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# Advances in the preparation and characterization of transuranium systems

**F Wastin, P Boulet, J Rebizant, E Colineau and G H Lander**

European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany

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**Abstract**

The most remarkable advance that one can report as regards transuranium systems is certainly the discovery of superconductivity above 18 K in $PuCoGa_5$. Motivated by this discovery, we have investigated bulk samples of both $PuCoGa_5$ and its Rh analogue. Characterizations of polycrystalline Co and Rh compounds are reported. The new $PuRhGa_5$ compound is also found to become superconducting above 8 K.

## 1. Introduction

During the past two decades, condensed matter physics has evolved in a climate of discovery in which many of the fundamental rules of solid-state physics have been brought into question by the finding of materials with unexpected properties. These 'emergent properties', such as high-temperature superconductivity, the coexistence of magnetism and superconductivity, and giant magnetoresistance, arise in complex materials in which electrons develop different states of organization and correlation. Many of these unusual electronic ground states are encountered in f-electron materials, and are linked to the notion of hybridization between the f-electron and ligand electron states. How these properties evolve with the progressive filling of the 5f shells remains an open question, but a key one for their understanding. For studying this process, families of isostructural lanthanide and uranium compounds are of considerable interest (see for example [1]). However, for the transuranium compounds very little is known. This is principally due to the intrinsic high radioactivity of the transuranium elements, complicating the experimental work and requiring cumbersome and costly infrastructures. Indeed, very few laboratories are able to handle these elements in appreciable quantities, limiting the progress on the physics and chemistry of these materials.

However, the recent discovery in Los Alamos Laboratory of superconductivity above 18 K in plutonium-based compounds, i.e. $PuCoGa_5$ single crystals [2], is certainly a remarkable advance that will strengthen transuranium research. Motivated by this discovery, we have started to investigate the $PuTGa_5$ series of isostructural compounds. We report on the preparation and characterization of $PuCoGa_5$ and $PuRhGa_5$ polycrystalline samples.

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## 2. Preparation and characterization of $PuTGa_5$ (T = Co, Rh)

Polycrystalline ingots of the compounds were obtained 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 alloy as an oxygen getter. The starting materials were in the form of ingots of pure elements as supplied by Merck A G (gallium 4N, cobalt and rhodium 5N) and electrorefined 3N6 plutonium metal. Classical methods for ensuring homogeneity of the arc-melted buttons and weight losses during the synthesis process were followed. Small single crystals with square shape, revealing a congruent melting of the compound, were formed on the surface of each button during the synthesis process and isolated from the crushed sample for x-ray structure determination and magnetic measurements.

The single-crystal x-ray diffraction data were collected with an Enraf-Nonius CAD-4 four-circle diffractometer using monochromated Mo K$\alpha$ radiation. The data processing was carried out using the Molen package [3]. The x-ray diffraction intensities were corrected for Lorentz and polarization effects and an absorption correction was applied using the program psiscan. The results are in close agreement with those obtained with the powder evaluation. In order to determine the purity of the sample and to investigate the phase relationship in the ternary phase diagram, x-ray powder diffraction data (Cu K$\alpha_{1,2}$ radiation) were systematically collected with a Bragg–Brentano Siemens D500/501 diffractometer using a $2\Theta$ step size of 0.02°. The diffraction patterns were analysed by a Rietveld-type profile refinement method using the Fullprof program [4]. The full profile x-ray powder analyses of the sample revealed nothing but pure $PuCoGa_5$ and $PuRhGa_5$ phases crystallizing in the tetragonal $HoCoGa_5$ structure type, which can be viewed as alternating planes of $PuGa_3$ and $TGa_2$ stacked along the $c$-axis.

The unit-cell parameters obtained are given in table 1. Investigations of other sample compositions in both ternary phase diagrams for lattice parameter evaluation revealed the 1:1:5 phase to exhibit a very small homogeneity domain.

