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Magnetic sublattices in Np_2Co_{17} and Np_2Ni_{17}

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Abstract Rare-earth-based compounds R_2T_{17} (R=Rare earth; T=Transition metal) have been extensively studied and developed for applications as permanent magnets. The actinide-based analogues, however, are much less documented and we report here about the magnetic properties of Np_2Co_{17} and Np_2Ni_{17}, as inferred from ^{237}Np Mössbauer spectroscopy, the best resonance in actinides, and specific heat.

Keywords Mössbauer spectroscopy · Neptunium · Actinides · Magnetism

1 Introduction

Among the large family of rare earth intermetallics, the R_2T_{17} (R=Rare earth; T=Transition metal) series has been particularly studied and developed for applications as permanent

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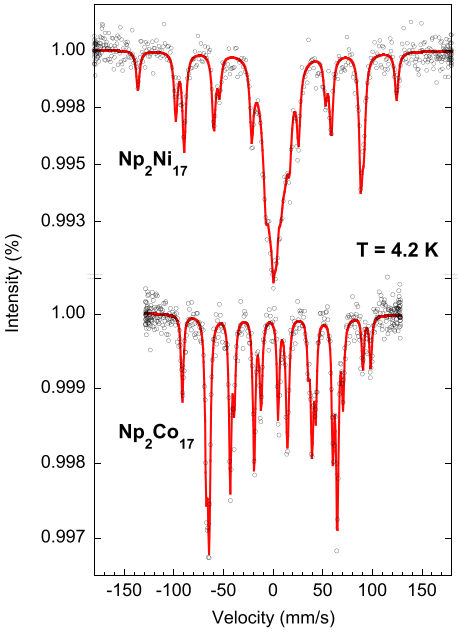

Fig. 1 ^{237}Np Mössbauer spectra recorded at T = 4.2 K for Np_2Ni_{17} and Np_2Co_{17}. The *circles* represent the experimental points and the *line* the fit assuming two distinct Np crystallographic sites

magnets [1]. It is interesting to extend these studies to actinide analogues, with their wider f-electrons wavefunctions, to enhance exchange interactions and tune the magnetic properties. Neptunium, with usually the $5f^4$ electronic configuration in intermetallic compounds, is a good candidate as, furthermore, ^{237}Np Mössbauer spectroscopy is the best resonance in actinides and allows to observe well-resolved hyperfine interactions [2].

We have recently synthesized Np_2Co_{17} [3, 4] and Np_2Ni_{17} [5], finding that they both crystallize in the Th_2Ni_{17}-type hexagonal structure ($P6_3/mmc$ space group), a structure with two non-equivalent crystallographic Np sites. Furthermore, we have studied their electronic and magnetic properties using an array of experimental and theoretical techniques. Magnetization, specific heat, XMCD and Mössbauer spectroscopy have shown that both compounds order magnetically, however with substantial differences: Np_2Co_{17} is a ferromagnet with a Curie temperature above room temperature [4], whereas Np_2Ni_{17} is a ferrimagnet with an ordering temperature of 17.5 K and a large ordered magnetic moment on just one of the two distinct crystallographic Np sites whereas the other Np site exhibits only a small induced magnetic moment [5]. In addition to the neptunium sublattices, the cobalt and nickel atoms also carry magnetic moments. ^{237}Np Mössbauer spectroscopy appears therefore extremely useful here to determine the microscopic ordered moments carried by neptunium ions and compare them with the macroscopic moments observed by other techniques. We focus in this paper on the Mössbauer results obtained for Np_2Co_{17} and Np_2Ni_{17}, the information gained about the magnetic sublattices and discuss the magnetic properties in comparison with rare earth and uranium analogues. We also show specific heat data to gain additional information about magnetic, electronic and phonon properties of both compounds.

