

## Structural and physical characterization of NpPt<sub>2</sub>In<sub>7</sub>

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### Abstract

A new neptunium intermetallic compound, NpPt<sub>2</sub>In<sub>7</sub>, has been synthesized in polycrystalline form and characterized by several macroscopic techniques. A Rietveld analysis of its powder x-ray diffraction pattern shows that NpPt<sub>2</sub>In<sub>7</sub> crystallizes in a tetragonal lattice with  $I4/mmm$  symmetry and lattice parameters  $a = 4.58471(3)$  Å,  $c = 21.5065(3)$  Å. Magnetic susceptibility, electrical resistivity, Hall effect, and heat capacity measurements indicate a metallic character and the occurrence of antiferromagnetic order below a Néel temperature  $T_N = 23$  K. The transition is exceptionally robust and  $T_N$  decreases by 0.2 K under a magnetic field of 9 T. A modified Curie-Weiss fit of the high-temperature magnetic susceptibility curve  $\chi(T)$  gives an effective magnetic moment  $\mu_{eff} = 2.54 \mu_B$  close to the value expected for trivalent Np. Low temperature heat capacity measurements give a reduced Sommerfeld linear coefficient close to 25 mJ mol<sup>-1</sup>.K<sup>-2</sup> and a Debye Temperature  $\Theta_D = 181$  K. First principles, correlated-band electronic structure calculations suggest that the neptunium magnetic moment in NpPt<sub>2</sub>In<sub>7</sub> is localized and that a quasi-two-dimensional antiferromagnetic structure could result from the competition of very weak interlayer interactions leading to very anisotropic properties.

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### 1. Introduction

The layered intermetallic family of compounds  $A_nM_mIn_{3n+2m}$  (where M is a transition metal Co, Rh, Ir, Pd, or Pt and A is Ce, U, Np, or Pu) has been the object of wide attention during the past two decades because some of its cerium- and plutonium-based heavy-fermion members exhibit unconventional superconductivity in presence of magnetism [1, 2, 3, 4, 5, 6]. Here, we report the results of an extensive investigation of a newly synthesized member of the family, NpPt<sub>2</sub>In<sub>7</sub>.

Typically, Np-based compounds exhibit a non-superconducting, magnetically ordered ground state, as the electrons in the Np 5*f* shell are usually too localized for forming Cooper pairs. Examples are given by members of the  $A_nM_mIn_{3n+2m}$  system, such as NpCoGa<sub>5</sub> [7, 8], NpRhGa<sub>5</sub> [9], and NpPtGa<sub>5</sub> [10]. Until now, only two Np-based superconductors have been reported: NpPd<sub>5</sub>Al<sub>2</sub>, a heavy-fermion *d*-wave superconductor with  $T_c = 4.9$  K [11, 12, 13, 14] and NpMo<sub>6</sub>Se<sub>8</sub> with  $T_c = 5.6$  K [15]. Investigating novel layered in-

termetallic compounds of neptunium is therefore interesting for making progress in the rationalization of the interplay between magnetism and superconductivity in correlated 5*f*-electron materials.

A Rietveld analysis of the X-ray diffraction pattern shows that NpPt<sub>2</sub>In<sub>7</sub> is an isostructural analogue of CePt<sub>2</sub>In<sub>7</sub> [16], which becomes a heavy fermion superconductor when compressed [17], and of the heavy-fermion paramagnet PuPt<sub>2</sub>In<sub>7</sub> [18]. The physical properties of NpPt<sub>2</sub>In<sub>7</sub> have been investigated by magnetic susceptibility, heat capacity and resistivity measurements. The results indicate the onset of antiferromagnetic (AF) order at  $T_N = 23$  K. Experimental data are complemented by electronic structure calculations based on the correlated extension of the density functional theory (DFT+U), where Coulomb and exchange correlations, U and J, are added to the *f*-shell. The results of the calculations suggest that the investigated compound could be a realization of a local-moment quasi-two-dimensional AF metal.

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## 2. Experimental details

A small (approx. 300 mg) polycrystalline sample of  $\text{NpPt}_2\text{In}_7$  was synthesized by the arc-melting technique under zirconium gettered ultra pure atmosphere. Constituent elements of purity 99.9% or higher were used in the atomic ratio 1:2:7.2 (Np:Pt:In). A small excess of indium was used to compensate its evaporation during melting. The sample was remelted three times to improve homogeneity and then it was wrapped in tantalum foil, sealed in an evacuated quartz ampoule and put in a furnace at 500 °C for 4 weeks, before being furnace quenched to room temperature.

Room temperature powder X-ray diffraction (PXRD) studies were conducted on a Bruker D8 Focus diffractometer (CuK $\alpha$  source). To avoid contamination, a small amount of  $\text{NpPt}_2\text{In}_7$  sample was carefully ground and the obtained powder was embedded in an epoxy glue. PXRD data were collected in the  $2\theta$  range of 10°–100° with a step size of 0.01°. The FullProf software package was used for Rietveld structure refinement [19] with the starting model reported in ref. [16] for  $\text{CePt}_2\text{In}_7$ .

Measurements of the magnetic susceptibility  $\chi(T)$  were performed by using a Magnetic Property Measurement System (MPMS – Quantum Design) in the temperature range 3 K–300 K in an applied magnetic field of 7 T. A chunk of sample with a mass of 47.5 mg was glued inside a plastic holder. The data were corrected for the small paramagnetic signal of the sample holder.

The temperature dependence of electrical resistivity and heat capacity was measured using a Physical Property Measurement System (PPMS – Quantum Design). The electrical resistivity was determined using a standard four-contact dc technique, with four 50  $\mu\text{m}$  diameter Pt wires connected to the flat polished sample by using silver epoxy (Epotek H20E). Magnetoresistance was measured with magnetic field of  $\mu_0 H = 9$  T. The heat capacity was measured by using a relaxation method. Due to high radioactivity and toxicity of neptunium, the sample was embedded in the heat conducting STYCAST 2850 FT resin to avoid contamination risks. The raw heat capacity data were corrected by subtracting the signal estimated for the resin and for the  $\text{Pt}_3\text{In}_7$  signal.

All technical operations were carried out in radioprotected glove boxes with low oxygen and water concentrations.

## 3. Experimental results

The room temperature PXRD pattern is shown in Fig. 1. Successful Rietveld refinement confirms that

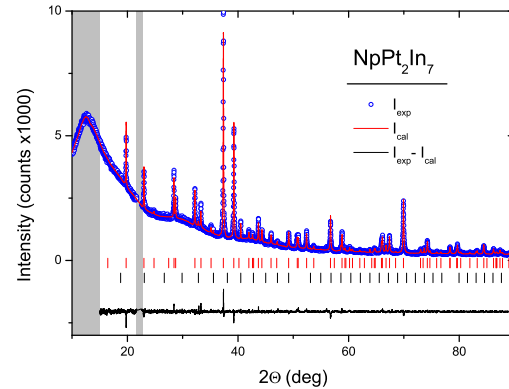


Figure 1: Rietveld refinement of room temperature powder X-ray diffraction data for  $\text{NpPt}_2\text{In}_7$ . Blue open circles ( $I_{exp}$ ) and a red solid line ( $I_{cal}$ ) represent observed and calculated data, respectively. Vertical tick marks are shown for two refined phases:  $\text{NpPt}_2\text{In}_7$  (upper, red) and about 20%  $\text{Pt}_3\text{In}_7$  impurity (lower, black). The differences between the observed and calculated pattern ( $I_{exp} - I_{cal}$ ) are represented by a black line.