## 3. Magnetization and transport property measurements

Magnetic susceptibility and electrical resistivity measurements were performed on bulk samples, using a Quantum Design SQUID magnetometer MPMS-7 and a PPMS-9 in the temperature range 2–300 K and in magnetic fields up to 70 and 90 kOe respectively. Samples were encapsulated as described in [5]. The resistivity was measured with a conventional four-probe ac method.

Figure 1 shows evidence of the $PuCoGa_5$ superconductivity properties as observed from magnetization and resistivity measurements. The zero-field-cooled magnetization reveals a sharp diamagnetic transition slightly above 18 K in agreement with the zero-resistivity transition observed around 18.2 K. Both values of $T_c$ are in very good agreement with ones reported for single crystals [2]. Figure 2 presents part of the magnetization loop $M(H)$ at 3 K. These data were taken while slowly increasing the field after zero-field cooling of the sample from a temperature well above $T_c$, and subsequently decreasing the field. A lower critical field $H_{c1}$ of $\sim$350 Oe is estimated. The substantial irreversibility of the magnetization is indicative of strong flux pinning which can be understood as due to the self-damage mechanism of Pu. The figure also displays the magnetization loop slightly above the superconducting transition, showing that paramagnetic behaviour is observed very close to the transition. In the paramagnetic state, the temperature dependence of the susceptibility was found to follow a modified Curie–Weiss law with an effective moment of $\sim 0.75\ \mu_B$ close to that expected for $Pu^{3+}$ and an interaction temperature $\sim -40$ K. These values differ from those reported from single-crystal measurements [2], which may indicate marked anisotropy.

**Table 1.** X-ray crystallographic data for $PuCoGa_5$ and $PuRhGa_5$ (of $HoCoGa_5$ type) and atom parameters.

| $PuCoGa_5$ | | | | | $PuRhGa_5$ |
|---|---|---|---|---|---|
| Crystal data | | | | | |
| Tetragonal, $P4/mmm$, no 123 | | | | | Tetragonal, $P4/mmm$, no 123 |
| $a = 0.423\,54(1)$ nm | | | | | $a = 0.430\,12(1)$ nm |
| $c = 0.679\,39(2)$ nm | | | | | $c = 0.685\,69(2)$ nm |
| $V = 0.1219(1)$ nm$^{-3}$ | | | | | $V = 0.1269(1)$ nm$^{-3}$ |
| $Z = 1$ | | | | | $Z = 1$ |
| $d_{calc} = 8.81$ g cm$^{-3}$ | | | | | $d_{calc} = 9.04$ g cm$^{-3}$ |
| Cu K$\alpha$ radiation, $T = 295$ K | | | | | Cu K$\alpha$ radiation, $T = 295$ K |
| Specimen shape: flat circle 13.00 mm × 0.2 mm | | | | | Specimen shape: flat circle 13.00 mm × 0.2 mm |
| Refinement | | | | | |
| $R_f$-factor = 0.079 | | | | | $R_f$-factor = 0.060 |
| $R_B = 0.102$ | | | | | $R_B = 0.079$ |
| $R_{exp} = 0.036$ | | | | | $R_{exp} = 0.033$ |
| Profile function: pseudo-Voigt | | | | | Profile function: pseudo-Voigt |
| Co: 204 reflections, 23 parameters | | | | | Rh: 168 reflections, 23 parameters |
| Orientation correction (March function): 001 | | | | | Orientation correction (March function): 001 |
| Atom parameters | | | | | |
| Atom | Site | $x$ | $y$ | $z_{Co}$ | $z_{Rh}$ |
| Pu | 1a | 0.0 | 0.0 | 0.0 | 0.0 |
| Co(Rh) | 1b | 0.0 | 0.0 | 1/2 | 1/2 |
| Ga | 4i | 0.0 | 1/2 | 0.3086(3) | 0.3064(3) |
| Ga | 1c | 1/2 | 1/2 | 0.0 | 0.0 |

