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Magnetic structures of the ternary stannide $U_2(Ni_{0.70}Pd_{0.30})_2Sn$

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Abstract

The Néel temperature T_N in the tetragonal (P4/mbm space group) antiferromagnetic $U_2(Ni_{1-x}Pd_x)_2Sn$ solid solution exhibits a minimum (T_N=12(1) K) at $x\approx$0.30–0.35; the end values being respectively equal to T_N=25 K (x=0) and T_N=42 K (x=1). In order to understand this T_N vs. x dependence, we have investigated the $U_2(Ni_{0.70}Pd_{0.30})_2Sn$ stannide by neutron powder diffraction. This alloy exhibits two magnetic transitions, at T_N=11.5(5) K and $T_{N'}$=8.0(5) K. Between $T_{N'}$ and T_N, the magnetic peaks are associated to $\mathbf{k}$=(0 0 1/2) propagation vector; below $T_{N'}$, two propagation vectors are present, $\mathbf{k}$=(0 0 1/2) and $\mathbf{k}'$=(1/2 1/2 1/2), which are associated to different volumes of the sample. We discuss this complex magnetic behaviour, in connection with the U_2Ni_2Sn ($\mathbf{k}$=(0 0 1/2)) and U_2Pd_2Sn ($\mathbf{k}''$=(0 0 0)) magnetic structures. © 1998 Elsevier Science S.A.

Keywords: Ternary stannides; Neutron diffraction; Magnetic structures; Magnetic phase diagram

1. Introduction

Recently, the magnetic properties of the $U_2(Ni_{1-x}Pd_x)_2Sn$ ternary stannides ($0\leq x\leq 1$), crystallizing in the tetragonal ordered U_3Si_2-type structure (P4/mbm space group, with U in (4h), (Ni, Pd) in (4g) and Sn in (2a) Wyckoff positions) were investigated [1]. All the compositions order antiferromagnetically, showing an interesting behaviour of the Néel temperature T_N: T_N first decreases from 25 K (x=0) to 12 K (x=0.30–0.35) and then increases up to 42 K (x=1.0). This $T_N=f(x)$ dependence was reproduced on account of an anisotropic RKKY (Ruderman–Kittel–Kasuya–Yosida) model [1], the occurrence of a minimum in $T_N(x)$ being associated to a change in magnetic structure, from the U_2Ni_2Sn, $\mathbf{k}$=(0 0 1/2) collinear magnetic structure described in Ref. [2] to the U_2Pd_2Sn, $\mathbf{k}''$=(0 0 0) non-collinear structure [3,4].

In order to prove this calculated magnetic phase, we performed neutron powder diffraction on the $U_2(Ni_{1-x}Pd_x)_2Sn$ system. In this paper, we discuss preliminary results concerning the $U_2(Ni_{0.70}Pd_{0.30})_2Sn$ ternary stannide.

2. Experimental

The $U_2(Ni_{0.70}Pd_{0.30})_2Sn$ sample was prepared by melting stoichiometric amounts of the constituent elements under argon atmosphere. The obtained alloy was then annealed for 1 month at 800°C under vacuum in a quartz crucible. Microprobe analysis and X-ray powder diffraction at T=300 K confirmed that this annealed alloy is single phase and crystallizes in the tetragonal U_3Si_2-type structure, with a=7.379(2) Å and c=3.714(1) Å as unit-cell parameters.

Magnetization measurements were carried out in the 2–20 K temperature range using a Superconducting QUantum Interference Device (SQUID) magnetometer.

Neutron diffraction experiments have been performed at the Orphée reactor (Saclay, France), on the G4.1 two-axis diffractometer (800 cell PSD, λ=2.4265 Å). Neutron data were analysed with the Rietveld-type FULLPROF program [5], with scattering neutron lengths from Ref. [6]: $b_U=0.8417\times10^{-12}$ cm, $b_{Ni}=1.03\times10^{-12}$ cm, $b_{Pd}=0.591\times$

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10^{-12} cm and $b_{Sn}=0.6225\times10^{-12}$ cm. The U^{3+} magnetic form factor was calculated as $\langle j_0\rangle$, with $\langle j_0\rangle$ values from Ref. [7].

3. Results

3.1. Magnetization measurements

Fig. 1 shows the temperature dependence of the magnetization M of $U_2(Ni_{0.70}Pd_{0.30})_2Sn$ below 20 K. Two features are observed in the derivative curve $dM/dT=f(T)$ (inset of Fig. 1): a well-defined maximum occurring at $T_N=12(1)$ K and a 'shoulder' occurring at $T_{N'}=7(1)$ K. These results suggest the existence of two magnetic transitions for this stannide.