$\text{NpPt}_2\text{In}_7$  is an isostructural analogue of the rare-earth  $\text{CePt}_2\text{In}_7$ , with the model described in Ref. [16]. Extra PXRD lines seen in the pattern correspond to  $\text{Pt}_3\text{In}_7$  (about 20% in weight). The used epoxy glue causes a large hump at low angle and a small peak at around 22°. Those regions were excluded for the Rietveld refinement. The crystallographic parameters and figures of merit derived from the fit are provided in Table 1.

Table 1: Refined structural parameters for  $\text{NpPt}_2\text{In}_7$  at room temperature. Space group  $I4/mmm$  (s.g. #139),  $a = 4.58471(3)$  Å,  $c = 21.5065(3)$  Å. Calculated density 10.51 g cm $^{-3}$ . Figures of merit: goodness of fit  $\chi^2 = 1.48$ , weighted profile residual  $R_{wp} = 4.33\%$ , profile residual  $R_p = 3.06\%$ .

Atom	Position	$z$	B	Occ
Np	2b (0, 0, 0.5)		0.644(44)	1
Pt	4e (0, 0, $z$ )	0.3257(1)	1.004(38)	1
In1	2a (0, 0, 0)		1.341(99)	1
In2	4d (0, 0.5, 0.25)		1.029(50)	1
In3	8g (0, 0.5, $z$ )	0.1067(1)	1.274(46)	1

The lattice parameters and the unit cell volume for  $\text{NpPt}_2\text{In}_7$  are larger than those previously reported for  $\text{PuPt}_2\text{In}_7$  [18], and smaller than those reported for  $\text{CePt}_2\text{In}_7$  [16] (see Table 2). The same trend is observed for a binary  $M\text{In}_3$  system, where  $M = \text{Ce}$  [20],  $\text{Np}$  [21] and  $\text{Pu}$  [22].

The magnetization  $M(T)$  was measured under applied fields  $\mu_0 H = 7$  T and  $\mu_0 H = 5$  T, and the magnetic susceptibility  $\chi$  was estimated as  $\Delta M / \Delta H$ . Its

Table 2: Unit cell parameters for CePt<sub>2</sub>In<sub>7</sub> (Ref. [16]), NpPt<sub>2</sub>In<sub>7</sub> (this work), and PuPt<sub>2</sub>In<sub>7</sub> (Ref. [18]). The parameters for CePt<sub>2</sub>In<sub>7</sub> and PuPt<sub>2</sub>In<sub>7</sub> were obtained from single crystal x-ray diffraction collected at 173 K and at room temperature, respectively. Refined parameters for NpPt<sub>2</sub>In<sub>7</sub> are based on room temperature powder x-ray diffraction.

	CePt <sub>2</sub> In <sub>7</sub> [16]	NpPt <sub>2</sub> In <sub>7</sub>	PuPt <sub>2</sub> In <sub>7</sub> [18]
a (Å)	4.5990(4)	4.58471(3)	4.5575(7)
c (Å)	21.580(2)	21.5065(3)	21.362(6)
V (Å <sup>3</sup> )	456.4(1)	452.06(1)	443.7(3)

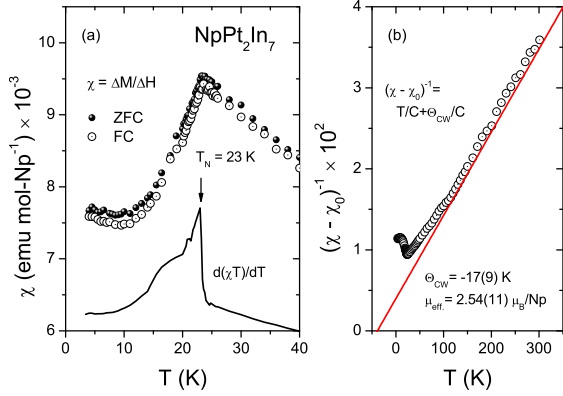


Figure 2: (a) Low temperature zero-field-cooling (ZFC) and field-cooling (FC) magnetic susceptibility for NpPt<sub>2</sub>In<sub>7</sub>. (b) Inverse magnetic susceptibility and a modified Curie–Weiss fit to the high temperature ( $T > 100$  K) data.

temperature dependence, obtained after zero-field cooling (ZFC) and field-cooling (FC) from the paramagnetic phase, is shown in Fig. 2(a). The low temperature anomaly reveals the onset of antiferromagnetic order. An accurate value of the Néel temperature,  $T_N = 23.0(5)$  K, is obtained from the maximum of the  $d(\chi T)/dT$  curve [23, 24]. As shown in Fig. 2(a), the cooling history has negligible effects on the phase transition.

The inverse magnetic susceptibility  $(\chi(T) - \chi_0)^{-1}$  in the  $T$  range 2 - 300 K is presented in Fig. 2(b). Above 100 K, the susceptibility follows a modified Curie–Weiss form:

$$\chi = \chi_0 + \frac{C}{T - \theta_{CW}}, \quad (1)$$

where  $\chi_0$  is temperature independent susceptibility,  $C$  is the Curie constant and  $\theta_{CW}$  is a Curie–Weiss temperature. The estimated fitting parameters are:  $\theta_{CW} = -17 \pm 9$  K, and  $C = 0.80 \pm 0.07$  emu K Np-mol<sup>-1</sup>. Having  $C$  we can calculate the effective moment per Np from  $\mu_{eff} = (8C)^{1/2} = 2.54 \pm 0.11 \mu_B$ . This

