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Magnetic and electronic properties of NpRhGe

E Colineau[1,5], J P Sanchez[2], F Wastin[1], P Javorský[3], E Riffaud[1], Y Homma[4], P Boulet[1,6] and J Rebizant[1]

[1] European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany
[2] CEA, Institut Nanosciences et Cryogénie, 38054 Grenoble cedex 9, France
[3] Charles University, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, The Czech Republic
[4] Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan

E-mail: eric.colineau@ec.europa.eu

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Abstract
NpRhGe is the neptunium homologue of the ferromagnetic superconductor URhGe, and has been investigated using magnetization, electrical resistivity, specific heat and ^{237}Np Mössbauer spectroscopy. NpRhGe exhibits antiferromagnetic ordering below $T_N \approx 21$ K with an ordered magnetic moment $\mu_{Np} = 1.14\ \mu_B$. The value of the isomer shift suggests a Np^{3+} charge state (configuration $5f^4$) and possible delocalization of the 5f electrons. The Brillouin-like ($J = 1/2$) thermal variation of the magnetic hyperfine field indicates that a doublet ground state of the neptunium ion may occur in this compound. The specific heat indicates a high Sommerfeld coefficient value for NpRhGe (195 mJ mol^{-1} K^{-2}).

1. Introduction

Among the equiatomic intermetallic AnTX (An = an actinide, T = a transition metal, X = a p metal), a long series of compounds crystallize in the orthorhombic TiNiSi-type structure where the An atoms form zigzag chains extended along the *a*-axis. Their properties, well documented for the uranium compounds, were shown to be driven by the hybridization between the 5f electrons and the d electrons of the transition metal T [1]. Hence, members of this family of compounds exhibit a variety of magnetic and electronic properties depending on the filling of the transition metal d states: long range magnetic order for highly filled d states; spin fluctuations or weak paramagnetism for few d electrons. The compounds at the borderline between the two extreme behaviours are of particular interest. Indeed unconventional superconductivity (SC) coexisting with ferromagnetism (FM) at ambient pressure was recently discovered in two members of this series: URhGe ($T_C = 9.5$ K, $T_s = 0.25$ K) [2] and UCoGe ($T_C = 3$ K, $T_S = 0.8$ K) [3]. Note that the latter compound is a weak ferromagnet with an ordered moment (0.03 μ_B) an order of magnitude smaller than the one (0.42 μ_B) observed in URhGe. The coexistence of SC and FM in these intermetallics suggests that the SC is mediated by magnetic interactions. So far only few transuranium systems crystallizing in the TiNiSi-type structure have been investigated. NpNiSn was shown to be a robust antiferromagnet with $T_N = 37$ K. The ordered Np moment inferred from the Mössbauer study amounts to 1.67 μ_B [4]. Preliminary results were obtained for the Np and Pu counterparts of URhGe [5]. NpRhGe was found to order antiferromagnetically at 21.5 K while PuRhGe was[7] shown to remain a paramagnet down to 2 K. The present work focuses on the electronic and magnetic properties of NpRhGe gained from magnetization, resistivity, specific heat and ^{237}Np Mössbauer measurements.

[5] Author to whom any correspondence should be addressed.
[6] Present address: Institut Jean Lamour, FR2797, Ecole des Mines, Parc de Saurupt, CS14234, F-54042 Nancy, France.

[7] The small anomaly observed at 15 K in the magnetization data of PuRhGe (see [5]) was shown later on to be due to an impurity phase, also confirmed by specific heat measurements. Hence it has been concluded that PuRhGe does not order magnetically at least down to 2 K.

