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Neutron powder-diffraction studies of U_2Ni_2In and U_2Pd_2In

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Abstract

We have performed neutron diffraction experiments on U_2Ni_2In and U_2Pd_2In. Both compounds crystallize with a tetragonal structure, U_3Si_2-type, space group P4/mbm, and are non-collinear antiferromagnets at low temperatures (U_2Ni_2In, $T_N = 15$ K; U_2Pd_2In, $T_N \leq 31$ K). Their magnetic structures are respectively described by propagation vectors $\mathbf{k} = (0, 0, 1/2)$ and $\mathbf{k} = (0, 0, 0)$. The uranium magnetic moments are perpendicular to the tetragonal c-axis, but their relative arrangement within the (001) plane is different for Ni and Pd compounds. At 1.5 K, the uranium magnetic moment value is $M_U = 0.85(5)\ \mu_B$ in U_2Ni_2In and $M_U = 1.55(5)\ \mu_B$ in U_2Pd_2In.

Keywords: Neutron diffraction; Magnetic structure

1. Introduction

The intermetallic compounds U_2T_2M (T = Co, Rh, Ir, Ni, Pd and Pt, M = Sn or In) crystallize in an ordered version of U_3Si_2-type structure [1–7]. This structure is tetragonal (space group P4/mbm) and can be described as built of two types of atomic planes: one at $z = 1/2$ containing only uranium atoms and the other at $z = 0$ filled with the T and M atoms. In this structure, each uranium atom occupies a (4h) crystallographic site of C_{2v}-symmetry and has three different types of uranium nearest neighbours at distances d(U–U) in the 3.45–3.80 Å range: two of these U nearest neighbours atoms correspond to the distance d_1(U–U) = c along the tetragonal axis; one, at distance d_2(U–U) and four, at d_3(U–U), are situated in the ab-plane. Magnetic measurements revealed that most of U_2T_2M order antiferromagnetically at low temperatures [4–7].

So far, neutron diffraction experiments have been performed only on U_2Ni_2Sn [8], U_2Pd_2Sn [9,10] and U_2Pd_2In [10]. The former compound shows a collinear antiferromagnetic order, with $\mathbf{k} = (0, 0, 1/2)$ and uranium magnetic moments equal to 1.05 μ_B at $T = 1.5$ K [8]. The latter compounds (T = Pd) show a non-collinear structure with $\mathbf{k} = (0, 0, 0)$ and uranium magnetic moments (U_2Pd_2Sn: 2.20 μ_B at $T = 1.5$ K [9], 2.00 μ_B at $T = 10$ K [10], U_2Pd_2In: 1.60 μ_B at $T = 10$ K [10]) lying in the basal plane.

The present neutron diffraction studies concern U_2Ni_2In and U_2Pd_2In, which, on the basis of ac-susceptibility [4] and specific heat measurements [5,6], have been concluded to order antiferromagneti-

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cally below $T_N = 14$–16 K for U_2Ni_2In and $T_N = 36$–40 K for U_2Pd_2In.

2. Experiment

The U_2Ni_2In and U_2Pd_2In samples were synthesised by arc melting stoichiometric amounts of the metallic elements in an argon atmosphere. The crystal structure checked by a X-ray analysis (Debye–Scherrer geometry) was found to be tetragonal, similar to that of U_2Ni_2Sn [8].

Neutron powder diffraction experiments were performed on the G4.1 diffractometer installed at the Orphée reactor (LLB-Saclay, France), with $\lambda = 2.426$ Å. The diffraction patterns were collected at several temperatures in the range 1.5–55 K. The refinements of the crystal and magnetic structures were carried out using the Rietveld profile method by the FULL-PROF program [11], with magnetic form factor of U^{3+} calculated in the dipolar approximation from $\langle j_0 \rangle$ and $\langle j_2 \rangle$ of A.J. Freeman et al. [12].