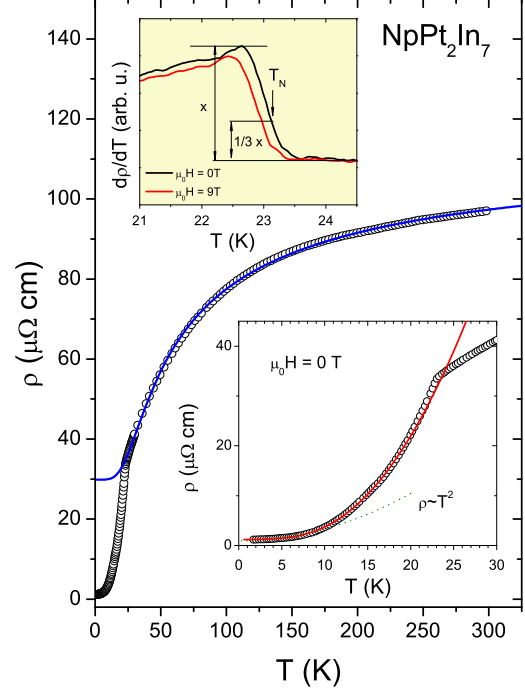


Figure 3: Temperature dependence of the electrical resistivity of NpPt<sub>2</sub>In<sub>7</sub> measured in zero magnetic field. Black points are the experimental data, blue line is the fit with Equation 2 Top Inset:  $d\rho(T)/dT$  in vicinity of the AFM transition measured under 0T and 9T applied magnetic field. Bottom Inset: Temperature dependence of the resistivity below  $T_N$ . The red solid curve is the fit to the data assuming the opening of a magnetic gap near  $T_N$ . The dashed green line is a low temperature fit with the Fermi liquid term.

value is close to  $\mu_{eff} = 2.755 \mu_B$  calculated for a trivalent Np<sup>3+</sup> in the intermediate coupling scheme, and to  $\mu_{eff} = 2.78 \mu_B$  obtained for NpFeAsO oxypnictide material [24]. On the other hand, it is much larger than  $\mu_{eff} = 1.5 \mu_B$  reported for NpCoGa<sub>5</sub> [7]. The negative value of the Curie–Weiss temperature,  $\theta_{CW} = -17$  K, might indicate the presence of antiferromagnetic interactions in NpPt<sub>2</sub>In<sub>7</sub>.

The temperature dependence of the electrical resistivity  $\rho(T)$  is shown in Fig. 3. The measurement was performed in the temperature range from 1.8 K to 300 K, in zero applied magnetic field and with a current  $I = 5$  mA. The  $\rho(T)$  reveals metallic-like character ( $d\rho/dT > 0$ ) with a sharp drop below 23 K, which is the onset of magnetic ordering. The  $\rho(T)$  curve at temperatures above  $T_N$  has been fitted to the formula for the so-called

parallel resistor model (PRM):

$$\rho^{-1}(T) = \rho_{max}^{-1} + (\rho_0 + \rho_{BG})^{-1}, \quad (2)$$

where

$$\rho_{BG}(T) = 4R\theta_R \left(\frac{T}{\theta_R}\right)^5 \int_0^{\theta_R} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}. \quad (3)$$

The model combines temperature independent resistors  $\rho_{max}$ ,  $\rho_0$ , and a the Bloch-Grüneisen resistor represented by  $\rho_{BG}(T)$ . The residual resistivity  $\rho_0 = 41 \mu\Omega cm$  estimated from the fit is one order of magnitude larger than the resistivity measured in the antiferromagnetic state  $\rho(2K) = 1 \mu\Omega cm$ . At high temperature, where the mean-free path approaches the interatomic distance, the resistivity starts saturating (Ioffe-Regel limit[25, 26]) to the estimated value of  $\rho_{max} = 112 \mu\Omega cm$ . The last parameter in the fit is  $\theta_R = 150$  K, the Debye temperature estimated from resistivity. The absence of any clear deviation of the resistivity curve from the fitted formula above  $T_N$  likely suggests the weakness of spin fluctuations in the paramagnetic regime.

The top inset (a) of Fig. 3 presents  $d\rho/dT$  versus temperature in the vicinity of the transition. The Néel temperature was determined as 1/3 of the jump of  $d\rho/dT$  [27] and is equal to  $T_N = 23.1$  K under zero field and decreases to  $T_N = 23.0$  K under  $\mu_0 H = 9$  T, in perfect agreement with  $T_N$  obtained from magnetic susceptibility and heat capacity experiments.

The low-temperature resistivity data are presented in the bottom (b) inset of Fig. 3. The  $\rho(T)$  curve cannot be fitted with the Fermi liquid term  $\rho(T) = \rho_0 + AT^2$ . Instead, the formula established for antiferromagnetic interactions with the opening of a magnetic gap [28] is found to successfully describe the low temperature resistivity, as demonstrated by a red solid line in top left Fig. 3:

$$\rho(T) = \rho_0 + aT^2 + bT \left(1 + \frac{2T}{\Delta}\right) \exp\left(-\frac{\Delta}{T}\right), \quad (4)$$

where  $\rho_0 = 1.17 \mu\Omega cm$ ,  $a = 10.4(8) n\Omega cm K^{-2}$ ,  $b = 1.29 \mu\Omega cm K^{-1}$ , and  $\Delta = 27(1)$  K.

Fig. 4 presents the Hall coefficient  $R_H$  for  $T = 2-100$  K for  $NpPt_2In_7$ .  $R_H$  is slightly enhanced compared to common metals (Cu:  $0.5 \times 10^{-10} m^3 C^{-1}$ ) approaching  $5.5 \times 10^{-10} m^3 C^{-1}$  at  $T_N$ , which is rather similar to values for neptunium intermetallic systems, e.g.,  $NpIr$  and  $NpCoGe$  [29, 30]. When decreasing the temperature,  $R_H$  increases slightly but collapses below  $T_N = 23$  K, saturating at low temperature at  $1.0 \times 10^{-10} m^3 C^{-1}$ . As  $R_H$  is the result of the combination of the electron and hole

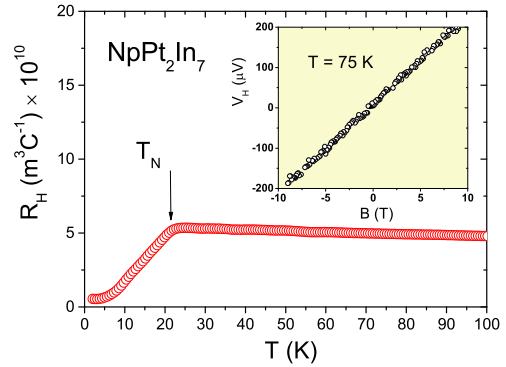


Figure 4: Temperature variation of the Hall Effect determined at 9 T from 2 to 100 K. The antiferromagnetic order is clearly visible at 23 K followed by a collapse of  $R_H$  below  $T_N$  while a small shoulder is marked around 17 K. In the paramagnetic state, Hall Effect is rising slowly when cooling down. Inset shows field dependence of  $V_H$  - Hall voltage - extracted perpendicular to the applied magnetic field on the sample at  $T = 75$  K and showing a pure linear regime and a positive variation.

contributions with different carrier velocities and relaxation times, the sign conservation in the full temperature range of  $R_H$  suggests that the nature and the mobility of the carriers are not changing drastically in the paramagnetic state with temperature and only the antiferromagnetic order is impacting hole carriers below  $T_N$ . A simple one-band model then provides an estimation of  $1.13 \times 10^{28} m^{-3}$  for the concentration of free holes in the paramagnetic state giving an upper limit for the actual carrier concentration in  $NpPt_2In_7$  converted into a rough estimate of 1.18 for the number of free holes per formula unit.