3.2. Neutron powder diffraction

At $T=16$ K$>T_N$, the neutron powder diffraction pattern of this stannide reveals reflections associated to nuclear scattering only: the $U_2(Ni_{0.70}Pd_{0.30})_2Sn$ unit-cell parameters are then equal to $a=7.3614(5)$ Å and $c=3.7306(3)$ Å.

Neutron powder diffraction diagrams at low temperatures (Fig. 2) clearly show the existence of new Bragg peaks, connected to 3D antiferromagnetic ordering in $U_2(Ni_{0.70}Pd_{0.30})_2Sn$. The type of antiferromagnetic order is temperature dependent: if all the magnetic Bragg peaks at $T=9.8$ K can be indexed with the help of a $\mathbf{k}=(0\,0\,1/2)$ propagation vector, two propagation vectors are necessary at $T=1.5$ K: $\mathbf{k}=(0\,0\,1/2)$ and $\mathbf{k}'=(1/2\,1/2\,1/2)$. From thermal variation of (1 0 1/2), (1 1 1/2) and (2 1 1/2) (Fig. 3), (1/2 1/2 1/2) and (3/2 1/2 1/2) (Fig. 4) magnetic intensities, two magnetic transition temperatures are obtained: $T_N=11.5(5)$ K and $T_{N'}=8.0(5)$ K, in excellent agreement with the values obtained from magnetization measurements. Moreover, the $\mathbf{k}=(0\,0\,1/2)$ magnetic structures below $T_{N'}$ and between $T_{N'}$ and T_N are different, as reflected by the differences in the magnetic $(h\,k\,1/2)$ intensity ratios in the intermediate and low temperature ranges (Fig. 3).

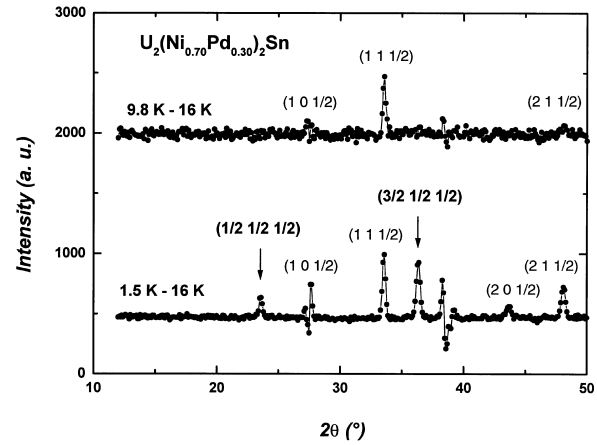

Fig. 2. $U_2(Ni_{0.70}Pd_{0.30})_2Sn$ neutron powder diffraction ($\lambda=2.4265$ Å) difference diagrams: T-($T=16$ K$>T_N$). Two diagrams are shown at, respectively, $T=9.8$ K [$T_{N'}<T<T_N$] and $T=1.5$ K [$T<T_{N'}$].

3.2.1. Magnetic structure at $T=9.8$ K

The analysis was done with the help of magnetic group theory for P4/mbm space group, (4h) Wyckoff position and $\mathbf{k}=(0\,0\,1/2)$ propagation vector [2]. In the intermediate temperature range ($T_{N'}<T<T_N$), the best fit

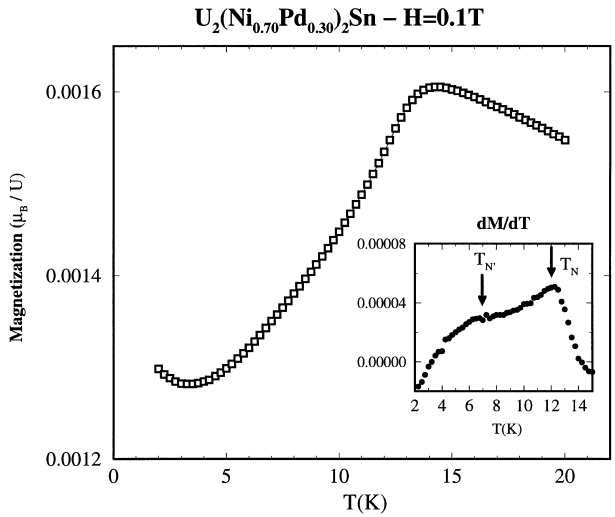

Fig. 1. Thermal variation of $U_2(Ni_{0.70}Pd_{0.30})_2Sn$ magnetization (external field $H=0.1$ T). The inset shows the derivative dM/dT (M, magnetization; T, temperature).