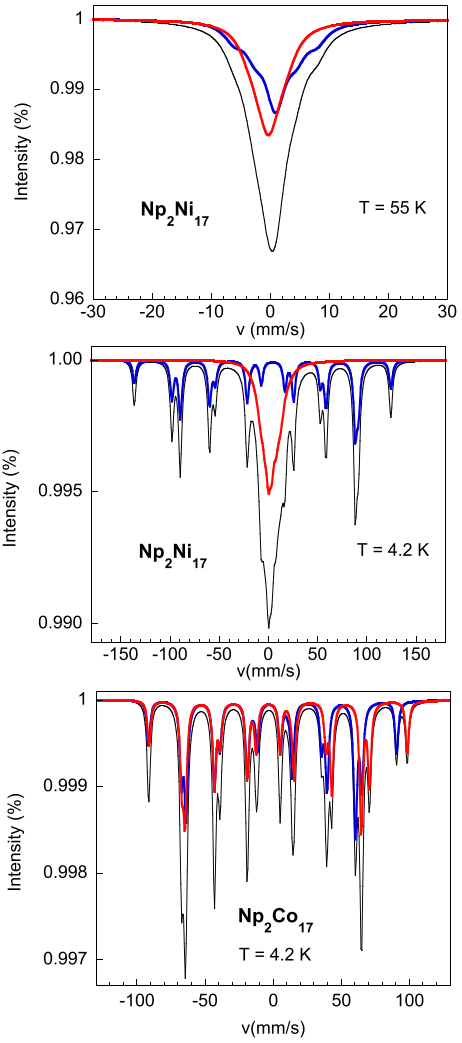

Fig. 2 Fits of the ^{237}Np Mössbauer spectra (not shown for clarity) recorded at T = 55K and T = 4.2 K for Np_2Ni_{17} and Np_2Co_{17} at T = 4.2K. The *bold lines* (*blue* and *red*) represent the two subspectra corresponding to the two 2b and 2d neptunium sites, respectively. The *thin line* (*black*) represents the resulting total fit (sum of the two subspectra)

2 Experimental

Due to the contamination risk generated by the radiotoxicity of the neptunium element, all operations of preparation and encapsulation have been carried out in shielded gloveboxes under inert nitrogen atmosphere following well-established safety procedures. The ^{237}Np Mössbauer spectra were recorded in a transmission-geometry spectrometer using the sinusoidal drive motion of a ∼100 mCi ^{241}Am metal source kept at a constant temperature of 4.2 K. The absorbers were prepared by grinding the samples to a fine powder to ensure a constant surface density with an optimal thickness of ∼140 mg of Np per square centimeter. A liquid-helium cryostat was used to vary the samples temperature. The velocity scale of the spectrometer was calibrated with reference to a $NpAl_2$ sample (B_{hf} = 330 T at 4.2

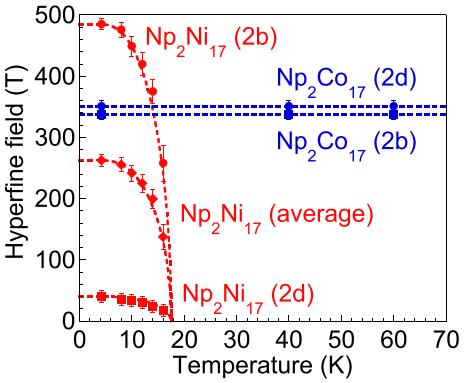

Fig. 3 Temperature dependence of the hyperfine magnetic fields (*symbols*), carried by the two non-equivalent Np sites, in Np_2Ni_{17} (*red*) and Np_2Co_{17} (*blue*), along with their corresponding Brillouin functions (*dotted lines*) for J=1/2

K). The crystallographic characterization and general physical properties of Np_2Co_{17} and Np_2Ni_{17} can be consulted in previous reports [3–5].

3 Results and discussion

The ^{237}Np Mössbauer spectra recorded at 4.2 K reveal complex patterns split by magnetic hyperfine interactions, indicating the occurrence of magnetic ordering in both compounds (Fig. 1). Two distinct magnetic sites are required to correctly reproduce the spectra: this can be immediately seen by the observation of a double external peak around 90 mm/s in Np_2Co_{17} and by the presence of a large weak-field component in Np_2Ni_{17} (central, unresolved peak). The detail of each subspectrum is shown in Fig. 2. It is obvious that the two sites in Np_2Co_{17} have hyperfine fields with relatively close values, namely $B_{hf} = 338$ T and $B_{hf} = 351$ T (here the magnetic exchange dominates the crystal field interaction), whereas in Np_2Ni_{17}, we observe the coexistence of a large-field ($B_{hf} = 483$ T) and a weak-field ($B_{hf} = 40$ T). The ordered moments carried by neptunium were deduced using the simple relation $B_{hf}/\mu_{Np} = 215$ T/μ_B [2].

