

## Structure and magnetism of $R_2T_2X$ compounds and their hydrides; comparison of lanthanides and actinides

Ladislav HAVELA<sup>1\*</sup>, Silvie MAŠKOVÁ<sup>1</sup>, Pavel SVOBODA<sup>1</sup>, Khrystyna MILIYANCHUK<sup>2</sup>, Alexandre KOLOMIETS<sup>1,3</sup>, Alexander V. ANDREEV<sup>4</sup>

<sup>1</sup> Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, 121 16 Prague 2, Czech Republic

<sup>2</sup> Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine

<sup>3</sup> Department of Physics, Lviv Polytechnic National University, Bandera St. 12, 79013 Lviv, Ukraine

<sup>4</sup> Institute of Physics, ASCR, Na Slovance 2, 18221 Prague 8, Czech Republic

\* Corresponding author. E-mail: havela@mag.mff.cuni.cz

Received September 25, 2013; accepted December 25, 2013; available on-line August 30, 2014

The group of “221” compounds crystallizing in the  $\text{Mo}_2\text{FeB}_2$  structure type comprises more than 400 members known so far. The onset of magnetic moments and their ordering can be studied in the actinide representatives by tuning the  $5f$ -ligand hybridization strength, including detailed investigations of the non-Fermi liquid regime. The mechanism of specific two-ion anisotropy, depending exclusively on the positions of the nearest-neighbor U atoms, can be tested due to the variety of coordinations observed within a single structure type. Possible dimerization of the magnetic structures, representing a practical realization of a Shastry-Sutherland lattice, has been the motivation for several studies of rare-earth based materials, and can be a reason for the tendency to magnetic frustration. Hydrogen absorption, being an additional degree of freedom for tuning the physical properties, was found to be limited to 2 H atoms per f.u. in U-based materials. The strengthening of U magnetism may be attributed to predominant volume expansion and consequent  $5f$ -band narrowing. In several rare-earth based compounds much higher H absorption has been observed (the limit seems to be 8 H/f.u.). The structure reacts either by distortion or amorphization in such cases. H absorption leads to weakening of the magnetic interactions, probably related to the reduced concentration of conduction electrons.