3. Results

3.1. Crystal structure

The neutron powder diffraction patterns obtained at 23 K for U_2Ni_2In and 53 K for U_2Pd_2In confirm that the samples are isostructural with U_3Si_2: tetragonal crystal structure, space group P4/mbm, with:

	U	in (4h)	$(x_U, \frac{1}{2}+x_U, \frac{1}{2})$
	Ni(Pd)	in (4g)	$(x_T, \frac{1}{2}+x_T, \frac{1}{2})$
and	In	in (2a)	(0, 0, 0)

The atomic positions x_U and x_T and the lattice parameters of both compounds at $T > T_N$ are given in Table 1. From the crystallographic data we can obtain the values of the nearest distances between uranium atoms: $d_1(U–U) = c$, $d_2(U–U) = 2\sqrt{2}\, x_U\, a$ and $d_3(U–U) = a((1/2)^2 + (\frac{1}{2} - 2x_U)^2)^{1/2}$ (see Table 1). For U_2Pd_2In at $T = 53$ K the distances $d_1(U–U)$ and $d_2(U–U)$ are identical (3.74 Å), while for U_2Ni_2In at $T = 23$ K, $d_1(U–U) = 3.57$ Å is smaller than $d_2(U–U) = 3.79$ Å. All of these values (> 3.5 Å) indicate that both compounds are located on the magnetic side of the Hill's limit.

Table 1
Crystallographic data for U_2Ni_2In and U_2Pd_2In

	U_2Ni_2In ($T = 23$ K)	U_2Pd_2In ($T = 53$ K)
a (Å)	7.381(5)	7.642(2)
c (Å)	3.571(1)	3.741(1)
x_U	0.1816(13)	0.1730(8)
x_T	0.3765(11)	0.3715(9)
R_B (%)	7.05	7.85
d_1(U–U) (Å)	3.571(1)	3.741(1)
d_2(U–U) (Å)	3.791(14)	3.739(9)
d_3(U–U) (Å)	3.826(14)	3.998(9)

3.2. Magnetic structrure

3.2.1. U_2Ni_2In

The U_2Ni_2In neutron diffraction pattern at 1.5 K, in comparison to the 23 K diagram, shows additional peaks of magnetic origin (Fig. 1). These magnetic Bragg peaks are indexed either $100^{\pm}$, $110^{\pm}$, $200^{\pm}$ and $210^{\pm}$, with a propagation vector $\mathbf{k} = (0, 0, 1/2)$ or (101), (111), (201) and (211) in the tetragonal magnetic unit cell (a, a, $2c$).

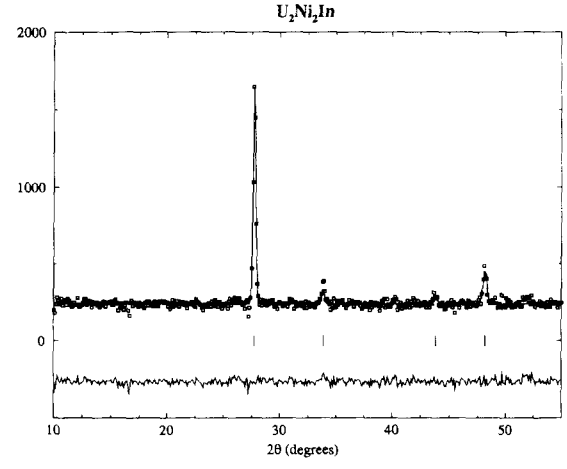

Fig. 1. Observed and calculated neutron powder diffraction pattern for U_2Ni_2In ($\lambda = 2.426$ Å): magnetic Bragg peaks (difference between 1.5 and 23 K neutron diagrams). The open squares represent the observed points, the solid lines the calculated profile and the difference between observed and calculated profiles (below).

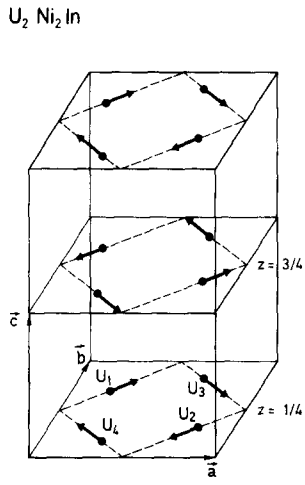

Fig. 2. Magnetic structure of U_2Ni_2In at 1.5 K. Only magnetic atoms (uranium) are drawn.