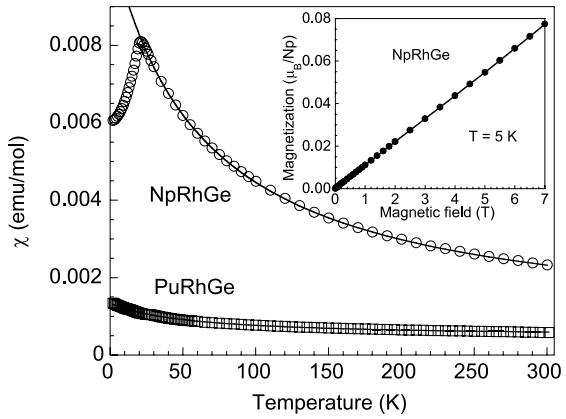

Figure 1. Magnetic susceptibility of NpRhGe versus temperature. The data for PuRhGe (a Curie–Weiss paramagnet with $\mu_{\rm eff} \approx 0.85\ \mu_{\rm B}$) are shown for comparison. The solid line represents the modified Curie–Weiss fit. The inset shows the magnetization of NpRhGe as a function of the magnetic field recorded at $T = 5$ K.

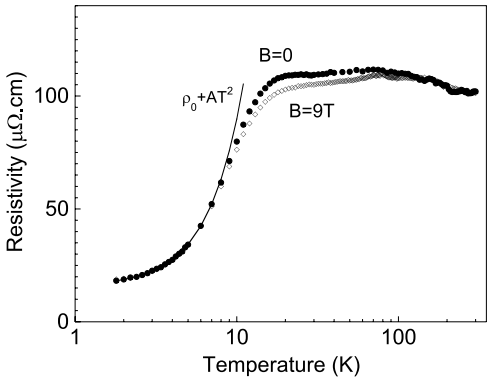

Figure 2. Electrical resistivity of NpRhGe in zero field (full circles) and with $B = 9$ T (open diamonds). The solid line shows the low temperature fit with a T^2 law (see the text).

2. Experimental details

A polycrystalline NpRhGe sample was prepared by arc melting the constituent elements (Np: 99.9%, Rh: 99.99% and Ge: 99.999%) in stoichiometric amounts under a high purity argon atmosphere in a water cooled copper hearth using a Zr getter. The as-cast sample was annealed for 10 days at 750 °C. Powder diffraction patterns recorded on a Bragg–Brentano Siemens diffractometer confirmed the TiNiSi-type structure (space group *Pnma*, No 62). The lattice parameters of the orthorhombic cell are $a = 6.987(1)$ Å, $b = 4.363(1)$ Å and $c = 7.493(1)$ Å. The smallest Np–Np spacing being of about 3.57 Å is above the Hill limit (∼3.2 Å).

DC magnetization measurements were carried out from 2 K up to 300 K on a Quantum Design (QD) SQUID magnetometer (MPMS-7) in magnetic field up to 7 T on a 44.0 mg sample. The specific heat experiments were performed using the relaxation method on a 23.7 mg sample in a QD PPMS-9 within the temperature range 1.8–300 K and in magnetic field up to 9 T. The electrical resistivity was measured between 1.8 and 300 K on the QD PPMS-9 system by the AC four-probe technique on a 3.6 mm^3 platelet sample taken from the ingot.

The ^{237}Np Mössbauer measurements were performed on a powder absorber with a thickness of 111 mg of Np cm^{-2}. The Mössbauer source of 108 mCi of ^{241}Am metal was kept at 4.2 K while the temperature of the absorber was varied from 1.5 to 40 K. The spectra were recorded with a sinusoidal drive system using conventional methods. The velocity scale was calibrated with reference to a $NpAl_2$ absorber ($B_{\rm hf} = 330$ T at 4.2 K).

3. Results and discussion

3.1. Magnetic measurements

The temperature dependence of the magnetic susceptibility is shown in figure 1. The susceptibility exhibits a pronounced and round maximum around 21.5 K attributed to the Néel temperature. No visible shift of $T_{\rm N}$ to lower temperature was observed up to 7 T. In the paramagnetic state the susceptibility can be fitted with a modified Curie–Weiss (MCW) law $\chi(T) = C/(T - \Theta_p) + \chi_0$ with $\mu_{\rm eff} = 2.23\ \mu_{\rm B}$ ($C = N\mu_{\rm eff}^2/3k_{\rm B}$) and $\Theta_p = -61$ K as expected for an antiferromagnet. The value of the effective moment $\mu_{\rm eff}$ is significantly below the free ion values of Np^{3+} (2.75 $\mu_{\rm B}$) and Np^{4+} (3.68 $\mu_{\rm B}$). The small temperature independent term $\chi_0 = 600 \times 10^{-6}$ emu mol^{-1} might be indicative of an electronic mass enhancement [6]. However, in actinide compounds, deviations from standard Curie–Weiss behaviour can be due to strongly anisotropic magnetic properties [7]. Therefore conclusions obtained from the use of the MCW law should be treated with caution. The magnetization curve measured at 5 K and displayed in the inset of figure 1 is shown to be linear. Thus, the application of a magnetic field up to 7 T does not induce any metamagnetic transition. This behaviour is in line with the strong magnetic anisotropy generally observed in the AnTX compound [1].