### Hydrides / Intermetallic compounds / Lanthanides / Actinides / Magnetic properties

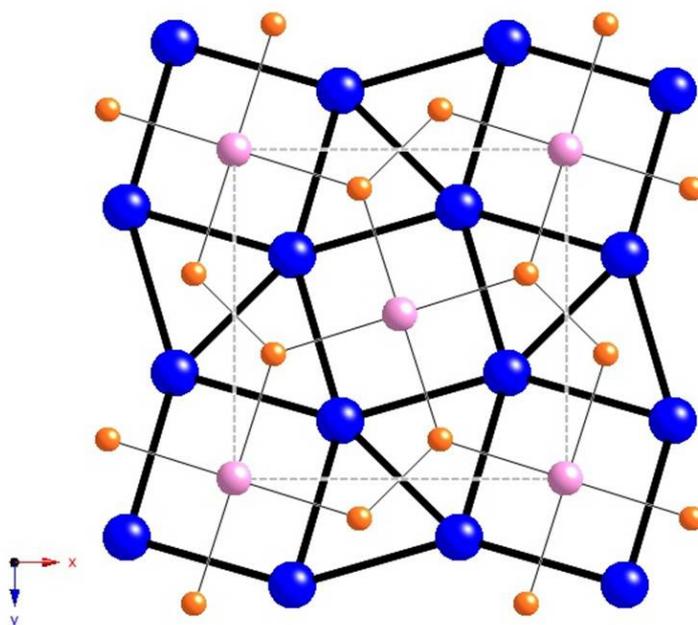
#### Introduction

The striking difference between the electronic properties of  $4f$  and  $5f$  systems becomes most clearly apparent when comparing isostructural compounds. There exist large families of intermetallics comprising lanthanides or actinides that crystallize in the same structure type and even have the same types of ligands. One of the largest ones is the family of  $R_2T_2X$  compounds, where  $R$  represents an actinide or lanthanide metal,  $T$  is a  $d$ -metal and  $X$  stands for a  $p$ -element. Here we concentrate on compounds that crystallize in the tetragonal structure of the  $\text{Mo}_2\text{FeB}_2$  type (space group  $P4/mbm$ ). In this structure type, each  $f$ -atom has three types of  $R$  neighbor. One type (two neighbors) is along the  $c$ -axis, the other types are in the basal plane, which is occupied by the  $f$ -atoms alone. There each  $f$ -atom has one neighbor within a

dimer and four others at slightly longer distances. This arrangement corresponds to a so called Shastry-Sutherland lattice [1], yielding magnetic frustration for some combinations of the effective inter-site exchange parameters  $J_1$  and  $J_2$  (see Fig. 1).

Although the first of the isotopic uranium compounds,  $\text{U}_2\text{Co}_2\text{Al}$ , was identified almost half a century ago [2], their magnetic properties started to be systematically studied 20 years ago for groups with  $X = \text{Sn}$  and  $\text{In}$  [3,4]. When the  $5f$  moments of U, Np, or Pu are not suppressed by too strong  $5f$ - $d$  hybridization, magnetic order appears. In most cases it is anti-ferromagnetism, with the Néel temperature lower than 50 K. The only exception is  $\text{Np}_2\text{Ni}_2\text{Sn}$  with  $T_N = 55$  K [5].

The rare-earth based materials have been studied mostly from the point of view of the crystal structure [6]. The 2002 review [7] lists more than



**Fig. 1** View of the tetragonal crystal structure of  $\text{Mo}_2\text{FeB}_2$ -type  $R_2T_2X$  compounds along the  $c$ -axis, revealing the dimers of actinide or rare-earth atoms (largest, blue spheres). Besides the dimer partner, each of these atoms has four other neighbors in the basal plane at somewhat higher distances. The  $X$  atoms (pink, medium size spheres) are at the corners of the unit cell, marked by a dashed square. Transition-metal atoms are represented by the smallest, yellow spheres.

400 representatives (which include also actinides), but magnetic properties have been determined only for part of them. For the magnetic rare earths, the ordering temperatures stay, despite much larger spin moments than at U, mostly below 50 K, reflecting the relative weakness of the indirect RKKY exchange interactions. Anomalous lanthanides (studied from 1996 [8]) and quantum magnetism effects (Shastry-Sutherland lattice [9]) were the main topics in the years after 2002.

A new dimension of the “221” compounds was opened by the H absorption studies, which offered very interesting tuning options, both for uranium and rare earths. Here we will show several cases where the H absorption is interesting from the point of view of forming metal hydrides or for solving general issues of  $f$ -magnetism.

The synthesis of the hydrides was performed by exposing activated samples of intermetallic compounds to hydrogen gas at pressures of up to  $p = 120$  bar, and followed by thermal treatment up to  $T = 923$  K. In each particular case the conditions for synthesis were optimized. To quantify the amount of absorbed hydrogen, a small quantity of hydride was decomposed in vacuum in a closed volume, by heating up to 1023 K. The phase composition of the initial alloys and the hydrogenated samples was checked by X-ray powder diffraction. In most cases the samples were single phase. Measurements of DC magnetization were performed using a PPMS

measuring system (Quantum Design), either on randomly oriented fixed powders, or on oriented single crystals, in the temperature range 1.8-300 K for applied external fields of up to 14 T.