Resistivity measurements in zero field and up to 90 kOe are displayed in figure 3. Up to 30 K the resistivity can be adjusted with an $AT^2$-type law with $A \sim 0.018$ $\mu\Omega$ cm K$^{-2}$, although an $AT^{1.35}$-type law applies up to 50 K (see the inset figure 3). A sharp superconducting transition is observed, slightly broadened with applied field. The critical temperature $T_c$ was followed as a function of the applied field (figure 4) and the resulting upper critical field $H_{c2}(0)$ inferred in the WHH [6] approximation to be ∼740 kOe. Experiments were repeated on the same sample aged for three months (inset, figure 4). The general properties are not affected by ageing, except for a shift of ∼0.4 K of $T_c$ and a slight increase of the resistivity (the curves are displaced almost parallel).

Figure 5 shows evidence of the $PuRhGa_5$ superconductivity properties as observed from magnetization and resistivity measurements. The zero-field-cooled magnetization reveals a sharp diamagnetic transition above 8 K in agreement with the zero-resistivity transition observed around 8.7 K. Comparing to $PuCoGa_5$, one can notice a less sharp diamagnetic transition as well as a less pronounced Meissner effect. For the paramagnetic state, the temperature dependence of the susceptibility follows perfectly a modified Curie–Weiss law with an effective moment of ∼0.60 $\mu_B$ and an interaction temperature ∼−36 K. These values are similar to those obtained for the Co compound. The inset of figure 5 presents the complete magnetization loop $M(H)$ at 3 K. The lower critical field $H_{c1}$ could not be precisely determined but seems to be lower than ∼100 Oe. For this compound too, large irreversibility of the magnetization is observed. The magnetization seems to cross the 0-axis around 50 kOe, indicating that the upper critical field is reached. However, resistivity

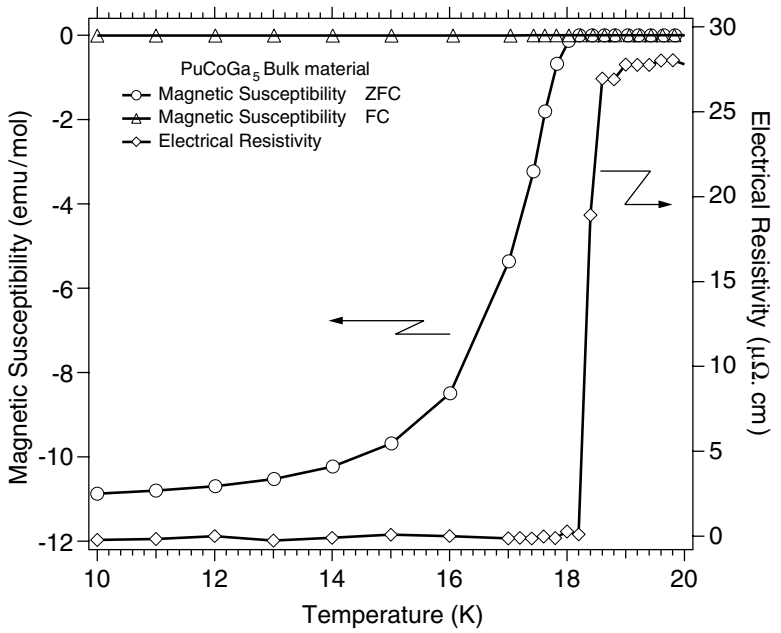


**Figure 1.** The zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility of $PuCoGa_5$ measured in 0.3 kOe for bulk material (left-hand side) and the electrical resistivity at zero field for material from the same batch (right-hand side).