These results are consistent with the trend observed in the rare earth analogues [6], however the one order of magnitude reduction of the magnetic moment on the (2d) site in Np_2Ni_{17} is uncommon and could be explained by a crystal field-exchange model where a non-magnetic singlet on the 2d site carries just an induced moment due to a small exchange field. Indeed, for an exchange field of 21 T oriented along the c-axis, one obtains $\mu_{Np}(2d) = 0.19\ \mu_B$ and $\mu_{Np}(2b) = 2.21\ \mu_B$, in agreement with experiment [5].

When temperature is increased, the magnetic moments in Np_2Ni_{17} rapidly decrease down to zero at $T_N = 17.5$ K, following a Brillouin function with an effective J = 1/2 (Fig. 3). It is worth mentioning that the moments of both sites decrease at the same rate, indicating that the same molecular field acts on both sites. Magnetic moments carried by neptunium in Np_2Co_{17} do not decrease significantly in the temperature range covered by Mössbauer spectroscopy (The Lamb-Mössbauer factor decreases rapidly with increasing temperature, due to the large energy (60 keV) of the Mössbauer transition used in ^{237}Np). However, as for this compound the saturated magnetic moment was measured by magnetization [4], using the values of the Np ordered moment inferred from Mössbauer spectroscopy it is possible to estimate the average contribution from the cobalt atoms (Fig. 4). Light rare earths moments couple ferromagnetically with cobalt moments in R2Co17, whereas the coupling is antiferromagnetic for heavy rare earths [1]. Depending on the sign of Np-Co

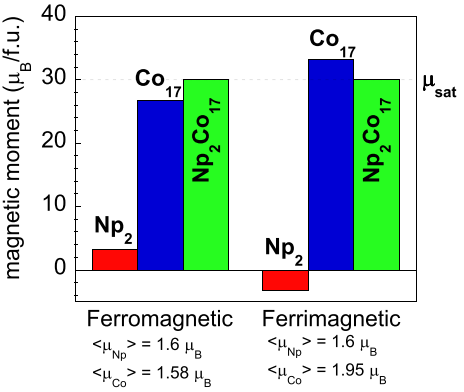

Fig. 4 Contributions from neptunium (*red*) and cobalt (*blue*) sublattices to the saturated magnetic moment per formula unit of Np_2Co_{17} (*green*), for ferromagnetic and ferrimagnetic (antiferromagnetic coupling of Np and Co) structures. First principles calculations provide an average ordered moment of 1.56 μ_B per Co ion, and indicate that the magnetic moments on the two sublattices are oriented parallel to each other

Table 1 Main ^{237}Np Mössbauer parameters obtained for Np_2Ni_{17} and Np_2Co_{17}

Compound	T (K)	Site	δ_{IS} (mm/s)	e^2 qQ (mm/s)	B_{hf}	μ_{Np} (μ_B)	W (mm/s)
Np_2Ni_{17}	4.2	(2b)	−12.5(6)	+17.6(3)	483(1)	2.25(4)	4.1(1)
		(2d)	−14.2(6)	−2.0(5)	40(2)	0.19(5)	4.1(1)
	55	(2b)	−12.8(5)	23.5(1)	0	0	4.1(1)
		(2d)	−14.0(5)	11.3(1)	0	0	4.1(1)
Np_2Co_{17}	4.2	(2b)	−15.4(2)	−4.5(3)	338(1)	1.57(4)	2.9(1)
		(2d)	−13.7(2)	−12.2(3)	351(1)	1.63(4)	2.9(1)

δ_{IS} is given versus the standard absorber $NpAl_2$

coupling in Np_2Co_{17}, the moment carried by cobalt is estimated to 1.58 or 1.95 μ_B per atom. The smaller value, corresponding to a ferromagnetic Np-Co coupling, compares well with the values observed in rare earths analogues (see for example [7]).