### $R_2T_2X$ compounds and hydrides containing actinides

Among the  $R_2T_2X$  compounds containing actinides, hydrogenation has been successfully attempted for U-based compounds [10-12]. The H concentration can reach up to 2 H atoms per f.u. It is assumed that H occupies interstices in one of two adjacent  $\text{U}_3\text{T}$  tetrahedra, which preserves the tetragonal symmetry. Comparing the magnetic properties of the parent compounds and the hydrides, we immediately see a strong tendency to support magnetism. This is demonstrated in the  $T_N$  values, which increase, *e.g.* from 14 K for  $\text{U}_2\text{Ni}_2\text{In}$  to 60 K for  $\text{U}_2\text{Ni}_2\text{InH}_{1.9}$ , or from 26 K for  $\text{U}_2\text{Ni}_2\text{Sn}$  to 87 K for  $\text{U}_2\text{Ni}_2\text{SnH}_{1.8}$ . This net tendency can be attributed to the volume expansion, which leads to enhanced U–U spacing and consequent narrowing of the  $5f$  band. Direct  $5f$ - $5f$  overlap is, besides  $5f$ -ligand hybridization, the most important mechanism of suppression of the  $5f$  magnetic moments. For the same transition metal, one may be surprised to see that the compounds with  $X = \text{Sn}$  exhibit a stronger tendency to magnetism than their In isotopes. This is in striking contrast to the

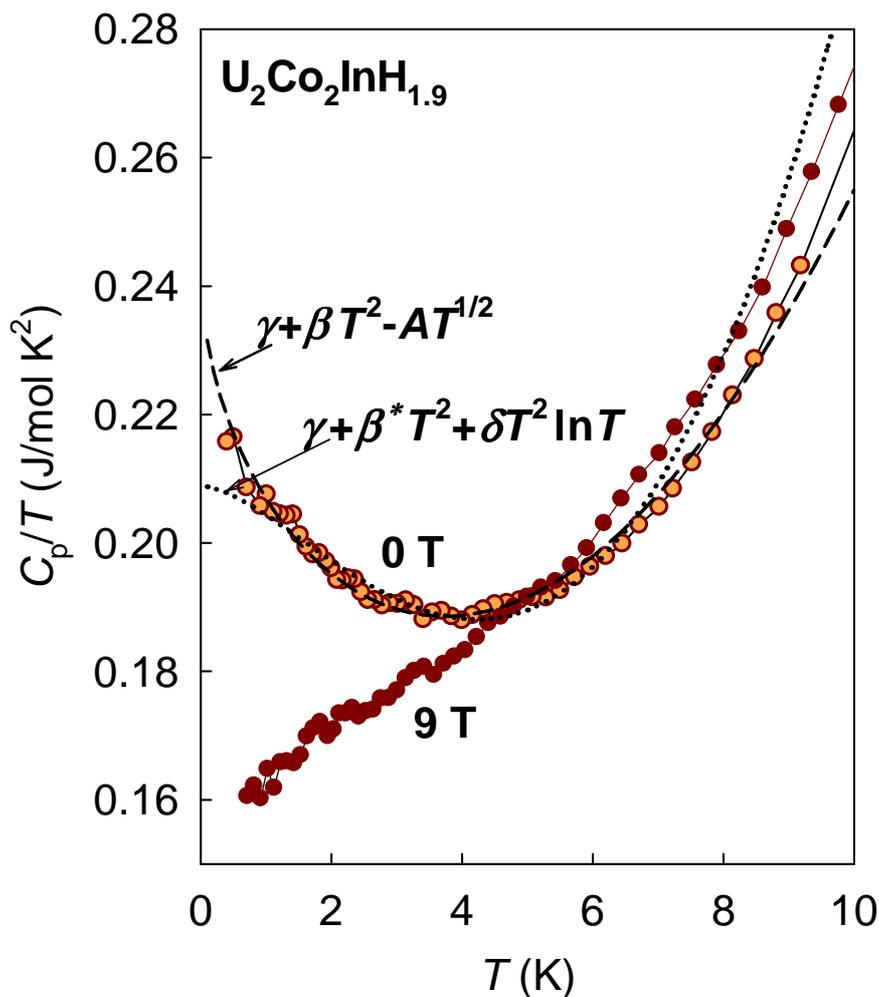
behavior of  $UX_3$  compounds and against common sense, assuming ionic radii of 168 pm for In and 158 pm for Sn. This situation deserves a more detailed analysis. The shortest U–U spacing is in most cases equivalent to the lattice parameter  $c$ . **Table 1** reveals that the weak paramagnet  $U_2Co_2In$  [13] has indeed a smaller shortest U–U spacing than the heavy fermion compound  $U_2Co_2Sn$ , with non-Fermi liquid features [13,14] appearing at the verge of magnetic order.