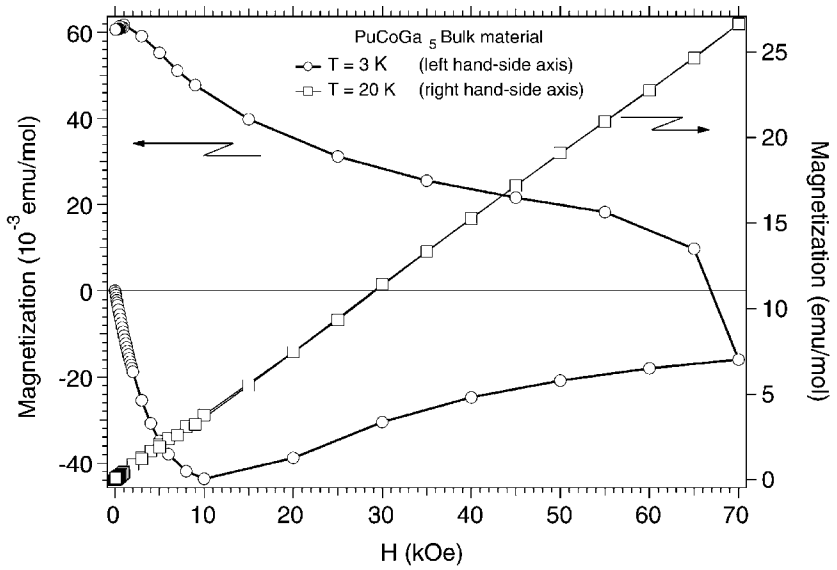


**Figure 2.** Magnetization loops $M(H)$ for $PuCoGa_5$ at 3 K (left-hand side) and in the paramagnetic region near the superconducting transition at 20 K (right-hand side).

measurements performed in a 90 kOe field still display a superconducting transition. This experimental disagreement between the two techniques can be understood in view of the difficulties regarding temperature stability/determination (due to self-heating effects of Pu)

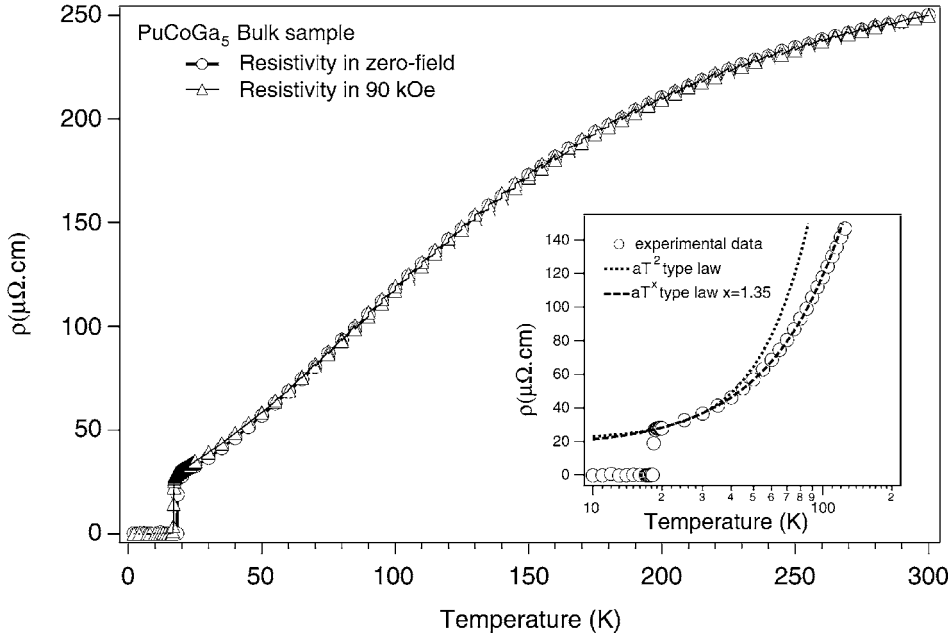


**Figure 3.** The electrical resistivity of $PuCoGa_5$ in zero and 90 kOe fields. The inset shows the results of the fitting to the $AT^n$ law ($n = 2$, 1.35) of the experimental data.