Fig. 5 presents the temperature dependence of the heat capacity ( $C_p$ ) of  $NpPt_2In_7$  corrected for the additional signal of the STYCAST and  $Pt_3In_7$ . Since the heat capacity for  $Pt_3In_7$  was not reported, we grew single crystals of  $Pt_3In_7$  and measured its  $C_p$ . At high temperature  $C_p$  saturates slightly above the expected Dulong-Petit value,  $3nR \approx 250 J mol^{-1} K^{-1}$ , where  $n = 10$  is the number of atoms per formula unit and  $R = 8.314 J mol^{-1} K^{-1}$  is the gas constant.

A clear anomaly, shown in the inset of Fig. 5, confirms a bulk character of the AFM transition with  $T_N = 23$  K in perfect agreement with magnetic susceptibility and transport results. It should be noted that the transition is very robust and the applied magnetic field only slightly suppresses the Néel temperature, i.e.  $T_N$  decreases by 0.2 K under 9 T.

We can describe heat capacity contributions at low temperature as  $C_p = C_e + C_{phonons} + C_{mag}$ , where  $C_e = \gamma T$

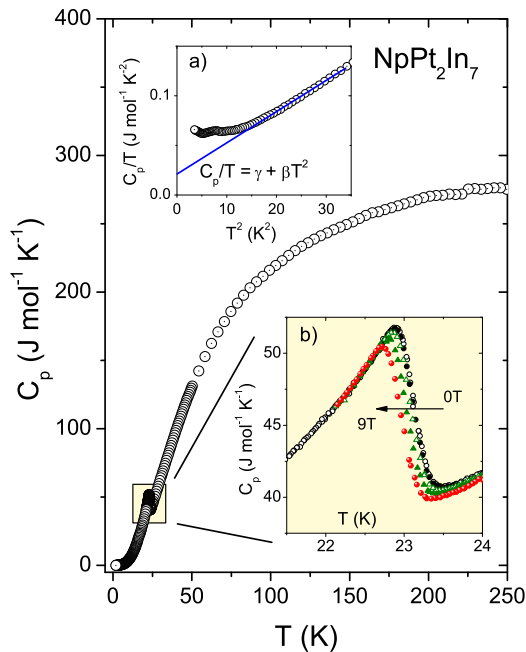


Figure 5: The specific heat versus temperature for  $\text{NpPt}_2\text{In}_7$ . Inset (a) shows the bulk antiferromagnetic transition with zero field and under applied magnetic field of  $\mu_0 H = 3$  T, 6 T and 9 T. The bottom right inset shows  $C_p/T$  vs.  $T^2$  plot with the fit  $\gamma_e + \beta T^2$  for the Sommerfeld linear coefficient determination and the Debye temperature estimation  $\Theta_D$ .

corresponds to the electronic contribution of carriers,  $C_{\text{phonons}} = \beta T^3$  lattice vibrations contribution at very low temperatures and  $C_{\text{mag}}$  takes into account antiferromagnetic interactions with the opening of a magnetic gap, following  $aT^{1/2}\exp(-\Delta/T)$  behavior [31]. Inset (a) of Fig. 5 presents the  $C_p/T$  vs.  $T^2$  behavior below 6 K. In this temperature range, typical magnetic contribution following previously quoted model of the antiferromagnetic interactions is negligible as  $\Delta$  is generally of the same order of magnitude to  $T_N = 23$  K, hence  $C_{\text{mag}}/C_p < 1\%$  - and only phonons and electronic carriers contribute significantly to heat capacity. We extract  $\gamma = 24 \text{ mJmol}^{-1}\text{K}^{-2}$  and  $\beta = 3.28 \text{ mJmol}^{-1}\text{K}^{-4}$ . Using Debye relation, we obtain an estimated Debye temperature  $\Theta_D = 181$  K, close to the 184 K reported for  $\text{CePt}_2\text{In}_7$  single crystal [32] and 189 K for polycrystal [17]. This value is also similar to the resistivity Debye temperature  $\theta_R = 150$  K from the previously presented resistivity model. The observed upturn in  $C_p/T$  seen at the lowest temperature originates from the

nuclear Schottky anomaly, which is often observed in Np compounds, e.g.  $\text{NpRh}_2\text{Sn}$  [27],  $\text{NpFeAsO}$  [24],  $\text{NpCoGa}_5$  [7].

#### 4. Electronic structure calculations

In order to theoretically analyze electronic structure and magnetic properties of  $\text{NpPt}_2\text{In}_7$ , we performed calculations in the framework of the correlated DFT+U method, an extension of the relativistic density functional theory (DFT), in which Coulomb- $U$  and exchange- $J$  are added to the correlated  $f$ -shell. We used the experimental crystal structure and a "state-of-the-art" full-potential linearized augmented plane-wave (FLAPW) basis set [33], taking into account both scalar-relativistic terms and spin-orbit coupling (SOC) implemented in the self-consistent second-variational procedure [34]. In the applied rotationally invariant implementation of the DFT+U including SOC [35, 36], all contributions to the  $f$ -manifold occupation matrix, including those nondiagonal in spin, are taken into account. The on-site Coulomb interaction in the correlated Np  $5f$  shell is given by Slater integrals  $F_0 = 3.00$  eV,  $F_2 = 7.43$  eV,  $F_4 = 4.83$  eV, and  $F_6 = 3.35$  eV [37]. They correspond to commonly accepted values of Coulomb interaction  $U = 3$  eV and exchange interaction  $J = 0.6$  eV.

As a preliminary step, we performed spin-polarized DFT calculations in a local-spin density approximation (LSDA) including SOC, setting the magnetization on the Np atoms along the  $z$ -[001] axis (out-of-plane). As shown in Table 3, this approximation does not provide a satisfactory description of the experimental data, neither assuming a ferromagnetic (FM) arrangements on the Np magnetic moments nor an antiferromagnetic (AF) one. In both cases, the spin  $\mu_S$  and orbital  $\mu_L$  magnetic moments are aligned antiparallel to each other and are close in magnitude, so that the ensuing small value of the total magnetic moment  $\mu_{\text{tot}} = \mu_S + \mu_L$  is not consistent with the experimental results.