An interesting option was proposed by tuning the structure by H absorption. As seen from **Table 1**, the

$c$ -parameter, representing the shortest U–U spacing, is practically equivalent for  $U_2Co_2InH_{1.9}$  and  $U_2Co_2Sn$ . It is therefore particularly tempting to investigate whether the non-Fermi liquid characteristics, especially the dramatic enhancement of  $C/T(T)$  following  $\gamma AT^{1/2}$  scaling, observed for  $U_2Co_2Sn$  [14], is reproduced for  $U_2Co_2InH_{1.9}$ . **Fig. 2** reveals that this is the case, and this type of scaling confirms the same type of non-Fermi liquid behavior, attributed to weakly interacting spin fluctuations.

**Table 1** Lattice parameters of selected  $U_2Co_2X$  compounds. The physical properties are mainly influenced by the  $c$ -parameter, representing the shortest U–U spacing in the listed compounds.

Compound	$a$ (pm)	$c$ (pm)	$\Delta V/V$ (%)
$U_2Co_2In$	736.5	343.4	–
$U_2Co_2InH_{1.9}$	759.0	350.7	8.46
$U_2Co_2Sn$	729.1	350.9	–
$U_2Co_2SnH_{1.8}$	751.0	358.2	8.30



**Fig. 2** Temperature dependence of the specific heat of  $U_2Co_2InH_{1.9}$  in the  $C_p/T$  vs.  $T$  representation, which shows the upturn attributed to weakly interacting spin fluctuations. The non-interacting spin fluctuation model, yielding a logarithmic term, gives a worse description. The upturn couples to the magnetic field, but very high fields are necessary to suppress it (after [12]).

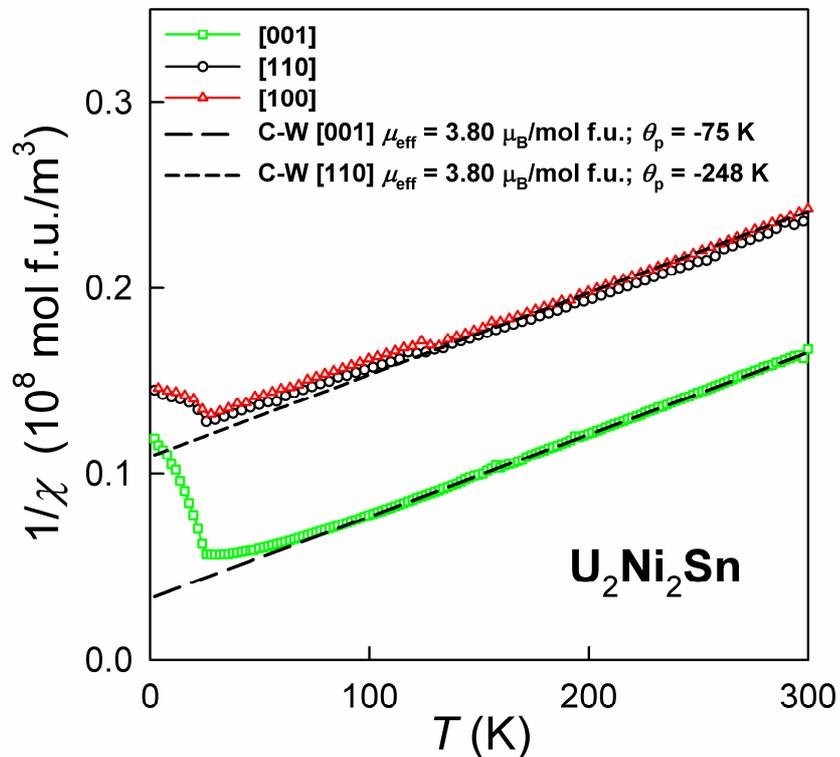
The fact that the expansion accompanying the H absorption can be strongly anisotropic, can be used to test whether the easy magnetization directions are always perpendicular to the shortest U–U distances, which represent the strong U–U bonding directions, irrespective of the positions of the other types of atom. Such a rule was deduced from studying the behavior of the U moments in various structure types [15], but the possibilities to study the exchange of nearest neighbors within one particular structure type are rare.