3.2. Resistivity measurements

The resistivity of NpRhGe (figure 2) is nearly temperature independent from $T_{\rm N}$ up to 300 K where it amounts to $\simeq$102 $\mu\Omega$ cm. Below $T_{\rm N}$, $\rho(T)$ decreases sharply to a low temperature limit $\rho_0 = 15.8\ \mu\Omega$ cm. The ratio of room temperature to residual resistivity (RRR $\simeq$ 6.5) is much smaller than the one (21–100) observed in the normal state of URhGe superconducting samples [8]. The analysis of the low temperature behaviour of the electrical resistivity indicates a quadratic (T^2) power law in the range 1.8–8 K. Writing $\rho(T) = \rho_0 + AT^2$ one obtains $A \simeq 0.74\ \mu\Omega$ cm K^{-2}. No hint of superconductivity was observed down to the lowest measured temperature (1.8 K). In agreement with the magnetization data no significant change is detected upon application of an external field up to 9 T. In heavy fermion compounds the coefficient A of the T^2 term in the resistivity is related to the linear specific heat coefficient by the expression [9]

$$A/\gamma^2 \simeq 10^{-5}\ \mu\Omega\ \text{cm mJ}^{-2}\ \text{mol}^2\ \text{K}^2.$$

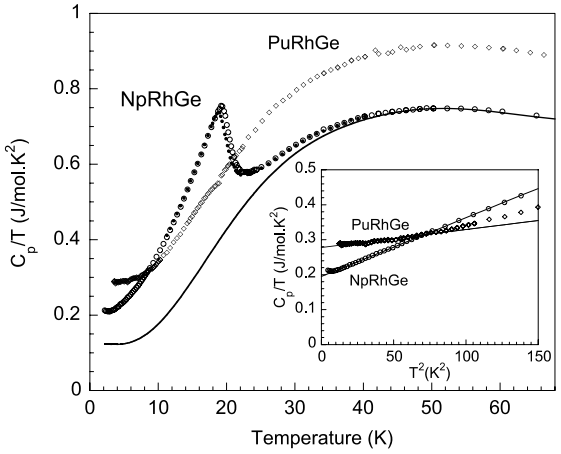

Figure 3. Specific heat of NpRhGe (open circles in zero field and full circles in $B = 9$ T) and PuRhGe (open diamonds in zero field). The solid line represents an estimation of the non-magnetic part in NpRhGe (see the text). The inset shows the low temperature data for NpRhGe and PuRhGe used to determine the γ-value.

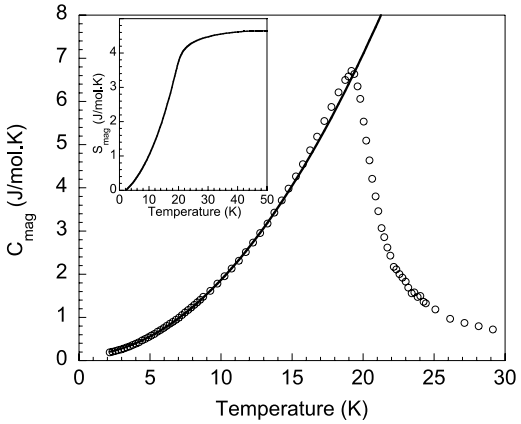

Figure 4. Magnetic specific heat of NpRhGe obtained as $C_{\rm mag} = C_p({\rm NpRhGe}) - C_p({\rm PuRhGe}) - \Delta\gamma T$ (see the text). The solid line represents a T^2 fit. The inset shows the magnetic entropy.