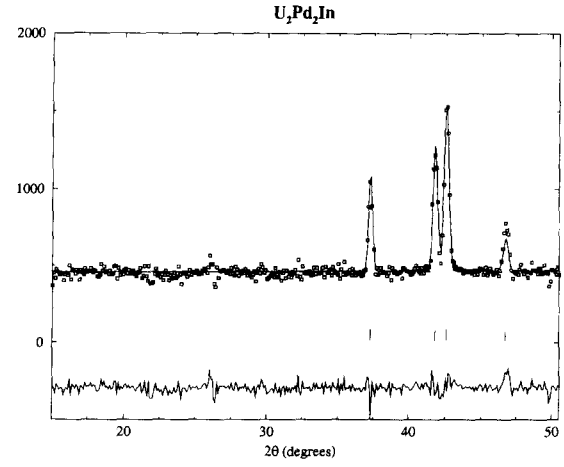

Fig. 3. Observed and calculated neutron powder diffraction pattern for U_2Pd_2In ($\lambda = 2.426$ Å): magnetic Bragg peaks (difference between 1.5 and 53 K neutron diagrams). The full squares represent the observed points, the solid lines the calculated profile and the difference between observed and calculated profiles (below).

As in other U_2T_2M intermetallic compounds [8–10], the only magnetic atoms in the structure are the U atoms. The (a, a, $2c$) magnetic unit cell contains eight U magnetic moments, $\mathbf{M}_1$, $\mathbf{M}_2$, $\mathbf{M}_3$, $\mathbf{M}_4$ and $\mathbf{M}'_1$, $\mathbf{M}'_2$, $\mathbf{M}'_3$ and $\mathbf{M}'_4$, respectively. Four of them are located at $z = 1/4$ and the remaining four at $z = 3/4$. The crystallographic positions of these magnetic moments are as follows:

$\mathbf{M}_1\,(x_U, \frac{1}{2}+x_U, \frac{1}{4})$ $\quad$ $\mathbf{M}'_1\,(x_U, \frac{1}{2}+x_U, \frac{3}{4})$

$\mathbf{M}_2\,(-x_U, \frac{1}{2}-x_U, \frac{1}{4})$ $\quad$ $\mathbf{M}'_2\,(-x_U, \frac{1}{2}-x_U, \frac{3}{4})$

$\mathbf{M}_3\,(\frac{1}{2}+x_U, -x_U, \frac{1}{4})$ $\quad$ $\mathbf{M}'_3\,(\frac{1}{2}+x_U, -x_U, \frac{3}{4})$

$\mathbf{M}_4\,(\frac{1}{2}-x_U, x_U, \frac{1}{4})$ $\quad$ $\mathbf{M}'_4\,(\frac{1}{2}-x_U, x_U, \frac{3}{4})$

The best fit ($R_M = 4.0\%$) between observed and calculated neutron powder diffraction patterns at $T = 1.5$ K (Fig. 1) is obtained for the non-collinear magnetic structure in Fig. 2 ($\mathbf{M}'_i = -\mathbf{M}_i$), which is described by magnetic moments in the basal plane (Γ_3 representation of Ref. [8]). The uranium magnetic moment is $M_U = 0.85 \pm 0.05\ \mu_B$ at $T = 1.5$ K (see Table 2).

Table 2
Magnetic structure data for U_2Ni_2In and U_2Pd_2In obtained at $T = 1.5$ K

	U_2Ni_2In	U_2Pd_2In
k	(0, 0, 1/2)	(0, 0, 0)
Γ	3	8
M_U (μ_B)	0.85(5)	1.55(5)
R_M (%)	4.0	6.1

3.2.2. U_2Pd_2In

Neutron powder diffraction patterns on U_2Pd_2In have been obtained at $T = 1.5$ K, $T = 5$ K, $T = 23.5$ K, $T = 31$ K and $T = 53$ K. No magnetic contribution is evidenced at $T = 31$ K. At 1.5 K, 5 K, 23.5 K, these patterns show that U_2Pd_2In develops a magnetic order different from those found in U_2Ni_2Sn [8] and U_2Ni_2In (see above). We only observe (Fig. 3, $T = 1.5$ K) magnetic Bragg peaks that can be indexed (200), (210), (101), (111) in a magnetic cell

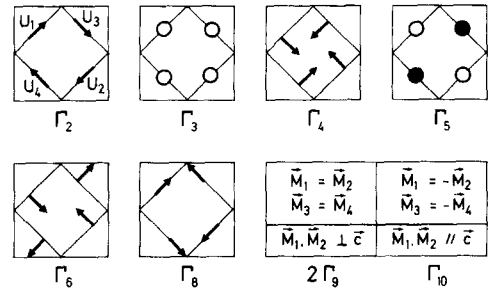

Fig. 4. Symmetry analysis of the 2:2:1 magnetic structures (wave vector $\mathbf{k} = (0, 0, 0)$): magnetic moments ($\mathbf{M}_1$, $\mathbf{M}_2$, $\mathbf{M}_3$, $\mathbf{M}_4$) of the uranium atoms at $z = 1/2$.