An interesting case in this context is  $U_2Ni_2SnD_{1.8}$ . The shortest U–U spacings along  $c$  and within the basal plane are practically equal, being 376.2(1) pm and 376.0(6) pm, respectively. The antiferromagnetic structure was identified as non-collinear, with the U moments perpendicular to the  $c$ -direction [16].  $U_2Ni_2Sn$  exhibits a distinct, short U–U spacing in the basal plane (355.8(8) pm, to be compared with  $c = 369.5(1)$  pm). Are the moments oriented along the  $c$ -axis in this case? Although neutron diffraction experiments have been undertaken, an accidental overlap of magnetic intensities with lattice reflections makes the analysis ambiguous [17,18]. Therefore we synthesized a single crystal of  $U_2Ni_2Sn$ . Susceptibility measurements along the principal crystallographic directions [19] show that the susceptibility is indeed higher along  $c$  (Fig. 3), *i.e.* perpendicular to the shortest U–U distances, and flipped with respect to the hydride.

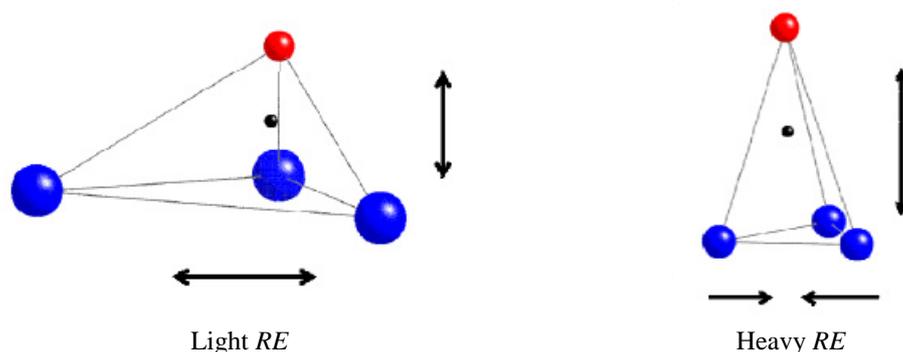
### Hydrides of $R_2T_2X$ compounds on the basis of rare-earths

The hydrides of U-based  $R_2T_2X$  compounds never contain more than 2 H atoms/f.u. This is the maximum occupancy, when considering that H enters the  $U_3T$  tetrahedral positions and occupies one of the two tetrahedra sharing a face. The H atoms are somewhat displaced out of the U planes, but the displacement is not sufficient to allow simultaneous occupancy of both adjacent tetrahedra. This is the situation for  $T = Fe, Co, Ni$ . Other transition metals do not allow hydrogenation at all, or their treatment leads to decomposition. For example,  $U_2Pd_2In$  decomposes into  $UPd_2In$  and  $UH_3$ .