A significant improvement on the predicted value for the total magnetic moment is obtained upon including many-body corrections by the DFT+U method. We performed these calculations using both the "around-mean-field" (AMF) and the "fully localized limit" (FLL) functionals for the double counting term, *i.e.* to subtract the correlation part from the DFT total energy. As seen from the results shown in Table 3, the DFT+U-FLL approximation fails to predict the observed AF ground state, as the calculated total energy difference between FM and AF configurations is negative ( $\Delta E =$

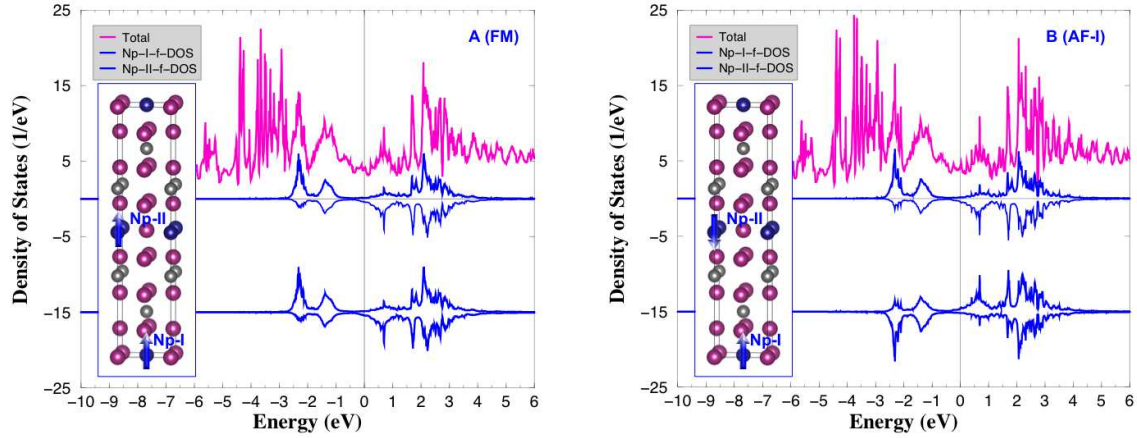


Figure 6: Total density of states (TDOS), and spin-resolved,  $f$ -projected DOS for the Np atoms in NpPt<sub>2</sub>In<sub>7</sub> (A) in the FM case, (B) in the AF-I case, as obtained from the DFT+U-AMF calculations described in the text.

Table 3: Spin ( $\mu_S$ ), orbital ( $\mu_L$ ) and total magnetic moment ( $\mu_{tot} = \mu_S + \mu_L$ ) in the units of  $\mu_B$  for Np atom from DFT+SOC and DFT+U (in FLL and AFM versions) for the FM and AF Np atom arrangements, together with the total energy difference  $\Delta E$  (in meV) between the FM and AF configurations.

	DFT+SOC		DFT+U-FLL		DFT+U-AMF	
	FM	AF	FM	AF	FM	AF
$\mu_S$	3.48	3.48	3.20	3.20	1.37	1.38
$\mu_L$	-3.16	-3.16	-5.20	-5.20	-4.19	-4.20
$\mu_{tot}$	0.32	0.32	-2.0	-2.0	-2.82	-2.82
$\Delta E$	4.2		-18.5		2.4	

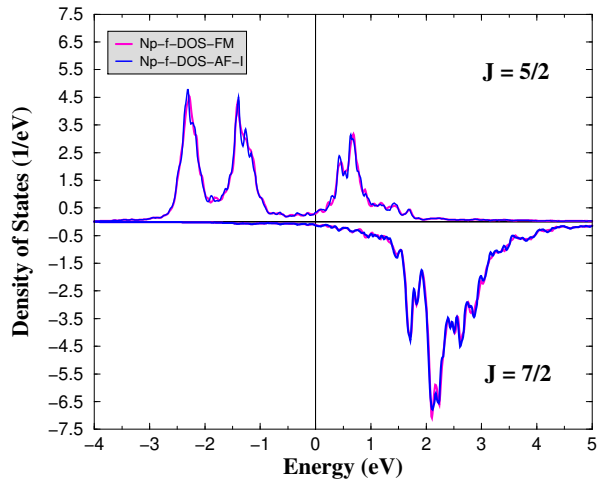


Figure 7: The  $J=5/2$  and  $J=7/2$  (shown as negative)  $f$ -projected DOS for the Np atoms in FM- and AF-I-NpPt<sub>2</sub>In<sub>7</sub>, as obtained from the DFT+U-AMF calculations.

-18.5 meV). On the contrary, in the DFT+U-AMF calculations the AF order is energetically favored, as  $\Delta E = +2.4$  meV.

The total magnetic moment obtained by DFT+U-AMF calculations is  $|\mu_{tot}| = 2.82 \mu_B$ , very close to the experimental value of the effective paramagnetic moment  $\mu_{eff} = 2.54 \pm 0.11 \mu_B$ . According to Rhodes-Wolfarth criterium [38], a ratio  $|\mu_{tot}|/\mu_{eff}$  close to one suggests a rather localized character of the  $f$ -shell magnetic moments in NpPt<sub>2</sub>In<sub>7</sub>.

The total density of states (DOS), and the Np atom spin-resolved  $f$ -projected DOS are shown in Fig. 6. The effects of electron-electron interactions are responsible for the splitting of the occupied and unoccupied Np  $f$ -states, which have indeed a fairly localized character. The Np- $f$  spin majority states are partially occupied and the spin minority ones are almost empty. The Np- $f$ -states spin splitting is fairly similar in the FM and AF-I cases (see Fig. 6). The spin-orbit splitting of the Np- $f$ -states is shown in Fig. 7, where the  $J=5/2$  and  $J=7/2$   $f$ -projected DOS are shown for both the FM and AF-I cases. Again, as in the case of spin projected DOS shown in Fig. 6, the  $J$ -projected DOS are very similar. The Fig. 7 illustrates mainly  $J=5/2$  character of the occupied  $f$ -manifold of the Np atom.

At the Fermi level, the total DOS of 4.0 1/eV per formula unit for the AF-I, and 3.94 1/eV for the FM cases are calculated. The total DOS includes the Np- $f$  (0.54 1/eV), Pt- $d$  (0.44 1/eV), and In- $p$  (0.63 1/eV) contributions for the AF-I, and the Np- $f$  (0.52 1/eV), Pt- $d$  (0.40 1/eV), and In- $p$  (0.49 1/eV) contributions for the FM cases.

The electronic specific heat coefficient  $\gamma$  can be es-

timated making use of the independent electron theory,  $\gamma = \frac{\pi^2 k_B^2}{3} N(E_F)$ , proportional to the DOS at the Fermi level,  $N(E_F)$ . This yields  $\gamma$  of 9.26 mJ K<sup>-2</sup> per mole for the FM solution, and  $\gamma$  of 9.39 mJ K<sup>-2</sup> per mole for the AF-I. The experimental Sommerfeld coefficient exceeds the theoretical estimate by a factor  $(1+\lambda)=2.56$ . The  $\lambda$  enhancement originates from the electron-phonon interaction, and the spin fluctuations.