Thus, a Sommerfeld coefficient $\gamma \simeq 272$ mJ mol^{-1} K^{-2} is estimated. This classifies NpRhGe as a moderately heavy fermion compound.

3.3. Specific heat measurements

The temperature dependence of the specific heat of NpRhGe divided by temperature (C_p/T) in zero and in 9 T applied magnetic fields is shown in figure 3. The most prominent feature is the peak connected with the Néel temperature ($\simeq$20.5 K). When applying the 9 T field the peak is only slightly ($\simeq$0.5 K) shifted to lower temperature which is the tendency expected for a rigid antiferromagnet. This behaviour agrees well with the magnetization and resistivity data.

The specific heat is generally assessed via three contributions: the lattice (phonon) specific heat $C_{\rm ph}$, the electronic part $C_{\rm el}$ and the magnetic specific heat $C_{\rm mag}$. At low temperatures, the phonon part can be approximated by a T^3 law and one obtains

$$C_{\rm el} + C_{\rm ph} = \gamma T + \beta T^3.$$

The Sommerfeld coefficient γ can be estimated from the C_p/T versus T^2 plot (inset of figure 3). Our data can be fitted to such a dependence between 3 and 10 K. The magnetic term can also contribute to the specific heat in this temperature region and would influence mainly the slope of the observed dependence. We cannot thus relate the β parameter obtained to the fit to phonons (i.e. to the Debye temperature through the relation $\Theta_{\rm D} = (\frac{12\pi^4 R}{5\beta})^{1/3}$) but the γ coefficient characterizing the electronic contribution can be estimated with reasonable accuracy: $\gamma \simeq 195$ mJ mol^{-1} K^{-2}, comparable to the value inferred from the resistivity data above. The small increase of C_p/T observed below 3 K (not considered in the fit) can be explained as arising from a nuclear hyperfine Schottky term due to the splitting of the $I = 5/2$ nuclear ground level of the ^{237}Np nuclei by the hyperfine field reported below [10].

To determine the magnetic part of C_p and the magnetic entropy $S_{\rm mag}$, one has to estimate the lattice contribution. In our case, we can use the specific heat data of the paramagnetic isostructural PuRhGe compound assuming that the phonon contributions are similar in the two compounds (figure 3). The magnetic specific heat of NpRhGe (figure 4) can be simply estimated by subtracting the PuRhGe data and a term ($\Delta\gamma \times T$) that describes the different electronic contributions of PuRhGe and NpRhGe. A difference in γ-value of 165 mJ mol^{-1} K^{-2} between the two compounds allows us to reproduce well the specific heat of NpRhGe from 40 to 210 K. Below about 16 K, the magnetic specific heat follows a T^2 dependence. This behaviour contrasts with a T^3 dependence characteristic of standard 3D antiferromagnets. A T^2 dependence is predicted to occur in the case of the 2D Heisenberg antiferromagnet [11]. We guess that the quadratic behaviour observed in NpRhGe could be linked to the anisotropic exchange interactions anticipated for this compound. The integration of $C_{\rm mag}/T$ gives a magnetic entropy of $S_{\rm mag} \simeq 4$ J K^{-1} mol^{-1} at $T_{\rm N}$ which is slightly below the value $R \ln 2$ (=5.76) expected for a doublet ground state (inset of figure 4). This reduced magnetic entropy is often taken as an argument for delocalized character of the Np 5f states. However more data, such as high pressure experimental results, would be needed to settle the exact nature of the 5f electron in NpRhGe. In this context it is worth recalling the unexpected results on $NpSn_3$, considered as an archetypal itinerant 5f electron antiferromagnet, whose high pressure behaviour is that typical for localized 5f electrons [12].

