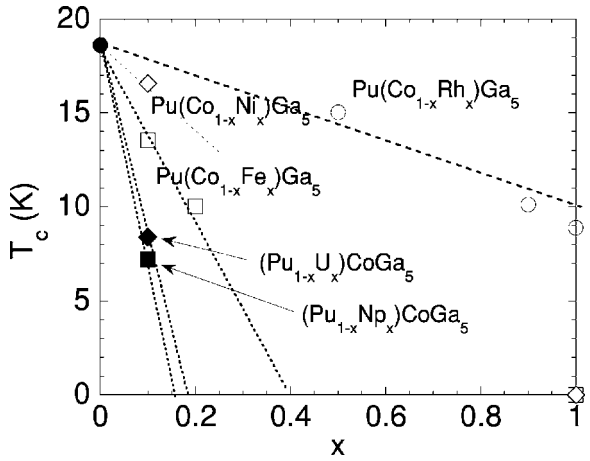

FIG. 10. Critical temperature as a function of the x concentration in $Pu(Co_{1-x}T_x)CoGa_5$ and $(Pu_{1-x}An_x)CoGa_5$ systems.

The variation of the critical temperature with substitution is represented in Fig. 10. It is clear that the substitution of the actinide affects more dramatically the critical temperature, which suggests that the $5f$ electrons are directly involved in superconductivity, as expected from theoretical calculations.[9–11] A rough linear extrapolation anticipates that T_c would vanish with ~18% Np or ~20% U. This rapid disappearance of the superconductivity makes the coexistence of superconductivity and magnetism unlikely in $(Pu_xNp_{1-x})CoGa_5$, as the magnetic order observed in $NpCoGa_5$ may not survive at such low Np concentrations. Substituting the transition metal appears less destructive for superconductivity in $PuCoGa_5$. We anticipate superconductivity to survive up to 40% Fe and an even higher Ni substitution. Finally, isoelectronic Rh substitution has only a small effect on T_c, as pure $PuRhGa_5$ is also a superconductor. These studies suggest that integrity of the Pu sublattice is more important for superconductivity than is periodicity of the d-electron elements.

The striking similarity of the properties between $PuTGa_5$ and $CeTIn_5$ has been recently demonstrated by the linear correlation in both systems between the critical temperature and the ratio of the tetragonal lattice parameters c/a.[2] Figure 11 shows the $T_c = f(c/a)$ plot extended to the solid solutions studied in the present paper. It clearly shows that these solid solutions do not fall on the same line as the $Pu(Co_{1-x}Rh_x)Ga_5$ materials. Their T_cs decrease much more rapidly with c/a. However, it seems that a linear relationship between T_c and c/a still applies individually for each series, with a steeper slope for actinide doping. The tendency for $Pu(Co_{1-x}Ni_x)Ga_5$ is less clear because only one substitution (10%) is available for this compound and it falls somewhere in between the other transition-metal doped systems, within an error bar distance of both slopes.

It is important to notice that Rh doping is iso-electronic (Co and Rh lie on the same column of the periodic table)

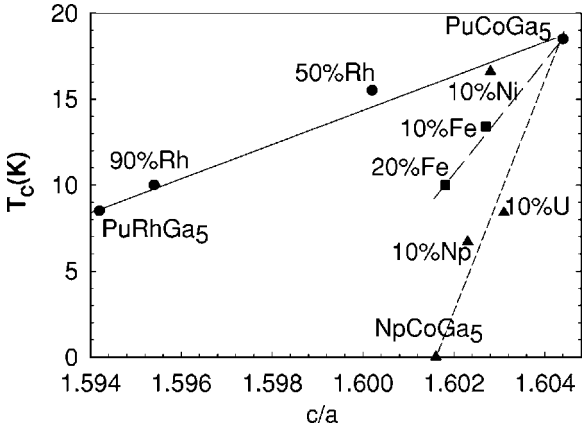

FIG. 11. Critical temperature T_c as a function of the c/a ratio for $Pu(Co_{1-x}T_x)CoGa_5$ and $(Pu_{1-x}An_x)CoGa_5$ systems. Dashed lines are only guides for the eye.

whereas Fe and Ni, as well as actinide-ion doping have different electron counts than $PuCoGa_5$. To illustrate the possible significance, key physical parameters are plotted as a function of the electron count in Fig. 12. Figure 12(a) shows a spectacular concentration of all $AnTGa_5$ superconducting compounds in a narrow band at 32 ± 0.2 electrons, whereas all compounds outside of this band (i.e., with a different electron count) are not superconducting. A similar trend is observed when plotting the critical field $H_{c2}(0)$. It is tempting to use these simple graphs to tentatively identify possible new superconducting compounds and/or interesting solid solutions. However, $PuIrGa_5$[18] and $NpNiGa_5$,[19] for example, are iso-electronic to $PuCoGa_5$ but so far no superconductivity was observed in these compounds.