Furthermore, we computed the crystal-field matrix  $\Delta_{CF}$  at the Np atomic site making use of the DFT+U local Green function as explained in Ref. [39]. Then we solved exactly the Anderson impurity hamiltonian [40] without hybridization, with the chemical potential given by the DFT+U  $f$ -occupation  $n_f=3.97$ , the SOC parameter  $\xi = 0.26$  eV, and the same Slater integrals as given above. We obtained the spin  $S=1.87$ , orbital  $L=5.84$ , and total  $J=4.01$  moment quantum numbers, and the Landé factor  $g_J=0.64$ . This gives the value of  $2.57 \mu_B$  for Np  $f$ -shell effective moment, in a very good agreement with the experimental effective moment of  $\mu_{eff}$ , and also supports the localized character of Np<sup>3+</sup> in NpPt<sub>2</sub>In<sub>7</sub>.

The calculated  $\Delta_{CF}$  matrix can be used to build the model crystal-field (CF) hamiltonian,

$$\hat{H}_{CF} = \sum_{kq} A_k^q \langle r^k \rangle \Theta_k(J) \hat{O}_k^q$$

where  $\hat{O}_k^q$  are the Stevens operator equivalents,  $\Theta_k(J)$  are the Stevens factors for a given ground state multiplet  $J$ , and  $A_k^q \langle r^k \rangle$ , the crystal field parameters (in standard notations) for given  $k$  and  $q$ .

The set of parameters  $A_k^q \langle r^k \rangle$  is obtained by a least-square fit of  $\Delta_{CF}$ . The calculated non-zero CF parameters [ $A_k^q \langle r^k \rangle$ ] for Np atom in NpPt<sub>2</sub>In<sub>7</sub> are shown in Table 4 in the AF-I case. Note that the CF parameters remain very similar in the FM case.

Table 4: The non-zero CF parameters [ $A_k^q \langle r^k \rangle$ ] (meV) for Np atom in NpPt<sub>2</sub>In<sub>7</sub> calculated in the AF-I case.

	$A_2^0 \langle r^2 \rangle$	$A_4^0 \langle r^4 \rangle$	$A_4^4 \langle r^4 \rangle$	$A_6^0 \langle r^6 \rangle$	$A_6^4 \langle r^6 \rangle$
CF (meV)	-28.85	-14.6	14.8	2.1	-234.1

So far, we have considered the direction of the magnetic moment along the  $z$ -[001] axis. In reality, it is determined by the magnetic anisotropy energy (MAE), and for the uniaxial crystal symmetry the MAE reads,  $E_A \approx K_1 \sin^2 \theta$ , where  $\theta$  is the angle between the magnetization and the  $z$ -[001] axis, and  $K_1$  is the first-order

anisotropy constant. An accurate total energy theoretical determination of  $K_1$  for NpPt<sub>2</sub>In<sub>7</sub> would be numerically a very demanding task. Assuming that, like in the rare-earth intermetallics, the MAE is dominated by the Np single-ion contribution, we can use the expression [41],

$$K_1 = -3J(J - \frac{1}{2})\Theta_2(J)A_2^0 \langle r^2 \rangle$$

for the semi-quantitative MAE estimate. It yields  $K_1=9.3$  meV per Np for the AF-I case, and  $K_1=9.6$  meV/Np for the FM case. The positive sign of the MAE indicates the easy axis is indeed  $z$ -[001].

A recent neutron diffraction experiment revealed a two-dimensional magnetic ordering for the isostructural CePt<sub>2</sub>In<sub>7</sub> compound [42]. Since the crystal structure of both materials is the same, it is plausible to expect some similarities in their magnetic properties and to assume that a layered magnetic superlattice appears below  $T_N$  also in the three dimensional bulk NpPt<sub>2</sub>In<sub>7</sub>. In analogy with CePt<sub>2</sub>In<sub>7</sub>, it is reasonable to assume the formation of an in-plane checkerboard AF arrangement. In a body centered tetragonal crystal structure the actual magnetic order of the AF planes along the  $z$ -[001] axis will be determined by competition of very weak interlayer interactions, as indeed suggested by the small energy difference between the FM and AF configurations (see Table 3). Also, it opens a possibility for metamagnetic transitions in the external field, which can play an important role for the occurrence of the giant magnetoresistance. We emphasize that a direct determination of the magnetic structure by neutron diffraction on a single crystal of NpPt<sub>2</sub>In<sub>7</sub> would be essential to explore this phenomenon further.

## 5. Conclusions

Our results indicate that NpPt<sub>2</sub>In<sub>7</sub> is a metallic antiferromagnet with a prevalently localized character of the Np magnetic moment, similarly to NpGoGa<sub>5</sub> [8]. The compound orders magnetically at  $T_N = 23$  K, which was confirmed by all performed experiments. From the magnetic susceptibility measurements, we estimated the Curie–Weiss temperature  $\theta_{CW} = -17 \pm 9$  K and the effective magnetic moment in the paramagnetic phase as  $\mu_{eff} = 2.54 \pm 0.11 \mu_B$ , which is close to the value calculated for trivalent neptunium in intermediate coupling scheme. Finally, we presented the results of a theoretical investigation of the compound, by means of correlated band theory DFT+U method. The calculations show very weak anti-ferromagnetic interlayer coupling between different Np-layers along the

z-[001] axis, and suggest localized magnetic moments and a positive uniaxial anisotropy. We propose that the actual magnetic structure shows an in-plane checkerboard AF arrangement. We notice that in presence of local moments in a quasi-two-dimensional antiferromagnetic structure a positive and large magnetoresistance could emerge if the external magnetic field promotes the formation of short-range antiferromagnetically correlated regions embedded in a field-induced ferromagnetic background. This has recently been predicted to occur in double perovskite systems [43] and observed in half-metallic double-perovskite  $\text{Sr}_2\text{CrWO}_6$  thin films[44].  $\text{NpPt}_2\text{In}_7$  could be a physical realization of such an uncommon phenomenon and we plan to investigate it once a single crystal specimen will become available.

## 6. Acknowledgments

This work has been performed at the at the Joint Research Centre within its Actinide User Laboratory program, with financial support to users provided by the European Commission. The Np metal required for the fabrication of the compound was made available through a loan agreement between Lawrence Livermore National Laboratory and the Joint Research Centre in the framework of a collaboration involving Lawrence Livermore National Laboratory, Los Alamos National Laboratory, and the US Department of Energy. This work was supported by the National Science Centre (Poland) grant No. DEC-2015/17/N/ST3/03790, by Operational Programme Research, Development and Education financed by European Structural and Investment Funds and the Czech Ministry of Education, Youth and Sports (Project No. SOLID21 - CZ.02.1.01/0.0/0.0/16-019/0000760), and by the Czech Science Foundation (GACR) grant No. 18-06240S. A.K. acknowledge the TASK Academic Computer Centre (Gdansk, Poland). Access to computing and storage facilities of the National Grid Infrastructure MetaCentrum provided under the programme "Projects of Projects of Large Research, Development, and Innovations Infrastructures" (CES-NET LM2015042), is acknowledged.