Very few studies of these systems exist in actinides, but a comparison can be done with the $U_2Co_{17-x}Si_x$ system [8], which also orders ferromagnetically well above room temperature. Contrarily to Np_2Co_{17}, in $U_2Co_{17-x}Si_x$, magnetization curves was measured up to 900 K and the Curie temperature was determined. The extrapolation to x=0 suggest a Curie temperature T_C ∼1000 K and a saturated magnetization M_S ∼26 μ_B/ f.u. for U_2Co_{17}. In this case, the respective contributions from U and Co could not be determined, but the global value compares well with Np_2Co_{17} (M_S ∼30 μ_B/ f.u.) and would suggest a smaller moment carried by uranium compared to neptunium, if one assumes similar contributions from the cobalt sublattice.

The Mössbauer spectrum of Np_2Ni_{17} in the paramagnetic state confirms the presence of two inequivalent Np sites, in agreement with the crystallographic structure (Fig. 2). The paramagnetic state of Np_2Co_{17} is out of the experimental temperature range for ^{237}Np Mössbauer spectroscopy. The main fitted Mössbauer parameters are listed in Table 1. The values of the isomer shifts in both compounds suggest that neptunium ions are in the trivalent state (electronic configuration $5f^4$).

Figure 5 shows the specific heat of Np_2Ni_{17} and Np_2Co_{17}, close to the Dulong-Petit value at room temperature. Both curves can be approximated by a simple Debye law plus an electronic term, that provides an estimate of the Debye temperature and Sommerfeld coefficient (Table 2).

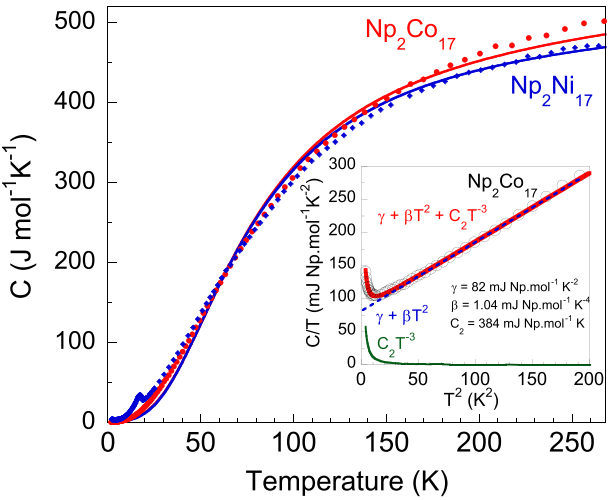

Fig. 5 Specific heat of Np_2Co_{17} (*red circles*) and Np_2Co_{17} (*blue diamonds*). The curves can be roughly reproduced (*red* and *blue lines*, respectively) by a simple Debye law, plus an electronic term ($\sim \gamma$ T) that provides an estimation of the Debye temperature and Sommerfeld coefficient. At room temperature, C(T) reaches closely the Dulong-Petit value. Inset: Specific heat of Np_2Co_{17} at low temperature. C(T)/T can be fully described by an electronic (γ), a phononic (βT^2) and a nuclear (C_2T^{-3}) contribution. γ is the Sommerfeld coefficient. The Debye temperature can be estimated to $\theta_D \approx 260$ K from the β value through the relation $\theta_D = (12\pi^4 nR/5\beta)^{1/3}$ where R is the molar gas constant and n the number of atoms in the formula unit (here half of the formula unit since we expressed the specific heat per mole of neptunium). The nuclear term is evaluated from the value of the hyperfine field

Table 2 Debye temperature (θ_D) and Sommerfeld coefficient (γ) estimated from the specific heat (C), at low temperature (LT) and for the full temperature range (FTR), for Np_2Ni_{17} and Np_2Co_{17}