The Sommerfeld specific heat coefficient γ shows an approximately linear dependence [Fig. 12(b)] versus the electron count and increases from a low 21 $mJmol^{-1}K^{-2}$($UCoGa_5$) up to a strongly enhanced 195 $mJmol^{-1}K^{-2}$($PuNiGa_5$). The idea that adding electrons to the system increases the electronic density of states is plausible, although a linear dependence seems surprisingly simple. $PuCoGa_5$, the 10% Fe, and the 50% Rh all slightly "deviate" from this approximately linear variation. However, these compounds are, with the 10% Ni, those with the highest T_cs and consequently the γ coefficients are extrapolated from high temperature, which limits their accuracy. The γ values of these compounds, estimated from the extrapolation to zero temperature of the simple $C_p/T=\gamma+\beta T^2$ law, which is known to be questionable for temperatures above $\sim$10 K, are not fully correct. Another way to estimate the γ coefficient is to use the phonon contribution of the nonsuperconducting and nonmagnetic $UCoGa_5$ homologue and fit the difference of $C_p(T)$ with $PuCoGa_5$ or other related compounds, over the whole available temperature range above T_c by the electronic contribution γT. Indeed, this method yields $\gamma=130$ $mJmol^{-1}K^{-2}$ for $PuCoGa_5$, placing it right on the linear $\gamma=f$(electron count) dependence and 180 $mJmol^{-1}K^{-2}$ for 10% Fe, shifting it from below to above the linear dependence. The γ values determined this way for the remaining compounds agree rather well with the low-temperature $C_p/T=\gamma+\beta T^2$ law extrapolating method.

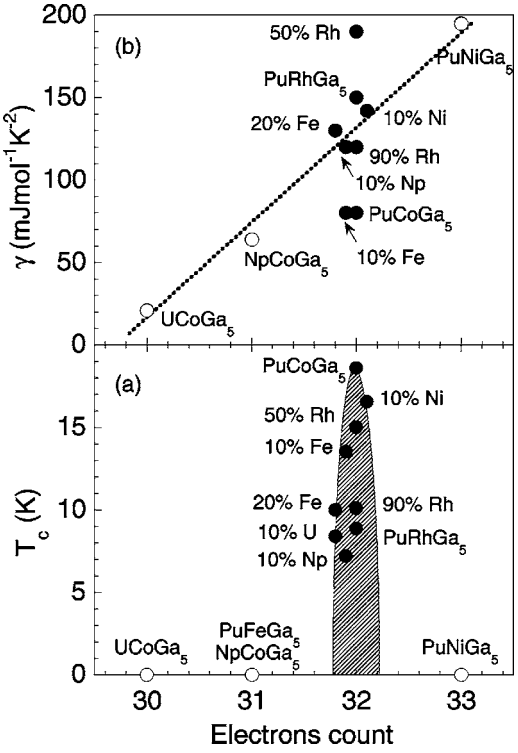

FIG. 12. Critical temperature T_c (a) and Sommerfeld specific heat coefficient γ (b) in $Pu(Co_{1-x}T_x)CoGa_5$ and $(Pu_{1-x}An_x)CoGa_5$ systems, as a function of the "valence" electrons count (taken as the total s, p, d and f electrons count from the outer shells, e.g., for $PuCoGa_5$, a total of 32 electrons is obtained by summing six $5f$ and two $7s$ for Pu, seven $3d$ and two $4s$ for Co and three valence electrons for each of the Ga atoms. Open symbols denote compounds that do not show superconductivity down to the lowest experimentally achieved temperatures and solid points correspond to compounds in which superconductivity is found and discussed in this paper.

