Crystal structure and physical properties of NpRh$_2$Sn, a new Np-based ternary compound

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Abstract. We report on the synthesis and physical characterization of a new compound, NpRh$_2$Sn, prepared by arc-melting under argon atmosphere. Rietveld analysis of the powder x-ray diffraction pattern reveals an orthorhombic, Fe$_3$C-type structure, with lattice parameters that are the shortest among the AnT$_2$Sn series (An = U, Np, Pu, and T = Pd, Rh). A fit of the high-temperature magnetic susceptibility curve, $\chi(T)$, gives a Curie-Weiss temperature $\Theta_{CW} = -29K$, and an effective magnetic moment $\mu_{eff} = 2.42\mu_B$. The stabilization of the antiferromagnetic order below $T_N = 34$ K is revealed by a cusp in $\chi(T)$ and by a small anomaly in the specific heat curve, $C_p(T)$. An enhanced value of the Sommerfeld coefficient, $\gamma \approx 107 \text{ mJ mol}^{-1} \text{ K}^{-2}$, indicates a moderate heavy-fermion state. NpRh$_2$Sn is the first member of the AnRh$_2$M family, and a rare representative of heavy-fermion systems amidst Np-intermetallics.

1. Introduction
The large family of the ternary actinide compounds AnT$_2$M, where An is an actinide element, T is a transition element, and M is a metalloid, forms mainly in the orthorhombic Fe$_3$C-type crystal structure (Pnma, $s.g. 62$). The uranium based alloys (UT$_2$M) have attracted considerable attention due to a wide range of physical properties, which originates from the sensitive nature of the uranium 5f-electrons. Very few compounds with An other than uranium have been reported, and most of them contain palladium as the transition element.

Here, we present the crystal structure and physical properties of a new intermetallic NpRh$_2$Sn compound, which is the first member of the AnRh$_2$M family.

2. Experimental
Polycrystalline NpRh$_2$Sn sample was synthesized by arc-melting stoichiometric amounts of elements under a zirconium gettered ultra pure argon atmosphere. The purity of the product was verified by powder X-ray diffraction (Bruker D8 Focus, CuK$_\alpha$ radiation, graphite monochromator). Data were collected in the 2$\theta$ range of 10° – 100° with a step size of 0.01°. The FullProf Suite package was used for Rietveld structure refinement [1]. The magnetic susceptibility was measured using a Magnetic Property Measurement System (MPMS, Quantum Design), whereas the specific heat and electrical
resistivity were determined using a Physical Properties Measurement System (PPMS, Quantum Design).

3. Results and discussion

The as-cast sample extracted from the batch was studied by x-ray powder diffraction and the result is presented in Figure 1. The known crystal structure of URh\(_2\)Sn was employed as a starting structural model [2]. As shown in Fig. 1, there is good agreement between the model and the data, suggesting that NpRh\(_2\)Sn is isostructural to the U analogue. The lattice parameters for NpRh\(_2\)Sn were calculated to be a=9.7208(6) Å, b=4.4221(3) Å and c=6.9043(4) Å and are smaller than the reported ones for NpPd\(_2\)Sn [3]. It was found that 8% of Np substitutes the Rh(1) site and 8% of Rh are located on the Np site.

Selected physical parameters for NpRh\(_2\)Sn and other members of the AnT\(_2\)M series are given in Table 1.

|                | a (Å)     | b (Å)     | c (Å)     | d\(_{An-An}\) (Å) | \(T_N\) (K) | \(\Theta_{CW}\) (K) |
|----------------|-----------|-----------|-----------|-------------------|--------------|---------------------|
| NpRh\(_2\)Sn   | 9.7208(6) | 4.4221(3) | 6.9043(4) | 3.9702            | 34           | -29                 |
| NpPd\(_2\)Sn   | 10.004(3) | 4.535(2)  | 6.961(1)  | 4.0606            | 15           | -80                 |
| PuPd\(_2\)Sn   | 10.053(9) | 4.502(4)  | 7.065(6)  | ---               | 11           | -30                 |
| URh\(_2\)Sn    | 9.7923(2) | 4.37474(7)| 6.9639(1)| 3.935             | ---          | -200                |
| UPd\(_2\)Sn    | 9.9787(1) | 4.58843(5)| 6.89166(8)| 4.1817           | ---          | -77                 |

Figure 1. Rietveld refinement of room temperature the x-ray diffraction pattern for NpRh\(_2\)Sn. Crosses represent observed data, red solid line is the calculated intensity. The black tick marks correspond to NpRh\(_2\)Sn and green set refers to the NpO impurity (~2% wt.). Figure of merits: \(R_p = 4.04\), \(R_wp = 5.97\), \(R_{exp} = 2.60\) and \(\chi^2 = 5.28\).
In Figure 2 we show the temperature dependence of magnetic susceptibility (χ(T)) and electrical resistivity (ρ(T)) of NpRh<sub>2</sub>Sn. The solid red line in panel a) is a fit by the modified Curie-Weiss law. The inset in panel b) shows the derivative of the electrical resistivity (dρ/dT) vs. temperature. The Néel temperature, defined as shown in the inset, is 34 K.