## References

- [1] C. Petrovic, P. G. Pagliuso, M. F. Hundley, R. Movshovich, J. L. Sarrao, J. D. Thompson, Z. Fisk, P. Monthoux, Heavy-fermion superconductivity in  $\text{CeCoIn}_5$  at 2.3 k, *Journal of Physics: Condensed Matter* 13 (17) (2001) L337.
- [2] C. Petrovic, R. Movshovich, M. Jaime, P. G. Pagliuso, M. F. Hundley, J. L. Sarrao, Z. Fisk, J. D. Thompson, A new heavy-fermion superconductor  $\text{CeIrIn}_5$ : A relative of the cuprates?, *EPL (Europhysics Letters)* 53 (3) (2001) 354.
- [3] H. Hegger, C. Petrovic, E. G. Moshopoulou, M. F. Hundley, J. L. Sarrao, Z. Fisk, J. D. Thompson, Pressure-induced superconductivity in quasi-2d  $\text{CeRhIn}_5$ , *Phys. Rev. Lett.* 84 (2000) 4986–4989. doi:10.1103/PhysRevLett.84.4986.
- [4] D. Kaczorowski, A. P. Pikul, D. Gnida, V. H. Tran, Emergence of a superconducting state from an antiferromagnetic phase in single crystals of the heavy fermion compound  $\text{Ce}_2\text{PdIn}_8$ , *Phys. Rev. Lett.* 103 (2009) 027003. doi:10.1103/PhysRevLett.103.027003.
- [5] M. Kratochvilova, M. Dusek, K. Uhlirova, A. Rudajevova, J. Prokleska, B. Vondrackova, J. Custers, V. Sechovsky, Single crystal study of the layered heavy fermion compounds  $\text{Ce}_2\text{PdIn}_8$ ,  $\text{Ce}_3\text{PdIn}_{11}$ ,  $\text{Ce}_2\text{PtIn}_8$  and  $\text{Ce}_3\text{PtIn}_{11}$ , *Journal of Crystal Growth* 397 (2014) 47 – 52. doi:http://dx.doi.org/10.1016/j.jcrysgro.2014.04.008.
- [6] E. D. Bauer, M. M. Altarawneh, P. H. Tobash, K. Gofryk, O. E. Ayala-Valenzuela, J. N. Mitchell, R. D. McDonald, C. H. Mielke, F. Ronning, J.-C. Griveau, E. Colineau, R. Eloirdi, R. Caciuffo, B. L. Scott, O. Janka, S. M. Kauzlarich, J. D. Thompson, *J. Phys. Condens. Matter* 24 (2012) 052206.
- [7] E. Colineau, P. Javorský, P. Boulet, F. Wastin, J. C. Griveau, J. Rebizant, J. P. Sanchez, G. R. Stewart, Magnetic and electronic properties of the antiferromagnet  $\text{NpCoGa}_5$ , *Phys. Rev. B* 69 (2004) 184411. doi:10.1103/PhysRevB.69.184411.
- [8] N. Magnani, A. Hiess, R. Caciuffo, E. Colineau, F. Wastin, J. Rebizant, G. H. Lander, Magnetic excitations in  $\text{NpCoGa}_5$ : Inelastic neutron scattering experiments, *Phys. Rev. B* 76 (2007) 100404.
- [9] B. Detlefs, S. B. Wilkins, R. Caciuffo, J. A. Paixão, K. Kaneko, F. Honda, N. Metoki, N. Bernhoeft, J. Rebizant, G. H. Lander, Resonant x-ray scattering study of  $\text{NpRhGa}_5$  and  $\text{NpCoGa}_5$ , *Phys. Rev. B* 77 (2008) 024425.
- [10] D. Aoki, Y. Haga, Y. Homma, Y. Shiokawa, E. Yamamoto, A. Nakamura, R. Settai, Y. Ōnuki, Magnetic properties and heavy electronic states in the antiferromagnet  $\text{NpPtGa}_5$ , *Journal of the Physical Society of Japan* 75 (11) (2006) 114715. doi:10.1143/JPSJ.75.114715.
- [11] D. Aoki, Y. Haga, T. D. Matsuda, N. Tateiwa, S. Ikeda, Y. Homma, H. Sakai, Y. Shiokawa, E. Yamamoto, A. Nakamura, R. Settai, Y. Ōnuki, Unconventional heavy-fermion superconductivity of a new transuranium compound  $\text{NpPd}_5\text{Al}_2$ , *Journal of the Physical Society of Japan* 76 (6) (2007) 063701. doi:10.1143/JPSJ.76.063701.
- [12] H. Chudo, H. Sakai, Y. Tokunaga, S. Kambe, D. Aoki, Y. Homma, Y. Shiokawa, Y. Haga, S. Ikeda, T. D. Matsuda, Y. Ōnuki, H. Yasuoka,  $^{27}\text{Al}$  NMR evidence for the strong-coupling d-wave superconductivity in  $\text{NpPd}_5\text{Al}_2$ , *Journal of the Physical Society of Japan* 77 (8) (2008) 083702. doi:10.1143/JPSJ.77.083702.
- [13] K. Gofryk, J.-C. Griveau, E. Colineau, J. P. Sanchez, J. Rebizant, R. Caciuffo, Kondo behavior in superconducting  $\text{NpPd}_5\text{Al}_2$ , *Phys. Rev. B* 79 (2009) 134525. doi:10.1103/PhysRevB.79.134525.
- [14] G. A. Ummarino, R. Caciuffo, H. Chudo, S. Kambe, Energy scale of the electron-boson spectral function and superconductivity in  $\text{NpPd}_5\text{Al}_2$ , *Phys. Rev. B* 82 (2010) 104510.
- [15] D. Damien, C. de Novion, J. Gal, Superconductivity in the neptunium chevrel phase  $\text{Np}_{1+x}\text{Mo}_6\text{Se}_8$ , *Solid State Communications* 38 (5) (1981) 437 – 440. doi:http://dx.doi.org/10.1016/0038-1098(81)90274-X.
- [16] T. Klimczuk, O. Walter, L. Muehler, J. W. Krizan, F. Kinart, R. J. Cava, Crystal structure and electronic structure of  $\text{CePt}_2\text{In}_7$ , *Journal of Physics: Condensed Matter* 26 (40) (2014) 402201.
- [17] E. D. Bauer, H. O. Lee, V. A. Sidorov, N. Kurita, K. Gofryk,