Rare earth  $R_2T_2X$ 's hydrogenate more willingly and offer more diversity in storing H. A situation analogous to that described for U was found for the  $R_2Pd_2In$  series. The impact on the crystal structure differs depending on the  $RE$  (rare earth metal) involved. For light  $RE$ 's, the lattice expands both in  $a$  and  $c$  upon absorbing up to 2 H atoms/f.u. For the smaller heavy  $RE$  atoms, the basis  $RE_3T$  tetrahedra is smaller, and insertion of H pushes the  $T$  atom far away, which allows compression of  $a$  (see Fig. 4). The crossover point is located at Tb, for which  $a$  does practically not change upon hydrogenation.



**Fig. 3** Temperature dependence of inverse magnetic susceptibility in an external magnetic field  $\mu_0H = 3$  T applied along the main axes of a  $U_2Ni_2Sn$  single crystal. The dashed lines are Curie-Weiss fits with parameters shown in the legend (after [12]).



**Fig. 4** Reaction of the  $R_3T$  tetrahedra in  $Mo_2FeB_2$ -type  $R_2T_2X$  compounds to H insertion for light (left) and heavy (right) rare earths.

The magnetic ordering temperatures, which indicate the strength of the exchange coupling, systematically decrease upon H absorption (for example, see Fig. 5). Such a dramatic and systematic effect cannot be attributed to the relatively small lattice variations. Reduction of the concentration of conduction electrons, affecting the efficiency of the RKKY interactions, is the most plausible reason. Such a tendency has been detected for other rare-earth hydrides. For  $RNiAl-H$  compounds, for example, a decrease of the density of states at the Fermi level due to hydrogenation was clearly indicated [20]. The relative electronegativity of H with respect to the strongly electropositive  $f$ -elements is undoubtedly in the background. The same effect is actually expected for  $5f$  elements. But here it is due to the higher concentration of conduction electrons related to the band character of the  $5f$  states (contrasting with the localized  $4f$  states in lanthanides), less pronounced and masked by the opposite effect of the  $5f$  band narrowing.

Higher H concentrations can be achieved in several cases. The price to pay is the change of the crystal structure. The option of amorphization at high H pressures is chosen *e.g.* by  $La_2Pd_2In$  [21] and  $Ce_2Pd_2In$  [22] with H concentrations exceeding 4 H/f.u.  $R_2Ni_2In$  compounds with early rare earths absorb up to 7 H/f.u., which is made possible thanks to an orthorhombic distortion of the structure (the symmetry decreases from  $P4/mbm$  to  $Pbam$ ) [23]. The volume expansion reaches 23%. Besides the  $8i$  positions, there are three other types of H position (Table 2), some of them apparently incompletely filled. Their full occupancy would give 8 H/f.u. The  $8i$  H site is very stable, as H is released only when heating to 720°C [23]. At ambient temperature the H pressure at which this site is saturated is at the level of a few mbar.

Even higher H concentrations have been reported for compounds with  $X = Mg$ , namely  $Ce_2Ni_2MgH_{7.7}$  [24] and  $La_2Ni_2MgH_8$  [25], the structures of which

become monoclinic. The latter work deduces that this hydride is actually more a complex hydride (with  $[Ni_2H_7]^{7-}$  and  $[Ni_4H_{12}]^{12-}$  anions) than a simple metal hydride. This correlates with allegedly irreversible decomposition properties [25].

### Concluding remarks and outlook

The large variety of known  $R_2T_2X$  compounds, accommodating very different metals and their combinations, allows addressing several important issues. The phenomenon of quantum criticality, appearing at the verge of the formation of magnetic moments and magnetic order in  $5f$  systems, can be achieved in several ways. The effect of tuning by appropriate substitutions of  $T$  and  $X$  metals can be compared with the effect of H absorption and the concomitant volume expansion. In this respect, we have lately been concentrating on the system  $U_2Ni_2Sn-U_2Fe_2Sn$  and its hydrides. The anisotropic character of the properties requires single crystal studies. Synthesis of single crystal hydrides, albeit difficult, is worth an attempt.