Electrical resistivity as a function of temperature (main panel) and the temperature derivative of the resistivity (inset) for NpRh<sub>2</sub>Sn are plotted in Figure 2b. At room temperature the resistivity is 129 μΩ cm which is very close to what is observed for PuPd<sub>2</sub>Sn [4] and NpPd<sub>2</sub>Sn [3]. With decreasing temperature the electrical resistivity slightly increases and at 50 K reaches a value of 133 μΩ cm. Interestingly the non-metallic behavior in the high temperature region was also reported for NpPd<sub>2</sub>Sn whereas PuPd<sub>2</sub>Sn exhibit metallicity in the whole temperature range. Below 40 K a rapid drop of resistivity, and a pronounced positive peak of dρ/dT, are visible. This behavior is caused by the antiferromagnetic transition. Using the derivative of the electrical resistivity we can determine the ordering temperature (1/3 of the dρ/dT peak). We found T<sub>N</sub> = 34 K, which is very close to the magnetic ordering temperature.

The temperature dependence of the specific heat (C<sub>p</sub>) and specific heat over temperature (C<sub>p</sub>/T) of NpRh<sub>2</sub>Sn are shown in Figure 3. At room temperature C<sub>p</sub> reaches a value that corresponds to the Dulong-Petit law: C<sub>p</sub>=3nR=99.77 J mol<sup>-1</sup> K<sup>-1</sup>, where n=4 and R=8.314 J mol<sup>-1</sup> K<sup>-1</sup>. The magnetic phase transition discussed above is not well pronounced in the specific heat measurement. Close to T=30K only a slight change of slope, as shown in the inset of Fig. 3a, is observed on the specific heat curve C<sub>p</sub>(T). Similar result, notably a marginal evidence of a specific heat anomaly was reported also for UPd<sub>2</sub>-xSn (x=0.05 and 0.15), as discussed in ref. [7].

Figure 3b shows C<sub>p</sub>/T versus T<sup>2</sup> (only low temperature region) where the Debye temperature (Θ<sub>D</sub>) and Sommerfeld parameter (γ) can be estimated from the linear fit: C<sub>p</sub>/T = C<sub>el</sub>/T +C<sub>ph</sub>/T = γ + βT<sup>2</sup>, where \( \beta = \frac{12\pi^4}{5} \frac{nR}{\Theta_D^3} \). Although the experimental data were fitted only up to 10K, which is three times lower than T<sub>N</sub>, we are aware of the magnetic contribution (C<sub>mag</sub>) to the specific heat. Subtracting C<sub>mag</sub> should not change the value of γ, but might slightly change β, and consequently the Debye temperature. The calculated Sommerfeld parameter for NpRh<sub>2</sub>Sn, γ = 107 mJ mol<sup>-1</sup> K<sup>-2</sup> indicates...
Figure 3. Temperature dependent specific heat (a) and specific heat over temperature (b) of NpRh₂Sn. The inset of the figure a) emphasises the magnetic transition region.

moderately heavy fermion state, and is of the same order of magnitude as reported for PuPd₂Sn and NpPd₂Sn, which are 180 mJ mol⁻¹ K⁻², and 400 mJ mol⁻¹ K⁻² respectively.

To summarize, we have synthesized and studied a new Np-based ternary NpRh₂Sn compound. Its properties are similar to those of NpPd₂Sn, although a shorter Np-Np distance causes an increase of the Néel temperature. NpRh₂Sn is a rare representative of heavy-fermion systems amidst Np-intermetallics.

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References
[1] J. Rodriguez-Carvajal 1993 Physica B 192 55
[2] P. Gravereau, H. Guengard, F. Mirambet, L. Trut, J. Granneck, B. Chevalier, A. Tressaud, J. Etourneau 1994 Mat. Sci. Forum 166-169 671
[3] D. Kaczorowski, K. Gofryk, P. Boulet, J. Rebizant, P. Javorský, E. Colineau, F. Wastin, G.H. Lander 2005 Physica B 359-361 1102
[4] K. Gofryk, D. Kaczorowski, J-C. Griveau, N. Magnani, R. Jardin, E. Colineau, J. Rebizant, F. Wastin and R. Caciuffo 2008 Phys. Rev. B 77 014431
[5] F. Mirambet, B. Chevalier, P. Gravereau, L. Fournès, J. Etourneau 1995 J. Magn. Magn. Mater. 140-144 1361
[6] M. Marezio, D.E. Cox, C. Rossel, M.B. Maple 1988 Solid State Commun. 67 831
[7] I. Maksimov, F. J. Litterst, H. Rechenberg, M. A. C. de Melo, R. Feyerherm, R. W. A. Hendrikx, T. J. Gortenmulder, J. A. Mydosh, and S. Süllow 2003 Phys. Rev. B 67 104405.