3.4. ^{237}Np Mössbauer measurements

^{237}Np Mössbauer spectra were recorded at different temperatures between 1.5 and 40 K. Typical spectra are shown in figure 5. At 30 K, in the paramagnetic state, the Mössbauer spectrum consists of a broad structureless line assigned to a poorly resolved quadrupolar pattern due to the non-axial point symmetry (.*m*.) of the Np ions in the TiNiSi-type structure. Owing to the strong correlation between the linewidth W of the individual Lorentzian lines and the quadrupole interaction

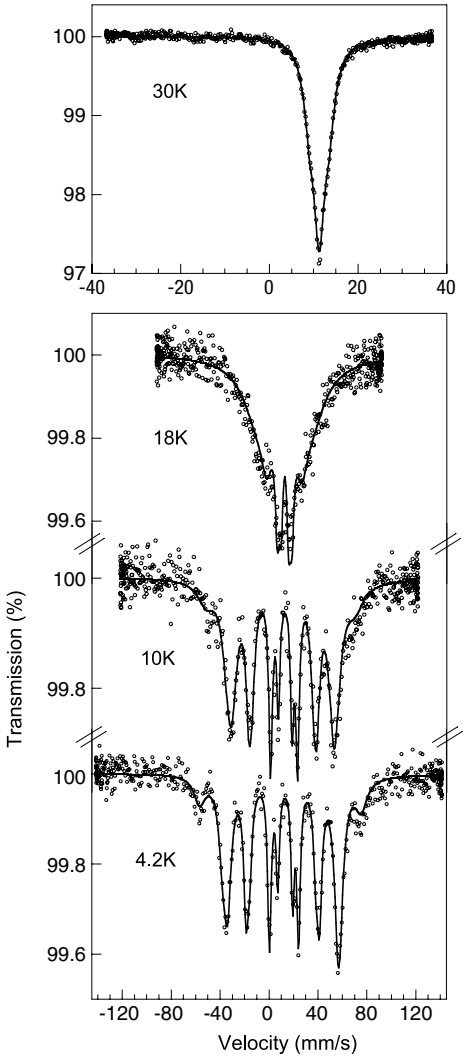

Figure 5. ^{237}Np Mössbauer spectra of NpRhGe recorded at typical temperatures between 4.2 and 30 K.

parameters (the quadrupole coupling constant e^2qQ and the asymmetry parameter η), we fixed W to 3 mm s^{-1} in the fitting procedure. Even then, we were unable to fit independently e^2qQ and η. Depending on the value assigned to η $(0 \rightarrow 1)$, $|e^2qQ|$ was found to range between 8.4 and 9.6 mm s^{-1}. The isomer shift ($\delta_{IS} = -2.5(1)$ mm s^{-1} versus $NpAl_2$) lies between those corresponding to the most ionic Np^{3+} (+37 mm s^{-1}) and Np^{4+} (−9 mm s^{-1}) compounds [13]. The presence of conduction electrons (or delocalization of the 5f electrons) was found to decrease δ_{IS}. Thus it may be anticipated that for a given charge state the isomer shift should be smaller than the value corresponding to the most ionic compound [13]. According to these systematics we assign a Np^{3+} ($^5I_4$) charge state to the Np ions in NpRhGe.

Upon cooling the sample, the spectra begin to broaden at 21 K indicating the onset of magnetic order. The situation in the ordered state is more complex. At 4.2 K, the spectrum can be analysed in terms of a unique set of hyperfine parameters ($B_{hf} = 245(1)$ T, $(e^2qQ)_{eff} = 6.5(8)$ mm s^{-1}) assuming that the magnetic hyperfine field axis coincides with the main principal axis of the electric field gradient tensor.

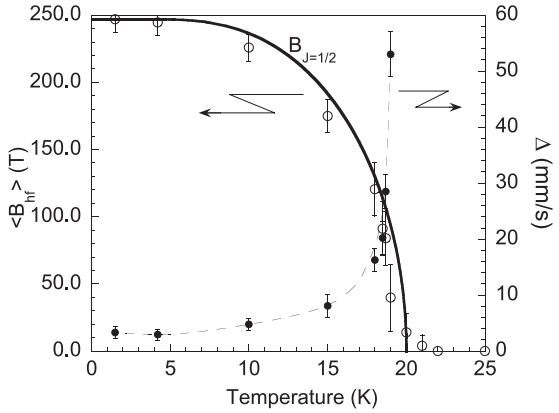

Figure 6. Temperature dependence of $\langle B_{hf}\rangle$ (open circles) and of the relaxation broadening parameter Δ (full circles). The thick line is a fit of $\langle B_{hf}\rangle$ to a $J = 1/2$ Brillouin curve whereas the thin line, $\Delta(T)$, is only a guide to the eye.