Compound	γ (mJ / Np.mol.K^2)		θ_D (K)		
	C (LT)	C (FTR)	C (LT)	C (FTR)	Mössbauer
Np_2Ni_{17}	126	48	182	309	236
Np_2Co_{17}	82	79	260	313	-

The Debye value inferred from Mössbauer for Np_2Ni_{17} is also given

At low temperature (inset), we notice for Np_2Co_{17} a sudden increase of C(T) when the temperature decreases below $\sim$ 5 K, which attributed to a nuclear Schottky term due to the splitting of the I = 5/2 nuclear ground level of the ^{237}Np nuclei by the hyperfine field: $C_N = C_2/T^2$, with $C_2 = (R/3)\ (\mu\ B_{hf}/\ k_B I)^2\ I\ (I+1) = 384$ mJ Np.mol^{-1} K, using the average value $B_{hf} = 344$ T inferred from Mössbauer spectroscopy. A similar behaviour has been reported for Np_2Ni_{17} [5] and a number of other neptunium systems (see for example [9–12]). The linear part of the $C(T)/T = f(T^2)$ plot (inset of Fig. 5) is reproduced assuming electronic (γ) and phonon (βT^2) contributions, which allow to estimate again the Sommerfeld coefficient and the Debye temperature (see Table 2). Note that the magnetic contribution for a ferro- or ferri-magnet is expected to vary as $C(T)/T \sim \sqrt{T}$, which was found to be negligible in the temperature range used here. Indeed, both low-temperature

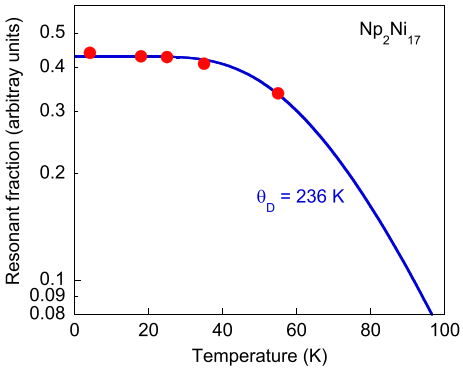

Fig. 6 Temperature dependence of the resonant fraction for Np_2Ni_{17}. Red *circles* represent experimental values whereas the *blue line* is a fit of the Lamb-Mössbauer fraction in the Debye model and yields a Debye temperature $\theta_D \approx 236$ K

and full temperature range estimates of the Sommerfeld coefficient and Debye temperature of Np_2Co_{17} agree relatively well (see Table 2). This is not the case for Np_2Ni_{17}, where the magnetic and Schottky anomalies [5] hamper the low temperature estimates of γ and θ_D that should therefore be taken with care.

Finally, despite a limited range of temperature in Mössbauer experiments, the thermal dependence of the resonant fraction in Np_2Ni_{17} can also provide an estimate of the Debye temperature: $\theta_D \approx 236$ K (Fig. 6). This value is consistent with the values estimated from specific heat data, average between the low-temperature estimate and the full temperature range estimate (see table 2).

4 Summary

The magnetic moments of the two neptunium sublattices in Np_2Co_{17} and Np_2Ni_{17} have been measured by ^{237}Np Mössbauer spectroscopy. The two Np sites in Np_2Co_{17} carry similar magnetic moments. As Np_2Co_{17} orders at high temperature, the temperature dependence of the magnetic moments could not be followed, but the ordered moments carried by cobalt atoms have been estimated by comparison with the macroscopic magnetization. On the contrary, only one Np site carries a large ordered moment in Np_2Ni_{17}, whereas the other site displays only a weak moment induced by the molecular field. The temperature dependence of the magnetic moment follows a Brillouin function with J = 1/2, as expected for a molecular field mainly associated with the Ni sublattice. The moment carried by nickel atoms could not be estimated since the macroscopic magnetization does not saturate. The hyperfine magnetic field inferred from Mössbauer spectroscopy was used to account for the low-temperature upturn of the specific heat in Np_2Co_{17}. The Debye temperature of Np_2Ni_{17} was estimated by the combination of Mössbauer spectroscopy and specific heat measurements.

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