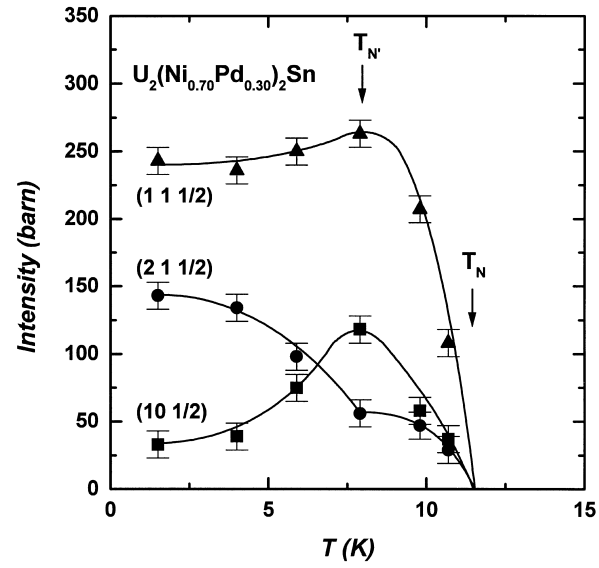

Fig. 3. $U_2(Ni_{0.70}Pd_{0.30})_2Sn$, thermal variation of (1 0 1/2), (1 1 1/2) and (2 1 1/2) magnetic intensities. These magnetic Bragg peaks are associated to $\mathbf{k}=(0\,0\,1/2)$ wave vector.

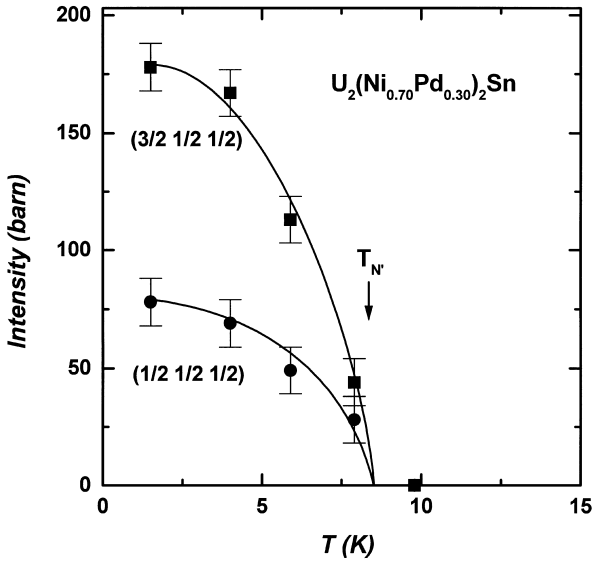

Fig. 4. $U_2(Ni_{0.70}Pd_{0.30})_2Sn$, thermal variation of (1/2 1/2 1/2) and (3/2 1/2 1/2) magnetic intensities. These magnetic Bragg peaks are associated to $\mathbf{k}'=(1/2\ 1/2\ 1/2)$ wave vector.