The value of the hyperfine field corresponds to an ordered magnetic moment $\mu_{Np} = 1.14\ \mu_B$, using the relation $1\ \mu_B = 215$ T [13, 14]. The spectrum recorded at the lowest achievable temperature of 1.5 K shows that the ordered moment of NpRhGe reaches saturation. However, the line broadening as well as the enhanced intensity of internal lines and reduced intensity of external lines are typical of relaxation effects. These are well accounted for using the Wegener relaxation model [15, 16] which assumes longitudinal fluctuations of the hyperfine field ($B_{hf} = \langle B_{hf}\rangle + B_f(t)$) around a time averaged value $\langle B_{hf}\rangle$. The linewidths are then given by

$$W = W_0 + 2\gamma_L(m_e, m_g)$$

where W_0 is the linewidth in the absence of relaxation broadening and

$$\gamma_L(m_e, m_g) = (g_e m_e - g_g m_g)^2\ \mu_N^2 \langle B_f^2\rangle \tau_c\ h^{-1}.$$

g_e, g_g, m_e, m_g are the nuclear g factors and the magnetic quantum numbers of the excited and ground state respectively; τ_c is the longitudinal correlation time. All spectra at $T < T_N$ were analysed in the framework of this model by constraining the intrinsic linewidth W_0 to the value of 3 mm s^{-1} fixed in the analysis of the paramagnetic spectra. It can be mentioned that similar effects were observed in $NpCo_2$ [17] and more recently in $NpCoGa_5$ [10] and $NpRhGa_5$ [18]. The temperature dependences of $\langle B_{hf}\rangle$ and of $\Delta = 2\mu_N^2\langle B_f^2\rangle\tau_c h^{-1}$ responsible for the line broadenings are presented in figure 6. It shows that the hyperfine field follows a $J = 1/2$ Brillouin behaviour which suggests that the ground state is a doublet. More surprising is the non-zero value of Δ at the lowest temperature ($\Delta = 3.32$ mm s^{-1} at 1.5 K) which indicates non-vanishing fluctuations of the hyperfine field (or magnetic moment) when $T \rightarrow 0$. Similar behaviour was previously observed for the Laves phase $NpCo_2$ compound [17] and is not yet understood.

4. Summary

The recent discovery of superconductivity at ambient pressure in the ferromagnet URhGe ($T_s \approx 0.25$ K and $T_C \approx 9.5$ K) [2] has attracted much interest in this system. The neptunium homologue, NpRhGe, has been investigated by means of magnetization, electrical resistivity, specific heat and ^{237}Np Mössbauer spectroscopy measurements. It is observed that NpRhGe exhibits antiferromagnetic ordering below $T_N \approx 21$ K and no hints of any further transition (of e.g. superconducting nature) down to 1.8 K have been found.

The value of the isomer shift ($\delta_{IS} = -2.5(1)$ mm s^{-1} versus $NpAl_2$) suggests a Np^{3+} charge state (configuration $5f^4$) and possible delocalization of the 5f electrons. The ordered magnetic moment amounts to $\mu_{Np} = 1.14\ \mu_B$ and the effective moment to $\mu_{eff} = 2.23\ \mu_B$. Both values are reduced compared to the Np^{3+} free ion values, respectively 2.46 μ_B and 2.75 μ_B. The Brillouin-like ($J = 1/2$) thermal variation of the magnetic hyperfine field indicates that a doublet ground state of the neptunium ion may occur in this compound. The magnetic entropy released at T_N (4 J K^{-1} mol^{-1}) is slightly below the $R \ln 2$ value expected for a doublet. Finally, the specific heat indicates a high density of states at the Fermi energy ($\gamma \approx$ 195 mJ mol^{-1} K^{-2}), a feature of a moderately heavy fermion.

A partially delocalized character of the 5f electrons in NpRhGe could account for the reduced values of the magnetic moment, the strong deviation of the isomer shift from the ionic value (+37 mm s^{-1} versus $NpAl_2$), the reduced magnetic entropy and the high Sommerfeld coefficient value.

Acknowledgments

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