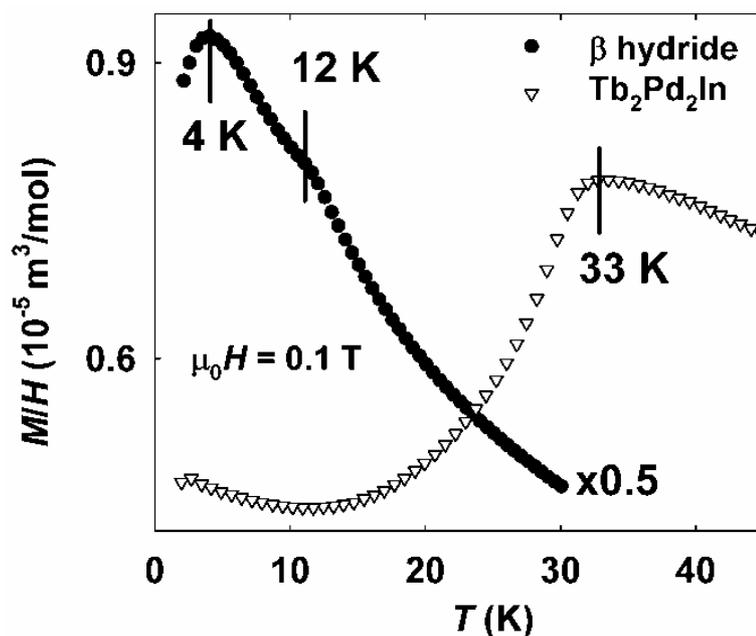
For rare-earth compounds, the possibility to investigate the crossover from metal to complex hydrides is particularly tempting. The oceans of materials listed in [7] have so far been explored only marginally. The majority of the materials still wait for detailed studies of their physical properties and interaction with hydrogen.

### Acknowledgements

This work was supported by the Czech Grant Agency under the grants Nos. P204/12/0285 and P108/10/1006. Experiments were performed at MLTL (<http://mltl.eu/>), which is supported within the program of Czech Research Infrastructures (project No. LM2011025).

**Table 2** Crystal structure of  $\text{Nd}_2\text{Ni}_2\text{InD}_{\approx 7}$ : 4 different deuterium sites and their site occupancy  $n$ . Space group  $P6mm$ .

Atom	Wyckoff position	Coordination	$n$
Nd	4h	–	1
Ni	4g	–	1
In	2a	–	1
D1	4h	$\text{Nd}_2\text{In}_2$	0.95
D2	4g	$\text{Nd}_4\text{NiIn}$	1
D3	4g	$\text{Nd}_4\text{NiIn}$	0.81
D4	8i	$\text{Nd}_3\text{Ni}$	0.5

**Fig. 5** Temperature dependence of magnetic susceptibility, revealing the reduction of the Néel temperature from  $T = 33$  K in  $\text{Tb}_2\text{Pd}_2\text{In}$  to 12 K in  $\text{Tb}_2\text{Pd}_2\text{InH}_{1.3}$ .