Although uranium possesses a potential magnetic moment arising from its unfilled $5f$ shell, it may be considered as a nonmagnetic impurity in $PuCoGa_5$ as the $UCoGa_5$ analogue is a temperature independent paramagnet. The fact that a nonmagnetic impurity affects the critical temperature[20] almost as dramatically as the Np *magnetic* impurity indicates that the superconductivity in the $PuCoGa_5$ host is probably unconventional. Note that although the significant amount of impurity phase in the 10%Np compound mentioned before does alter the superconducting volume fraction of the sample, it is expected that the critical temperature of the intrinsic superconducting phase is unchanged.

The influence of magnetic impurities on the T_c of a superconductor is described by the Abrikosov and Gorkov pair breaking theory,[21] which considers a term arising from exchange interaction between conduction electron spin and localized impurity spin, leading to a finite lifetime τ_{AG} of the electron pairs:

$$1/\tau_{AG} = xN(E_F)2\pi(J_{ex}/2)^2S(S+1)$$

where x is the concentration of magnetic impurities, $N(E_F)$ is the single spin density of states at the Fermi surface, J_{ex} is

the exchange integral, and S is the spin of the impurity. For low concentrations of impurities, the critical temperature decreases linearly as :

$$\Delta T_c(x) = T_c(x=0) - T_c(x) = (\pi\hbar/4k_B\tau_{\mathrm{AG}})$$

For a given impurity, such as Fe, we can evaluate the relative changes in T_c expected from these relationships by assuming that J_{ex} depends weakly on x and that $\mathrm{N}(E_F)$ is proportional to the measured Sommerfeld coefficient. With these assumptions and taking values of $T_c(x)$ and $\gamma(x)$ for 10% and 20% Fe from Table I, the Abrikosov-Gorkov relations predict $\Delta T_c(0.2)/\Delta T_c(0.1)=3.2$; whereas, experimentally, this ratio is 1.7. If this discrepancy is real, it suggests that Fe substitutions on the transition-metal site do not break Cooper pairs as effectively as expected by theory.

We also make the following qualitative observations:

The pair breaking parameter $1/\tau_{\mathrm{AG}}$ increases with the doping x, which is observed experimentally.

The critical temperature T_c is expected to decrease linearly with $1/\tau_{\mathrm{AG}}$, thus quasi-linearly with x if $N(E_F)$ does not depend too much on x. A quasi-linear experimental T_c decrease is observed for dopings where we have at least 3 points (Fe, Rh). This validates our proposed linear extrapolations to $T_c=0$.

The Abrikosov and Gorkov formula can also account for the T_c decrease induced by nonmagnetic impurities if the pairing states have non-s-wave symmetry.[22] As mentioned above, U and Np substitution have, neglecting potential impact of the impurity phase in the 10%Np sample, comparable effect on the T_c of $PuCoGa_5$ and this further suggests that non-s-wave symmetry occurs in this compound.

As discussed earlier in this section, electron count and changes in c/a ratios also strongly influence T_c and compromise an unambiguous interpretation of pair breaking effects by chemical substitutions.

V. CONCLUSION

When substituting Pu with actinides (U, Np) or Co with transition metals (Fe, Ni, Rh) in $PuCoGa_5$, the critical parameters decrease and different trends emerge. Some of these trends have to be taken with care when few experimental points are available and in particular "magnetic" parameters that may be influenced by impurity phases observed in some compounds (see experimental section). However, the present paper is focused on superconducting properties and these are not affected greatly by nonsuperconducting impurity phases and this allows solid conclusions to be drawn. We have adopted the "electron count" as suggested by Maehira *et al.*[10] and found that many parameters appear to be dependent on this quantity. This, in turn, implies that a description in terms of itinerant electron states may be appropriate for these materials.[9–11] Iso-electronic substitution is the least destructive for superconductivity. On the contrary, for nonisoelectronic substitution, the T_c decrease versus c/a does not follow the trend observed in the iso-electronic doping of cerium or plutonium compounds of this type.[2] The most dramatic effects happen when Pu is substituted suggesting that the $5f$ electrons are crucial in driving the superconductivity. In particular, superconductivity is expected to vanish in $PuCoGa_5$ with approximately 20% Np. Further investigation of the $(Pu_{1-x}Np_x)CoGa_5$ system with higher Np content would be worthwhile to check where the superconductivity is destroyed and where magnetism appears.

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*Corresponding author.

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