- J.-X. Zhu, F. Ronning, R. Movshovich, J. D. Thompson, T. Park, Pressure-induced superconducting state and effective mass enhancement near the antiferromagnetic quantum critical point of CePt<sub>2</sub>In<sub>7</sub>, *Phys. Rev. B* 81 (2010) 180507. doi:10.1103/PhysRevB.81.180507.
- [18] H. B. Rhee, F. Ronning, J.-X. Zhu, E. D. Bauer, J. N. Mitchell, P. H. Tobash, B. L. Scott, J. D. Thompson, Y. Jiang, C. H. Booth, W. E. Pickett, PuPt<sub>2</sub>In<sub>7</sub>: A computational and experimental investigation, *Phys. Rev. B* 86 (2012) 115137. doi:10.1103/PhysRevB.86.115137.
- [19] J. Rodriguez-Carvajal, FULLPROF: A program for Rietveld refinement and pattern matching analysis, in: Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr, Toulouse, France, 1990, p. 127.
- [20] E. G. Moshopoulou, R. M. Ibberson, J. L. Sarrao, J. D. Thompson, Z. Fisk, Structure of Ce<sub>2</sub>RhIn<sub>8</sub>: an example of complementary use of high-resolution neutron powder diffraction and reciprocal-space mapping to study complex materials, *Acta Crystallographica Section B* 62 (2) (2006) 173–189. doi:10.1107/S0108768106003314. URL <https://doi.org/10.1107/S0108768106003314>
- [21] J. Gal, I. Yaar, S. Fredo, I. Halevy, W. Potzel, S. Zwirner, G. M. Kalvius, Magnetic and electronic properties of cubic npx<sub>3</sub> intermetallics, *Phys. Rev. B* 46 (1992) 5351–5356. doi:10.1103/PhysRevB.46.5351.
- [22] F. Ellinger, C. Land, K. Johnson, The plutonium-indium system, *Transactions of the metallurgical society of AIME*.
- [23] P. Dutta, M. S. Seehra, S. Thota, J. Kumar, A comparative study of the magnetic properties of bulk and nanocrystalline Co<sub>3</sub>O<sub>4</sub>, *Journal of Physics: Condensed Matter* 20 (1) (2008) 015218.
- [24] T. Klimczuk, H. C. Walker, R. Springell, A. B. Shick, A. H. Hill, P. Gaczyński, K. Gofryk, S. A. J. Kimber, C. Ritter, E. Colineau, J.-C. Griveau, D. Bouëxière, R. Eloirdi, R. J. Cava, R. Caciuffo, Negative thermal expansion and antiferromagnetism in the actinide oxypnictide NpFeAsO, *Phys. Rev. B* 85 (2012) 174506. doi:10.1103/PhysRevB.85.174506.
- [25] N. H. , K. Takenaka, H. Takagi, Universality of the mottiof-ferregel limit in metals, *Philosophical Magazine* 84 (27) (2004) 2847–2864. doi:10.1080/14786430410001716944.
- [26] A. F. Ioffe, A. R. Regel, Non-crystalline, amorphous, and liquid electronic semiconductors, *Prog. Semicond.* 4 (1960) 237–291.
- [27] T. Klimczuk, J.-C. Griveau, P. Gaczyński, R. Eloirdi, E. Colineau, R. Caciuffo, Crystal structure and physical properties of nprh 2 sn, a new np-based ternary compound, *Journal of Physics: Conference Series* 273 (1) (2011) 012024.
- [28] N. H. Andersen, Electrical resistivity investigations on metallic rare-earths, in: J. E. Crow, R. P. Guertin, T. W. Mihalisin (Eds.), *Crystalline Electric Field and Structural Effects in f-Electron Systems*, Springer US, 1980, pp. 373–387.
- [29] H. C. Walker, K. A. McEwen, J.-C. Griveau, R. Eloirdi, P. Amador, P. Maldonado, P. M. Oppeneer, E. Colineau, Magnetic, electrical, and thermodynamic properties of npir: Ambient and high-pressure measurements, and electronic structure calculations, *Phys. Rev. B* 91 (2015) 195146. doi:10.1103/PhysRevB.91.195146.
- [30] E. Colineau, J.-C. Griveau, R. Eloirdi, P. Gaczyński, S. Khmelevskyi, A. B. Shick, R. Caciuffo, Antiferromagnetic ground state in npcoge, *Phys. Rev. B* 89 (2014) 115135. doi:10.1103/PhysRevB.89.115135.
- [31] N. H. Andersen, H. Smith, Electron-magnon interaction and the electrical resistivity of tb, *Phys. Rev. B* 19 (1979) 384–387. doi:10.1103/PhysRevB.19.384.
- [32] P. H. Tobash, F. Ronning, J. D. Thompson, B. L. Scott, P. J. W. Moll, B. Batlogg, E. D. Bauer, Single crystal study of the heavy-fermion antiferromagnet CePt<sub>2</sub>In<sub>7</sub>, *Journal of Physics: Condensed Matter* 24 (1) (2012) 015601.
- [33] E. Wimmer, H. Krakauer, M. Weinert, A. J. Freeman, Full-potential self-consistent linearized-augmented-plane-wave method for calculating the electronic structure of molecules and surfaces: O<sub>2</sub> molecule, *Phys. Rev. B.* 24 (1981) 864. doi:10.1103/PhysRevB.24.864.
- [34] A. B. Shick, D. L. Novikov, A. J. Freeman, Relativistic spin-polarized theory of magnetoelastic coupling and magnetic anisotropy strain dependence: Application to Co/Cu(001), *Phys. Rev. B* 56 (1997) R14259–R14262.
- [35] A. B. Shick, W. E. Pickett, Magnetism, spin-orbit coupling, and superconducting pairing in UGe<sub>2</sub>, *Phys. Rev. Lett.* 86 (2001) 300–303.
- [36] A. B. Shick, V. Drchal, L. Havela, *Europhys. Lett* 69 (2005) 588.
- [37] K. T. Moore, G. van der Laan, Nature of the 5f states in actinide metals, *Rev. Mod. Phys.* 81 (2009) 235–298.
- [38] Y. Izymov, M. Katsnelson, Y. Skryabin, Itinerant electron magnetism, Moscow, "Nauka" (in Russian), 1993.
- [39] A. Shick, D. Shapiro, J. Kolorenč, A. Lichtenstein, *Scientific Reports* 7 (2017) 2752.
- [40] A. Hewson, *The Kondo Problem to Heavy Fermions*, Cambridge University Press, 1993.
- [41] M. Richter, P. M. Oppeneer, H. Eschrig, B. Johansson, *Phys. Rev. B* 46 (1992) 13919.
- [42] M. Raba, E. Ressouche, N. Qureshi, C. V. Colin, V. Nassif, S. Ota, Y. Hirose, R. Settai, P. Rodière, I. Sheikin, Determination of the magnetic structure of cept<sub>2</sub>in<sub>7</sub> by means of neutron diffraction, *Phys. Rev. B* 95 (2017) 161102. doi:10.1103/PhysRevB.95.161102.
- [43] V. N. Singh, P. Majumdar, *J. Phys. Condens. Matter* 26 (2014) 296001.
- [44] J. Zhang, W.-J. Ji, J. Xu, X.-Y. Geng, J. Zhou, Z.-B. Gu, S.-H. Yao, S.-T. Zhang, Giant positive magnetoresistance in half-metallic double-perovskite sr2crw6 thin films, *Science Advances* 3 (2017) e1701473.