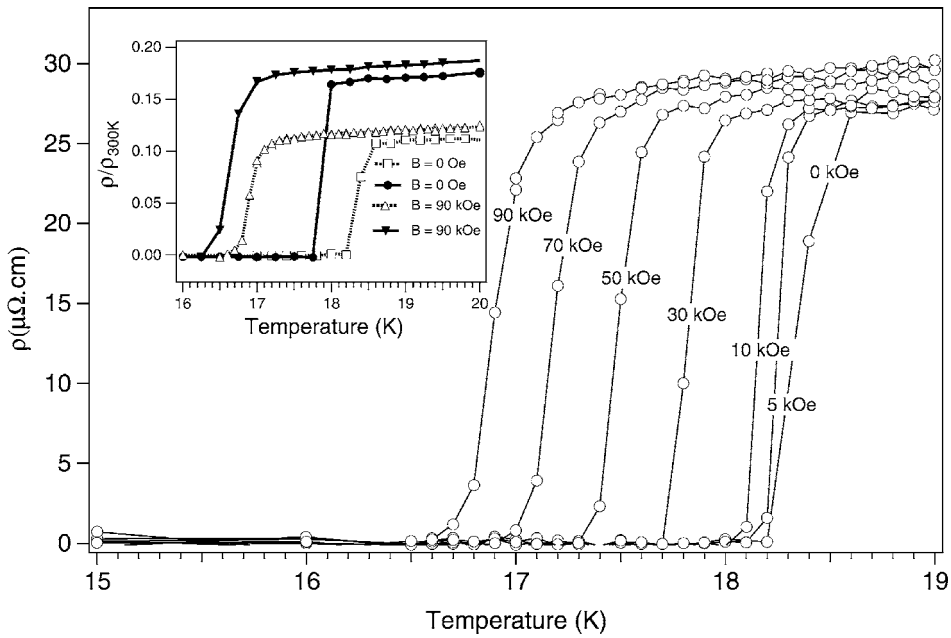


**Figure 4.** Field-dependent resistivity measurements for $PuCoGa_5$ . The inset shows the experiments repeated at zero and 90 kOe fields for a 'fresh' sample (open symbols) and the same sample aged for three months (full symbols).

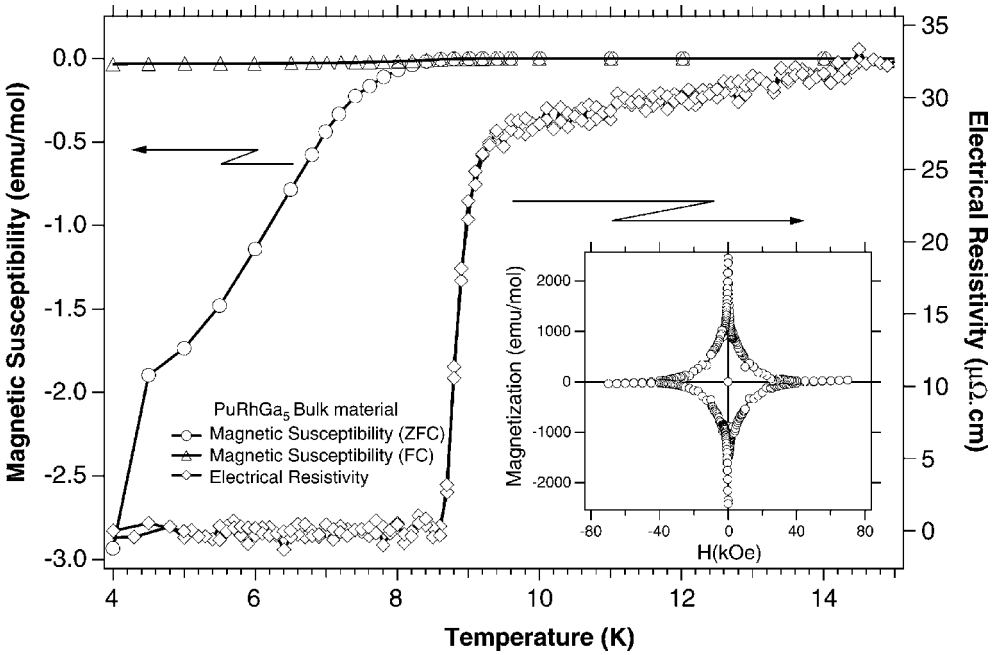


**Figure 5.** The zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility of $PuRhGa_5$ measured in 0.5 kOe for bulk material (left-hand side) and the electrical resistivity at zero field for material from the same batch (right-hand side). The inset shows the magnetization loops $M(H)$ for $PuRhGa_5$ at 3 K.