## References

- [1] B. Shastry, B. Sutherland, *Physica B+C* 108 (1981) 1069.
- [2] A.O. Sampaio, E. Santa Marta, H.L. Lukas, G. Petzow, *J. Less-Common Met.* 14 (1968) 472.
- [3] M.N. Peron, Y. Kergadallan, J. Rebizant, D. Meyer, S. Zwirner, L. Havela, H. Nakotte, J.C. Spirlet, G.M. Kalvius, E. Colineau, J.L. Oddou, C. Jeandey, J.P. Sanchez, J.M. Winand, *J. Alloys Compd.* 201 (1993) 203.
- [4] F. Mirambet, P. Gravereau, B. Chevalier, L. Trut, J. Etourneau, *J. Alloys Compd.* 191 (1993) L1.
- [5] J.P. Sanchez, E. Colineau, C. Jeandey, J.L. Oddou, J. Rebizant, A. Seret, J.C. Spirlet, *Physica B: Condens. Matter* 206-207 (1995) 531.
- [6] Y.M. Kalychak, V.I. Zarembo, V.M. Baranyak, P.Y. Zavaliy, V.A. Bruskov, L.V. Syya, O.V. Dmytrakh, *Inorg. Mater.* 26 (1990) 74.
- [7] M. Lukachuk, R. Pöttgen, *Z. Kristallogr.* 218 (2002) 767.
- [8] D. Kaczorowski, P. Rogl, K. Hiebl, *Phys. Rev. B* 54 (1996) 9891.
- [9] Y. Shimura, T. Sakakibara, K. Iwakawa, K. Sugiyama, Y. Onuki, *J. Phys. Soc. Jpn.* 81 (2012) 103601.
- [10] K. Miliyanchuk, L. Havela, A.V. Kolomiets, A.V. Andreev, *Physica B: Condens. Matter* 359-361 (2005) 1042.
- [11] K. Miliyanchuk, L. Havela, A.V. Kolomiets, S. Daniš, L.C.J. Pereira, A.P. Gonçalves, *Physica B: Condens. Matter* 378-380 (2006) 983.
- [12] L. Havela, K. Miliyanchuk, L.C.J. Pereira, E. Šantavá, *Z. Naturforsch. B* 62 (2007) 977.

- [13] L. Havela, V. Sechovský, P. Svoboda, H. Nakotte, K. Prokeš, F.R. de Boer, A. Seret, J.M. Winand, J. Rebizant, J.C. Spirlet, A. Purwanto, R.A. Robinson, *J. Magn. Magn. Mater.* 140-144 (1995) 1367.
- [14] J.S. Kim, J. Alwood, S.A. Getty, F. Sharifi, G.R. Stewart, *Phys. Rev. B* 62 (2000) 6986.
- [15] L. Havela, V. Sechovský, F.R. de Boer, E. Brück, H. Nakotte, *Physica B* 177 (1992) 159.
- [16] K. Miliyanchuk, L. Havela, L.C.J. Pereira, A.P. Gonçalves, K. Prokeš, *J. Magn. Magn. Mater.* 310 (2007) 945-947.
- [17] F. Bourée, B. Chevalier, L. Fournès, F. Mirambet, T. Roisnel, V.H. Tran, Z. Zolnierek, *J. Magn. Magn. Mater.* 138 (1994) 307.
- [18] D. Laffargue, B. Chevalier, S.F. Matar, F. Bourée, *Proc. 26ièmes Journées des Actinides*, Sklarska Poreba, Poland, 1996, p. 53.
- [19] S. Mašková, L. Havela, A.V. Andreev, S. Daniš, Y. Skourski, J. Wosnitza, K. Kothapalli, H. Nakotte, *Proc. 41èmes Journées des Actinides*, Stará Lesná, Slovakia, 2011, pp. 27-28.
- [20] K. Eichinger, L. Havela, J. Prokleška, O. Stelmakhovych, S. Daniš, E. Šantavá, K. Miliyanchuk, *Int. J. Mater. Res.* 100 (2009) 1200.
- [21] A.V. Kolomiets, S. Mašková, L. Havela, Z. Matěj, R. Kužel, *J. Alloys Compd.* 509 (2011) 4185.
- [22] W. Iwasieczko, D. Kaczorowski, *J. Alloys Compd.* 509 (2011) 1384.
- [23] S. Mašková, L. Havela, S. Daniš, A. Llobet, H. Nakotte, K. Kothapalli, R. Černý, A. Kolomiets, *J. Alloys Compd.* 566 (2013) 22.
- [24] B. Chevalier, A.A. Krolak, J.-L. Bobet, E. Gaudin, F. Weill, W. Hermes, R. Pöttgen, *Inorg. Chem.* 47 (2008) 10419.
- [25] J.N. Chotard, Y. Filinchuk, B. Revaz, K. Yvon, *Angew. Chem. Int. Ed.* 45 (2006) 7770.