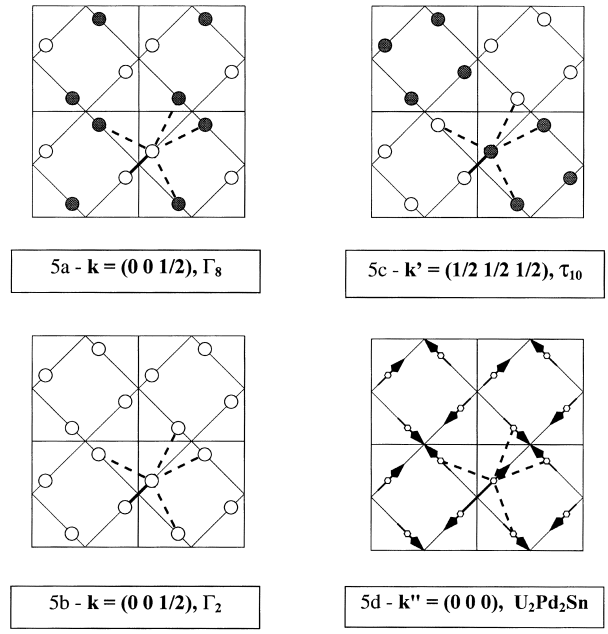

Fig. 5. (a) $\mathbf{k}=(0\ 0\ 1/2)$, Γ_8 magnetic structure; (b) $\mathbf{k}=(0\ 0\ 1/2)$, Γ_2 magnetic structure; (c) $\mathbf{k}'=(1/2\ 1/2\ 1/2)$, τ_{10} magnetic structure; (d) $\mathbf{k}''=(0\ 0\ 0)$, U_2Pd_2Sn magnetic structure. For $\mathbf{k}'=(1/2\ 1/2\ 1/2)$, an **a**-, **b**- or **c**-translation implies a change in the sign of the U magnetic moment. For $\mathbf{k}=(0\ 0\ 1/2)$, only a **c**-translation changes this sign. Four crystalline unit-cells, i.e. $2a\times2a\times c$, are shown in the figures. For all these magnetic structures, except U_2Pd_2Sn (d), the U magnetic moments are parallel to the tetragonal **c**-axis (open circles, spins 'up'; full circles, spins 'down'). The shortest d_{U-U} distances within (**a**,**b**)-plane are indicated either by continuous (one distance, d_{1U}) or dashed lines (four distances, d_{4U}).

between observed and calculated data is obtained for Γ_8 irreducible representation (Fig. 5a), with $M_U=0.55(5)\ \mu_B$ at $T=9.8$ K (reliability factor $R_M=9\%$).

3.2.2. Magnetic structure at T=1.5 K

Contrary to what happens in the intermediate temperature range, the $\mathbf{k}=(0\ 0\ 1/2)$ magnetic diagram at $T=1.5$ K cannot be accounted for by a unique irreducible representation Γ_i ($i=1$–10): two of them are now present, Γ_8 and Γ_2. For both of these magnetic arrangements, the U-magnetic moments are parallel to the tetragonal **c**-axis: Γ_2 magnetic structure is characterized by ferromagnetic (001) planes, with the '+−+−' stacking sequence along the **c**-axis (Fig. 5b).

From magnetic group theory applied to the P4/mbm space group, (4h) Wyckoff position and $\mathbf{k}'=(1/2\ 1/2\ 1/2)$ propagation vector [8], as many as 10 irreducible representations τ_j ($j=1$–10) are obtained. In $U_2(Ni_{0.70}Pd_{0.30})_2Sn$, the $\mathbf{k}'=(1/2\ 1/2\ 1/2)$ magnetic structure at $T=1.5$ K is accounted for by τ_{10}: for this arrangement (magnetic unit cell $2a\times2a\times2c$), the U-magnetic moments are also parallel to the **c**-axis (Fig. 5c).

Three different types of magnetic ordering are then observed at $T=1.5$ K for U-magnetic moments. Two assumptions can be made (and neutron powder diffraction is not able to choose between these two): either '$\mathbf{k}=(0\ 0\ 1/2)$, Γ_8', '$\mathbf{k}=(0\ 0\ 1/2)$, Γ_2' and '$\mathbf{k}'=(1/2\ 1/2\ 1/2)$, τ_{10}' are all associated to the whole volume of the sample, or each of these magnetic arrangements is associated to a partial volume in the sample. We selected the partial volume assumption, from the criterium of identical magnetic moment values for the four U atoms in the nuclear unit cell. The results of the neutron powder diffraction ($T=1.5$ K) magnetic data refinement are given in Table 1. At $T=1.5$ K, the U-magnetic moment is equal to 1.05(10) μ_B/U, identical to the value obtained at the same temperature for $x=0$ [2], and far below the '$x=1$' value (2.20 μ_B/U [3]).

Table 1
$U_2(Ni_{0.70}Pd_{0.30})_2Sn$ magnetic structures at $T=1.5$ K: propagation vector (**k** or **k**′), magnetic structure type (Γ_i or τ_j), U magnetic moment and volume of the associated magnetic domain

Propagation vector	Magnetic structure	Magnetic moment (μ_B)	Volume (%)	Reliability factor, R_M (%)
$\mathbf{k}=(0\ 0\ 1/2)$	Γ_8	$M_U=1.05(10)$	30(5)	2.10
$\mathbf{k}=(0\ 0\ 1/2)$	Γ_2	$M_U=1.05(10)$	25(5)	5.05
$\mathbf{k}'=(1/2\ 1/2\ 1/2)$	τ_{10}	$M_U=1.05(10)$	45(5)	9.35

These values are obtained from neutron powder diffraction FULLPROF [5] data refinement.