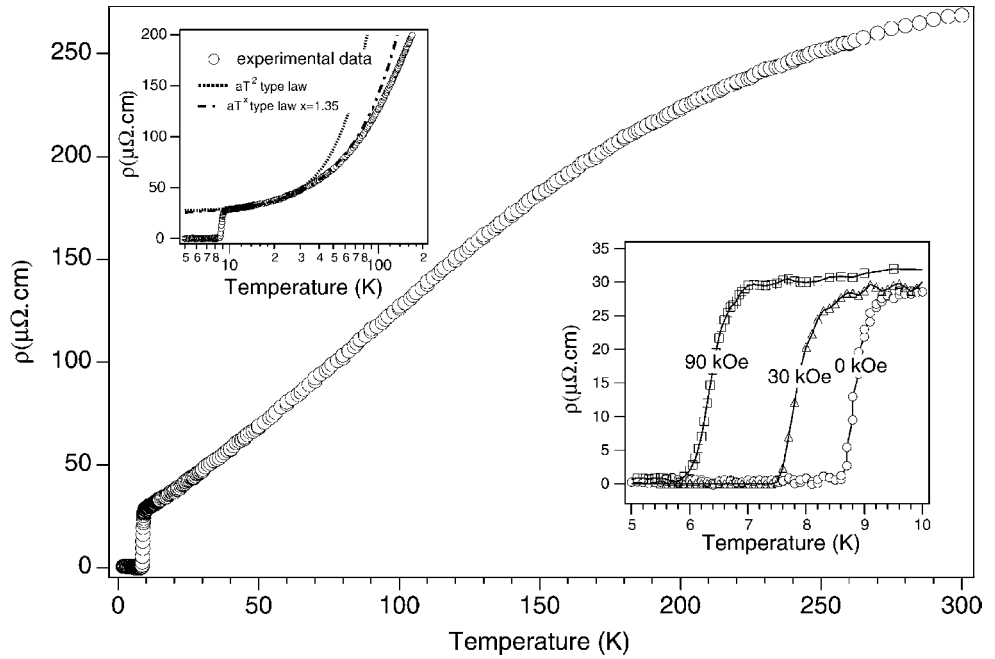


**Figure 6.** The electrical resistivity of $PuRhGa_5$ in zero field. The upper inset shows the results of a fitting to an $AT^n$ law ($n = 2$, 1.35) of the experimental data and the lower inset the variation of $T_c$ with applied magnetic field.

and/or sample encapsulation techniques. More careful experiments are necessary, preferably with a non-fissile Pu isotope (242).

Resistivity measurements in zero field are displayed in figure 6. The resistivity behaviour of $PuRhGa_5$ is very similar to that of its Co analogue and the experimental data can be adjusted according to an $AT^n$-type law with almost identical parameters ($A \sim 0.024\ \mu\Omega$ cm $K^{-2}$ for $n = 2$ or $n = 1.35$; see the inset of figure 6). The critical temperature $T_c$ was followed as a function of the field applied and the resulting upper critical field $H_{c2}(0)$ inferred in the WHH [6] approximation to be ∼210 kOe.

## 4. Conclusions

$PuCoGa_5$ and $PuRhGa_5$ are two new Pu-based superconducting compounds with critical temperatures of 18 and 8 K, respectively. The two compounds display very similar properties, suggesting that they are type-II superconductors. They are the first series of superconducting compounds found among transuranium-based compounds and are certainly represent a notable advance in transuranium compound solid-state physics.

## Acknowledgments

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