Table 2
$U_2(Ni_{1-x}Pd_x)_2Sn$ alloys, magnetic exchange interactions between nearest U neighbours, at distances d_{1U}, d_{2U} and d_{4U} (the number of such neighbours is indicated by the digit in the index of d_{nU}; neighbours within (**a**,**b**)-plane, at distances d_{1U} and d_{4U}, are shown in Fig. 5)

	Propagation vector	Magnetic structure	d_{1U} ($\perp$**c**-axis)	d_{2U}=c ($\parallel$**c**-axis)	d_{4U} ($\perp$**c**-axis)
U_2Ni_2Sn	**k**=(0 0 1/2)	Γ_{10}	F	AF	AF
	k=(0 0 1/2)	Γ_8	F	AF	AF
$U_2(Ni_{0.7}Pd_{0.3})_2Sn$	**k**=(0 0 1/2)	Γ_2	F	AF	F
	k′=(1/2 1/2 1/2)	τ_{10}	AF	AF	2F & 2AF
U_2Pd_2Sn	**k**″=(0 0 0)	Γ_8'	AF	F	—

F, ferromagnetic; AF, antiferromagnetic.

4. Discussion

Contrary to the end compounds, U_2Ni_2Sn and U_2Pd_2Sn, where only one magnetic transition occurs, two magnetic transition temperatures are obtained for $U_2(Ni_{0.70}Pd_{0.30})_2Sn$: T_N=11.5(5) K and $T_{N'}$=8.0(5) K.

Let us now compare the magnetic structures in the $U_2(Ni_{1-x}Pd_x)_2Sn$ series: they are known, up to now, for x=0 [2], x=1 [3,4] (Fig. 5d) and x=0.30 (this work). All are antiferromagnetic, but all are different (Table 2, Fig. 5). Let us just recall that the U_2Ni_2Sn magnetic structure ['**k**=(0 0 1/2), Γ_{10}'] is similar to the '**k**=(0 0 1/2), Γ_8' structure (Fig. 5a), except for the direction of the U-moments, which are either perpendicular (U_2Ni_2Sn) or parallel ($U_2(Ni_{0.70}Pd_{0.30})_2Sn$) to the tetragonal **c**-axis. At the other end of the series (i.e. for x=1, U_2Pd_2Sn), the magnetic structure is associated to '**k**″=(0 0 0), Γ_8'' [9] and depicted in Fig. 5d. So, for U_2Ni_2Sn and U_2Pd_2Sn, the magnetic interactions between nearest U neighbours (at d_{1U} and d_{2U} distances, Table 2) are respectively F, AF (U_2Ni_2Sn) and AF, F (U_2Pd_2Sn), which means an inversion of the sign of interactions (F$\Leftrightarrow$AF) when going from x=0, U_2Ni_2Sn to x=1, U_2Pd_2Sn. Some equilibrium between these competing magnetic interactions is then to be found at intermediate x values. For $U_2(Ni_{1-x}Pd_x)_2Sn$, x=0.30, the 'equilibrium' at low temperature ($T<T_{N'}$) is obtained via different volumes of the same sample, associated to different magnetic structures. For these magnetic structures, the magnetic interactions between U nearest neighbours are either F, AF or AF, AF (Table 2).

The $U_2(Ni_{1-x}Pd_x)_2Sn$ magnetic ground state and $T_N(x)$ value have been accounted for in the frame of an anisotropic RKKY model [1]: for this calculation of magnetic RKKY exchange interaction, not only three (at d_{1U} and d_{2U} distances) or seven (at d_{1U}, d_{2U} and d_{4U} distances) U neighbours were considered, but about 300, which are included in a sphere of 15 Å radius. It was then shown that the minimum of $T_N(x)$ observed at $x\approx$0.30–0.35 in the $U_2(Ni_{1-x}Pd_x)_2Sn$ solid solution was associated to a change of magnetic structure type, from U_2Ni_2Sn to U_2Pd_2Sn-type magnetic structure. Let us note that the '**k**=(0 0 1/2), Γ_{10}' (U_2Ni_2Sn) and '**k**=(0 0 1/2), Γ_8' ($U_2(Ni_{0.70}Pd_{0.30})_2Sn$) magnetic structures, as they are similar except for the direction of the U magnetic moments, are associated to the same magnetic exchange energy. An extension of this anisotropic RKKY model to the '**k**′=(1/2 1/2 1/2)' magnetic states, which have not been taken into account in Ref. [1], has to be done now, together with neutron powder diffraction on other compounds in the series ($0.30<x<1$), in order to get a deeper insight in the complex $U_2(Ni_{1-x}Pd_x)_2Sn$ magnetic phase diagram.

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