Table 3
Magnetic group theory, P4/mbm space group, (4h) crystallographic site, propagation vectors $\mathbf{k} = (0, 0, 0)$ and $\mathbf{k} = (0, 0, 1/2)$. We have $\Gamma = \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5 + \Gamma_6 + \Gamma_8 + 2\Gamma_9 + \Gamma_{10}$ for $\mathbf{k} = (0, 0, 0)$ and $\Gamma = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_5 + \Gamma_7 + \Gamma_8 + \Gamma_9 + 2\Gamma_{10}$ for $\mathbf{k} = (0, 0, 1/2)$ [8]. This table indicates the correspondence between magnetic representations Γ_i, $\mathbf{k} = (0, 0, 0)$ and Γ_j, $\mathbf{k} = (0, 0, 1/2)$ for which the magnetic monents of uranium atoms in $z = 1/2$ are identical (see Fig. 4)

$\mathbf{k} = (0, 0, 0)$	$\mathbf{k} = (0, 0, 1/2)$
Γ_2	Γ_3
Γ_3	Γ_2
Γ_4	Γ_1
Γ_5	Γ_8
Γ_6	Γ_7
Γ_8	Γ_5
Γ_9	Γ_{10}
Γ_{10}	Γ_9

identical to the crystallographic one, i.e. the propagation vector is $\mathbf{k} = (0, 0, 0)$. Magnetic group theory with $\mathbf{k} = (0\ 0\ 0)$ leads to the magnetic ordering schemes drawn in Fig. 4 (see [8] for $\mathbf{k} = (0, 0, 1/2)$). Let us note that, if the irreducible representations Γ_i ($i = 1$–10) are identical for $\mathbf{k} = (0, 0, 0)$ and $\mathbf{k} = (0, 0, 1/2)$, the basis vectors are different: the relationships between the two cases are listed in Table 3.

Comparing the results obtained for the above mentioned magnetic structures (basis vectors of irreducible magnetic representations), we can conclude that at 1.5 K the magnetic structure of U_2Pd_2In is

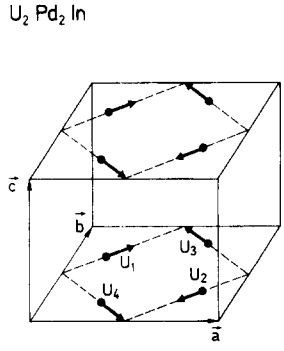

Fig. 5. Magnetic structure of U_2Pd_2In at low temperature. Only magnetic atoms (uranium) are drawn.

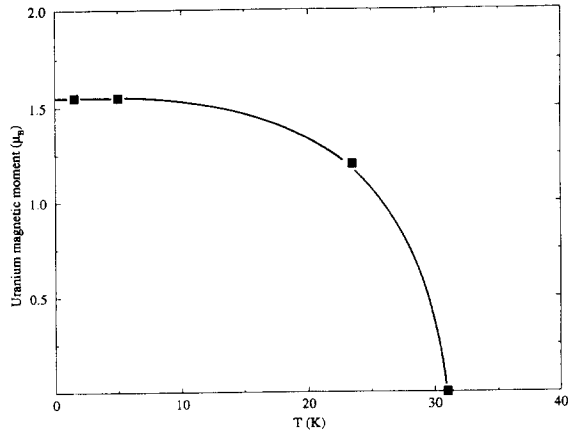

Fig. 6. Thermal variation of the uranium magnetic moment in U_2Pd_2In. The line in this figure results from a mean field approximation calculation of the magnetic moment, with a $S = 1/2$ magnetic ground state, an ordering temperature $T_N = 31$ K and a saturated magnetic moment equal to 1.55 μ_B. This line must be considered only as a guide for the eyes.

described by the $\mathbf{k} = (0, 0, 0)$ Γ_8-model ($R_M = 6.1\%$) with $M_U = 1.55(5)$ μ_B (Fig. 5).

Even if all magnetic space-groups were not considered in Ref. [10] (Γ_9 omitted), the same magnetic structure is obtained for U_2Pd_2In in this work and Ref. [10], with an identical value M_U of the uranium magnetic moment at low temperature: 1.55(5) μ_B and 1.6(1) μ_B, respectively. A direct comparison of experimental data (Fig. 3, this work; Fig. 6d, Ref. [10]) shows however that our NPD data have been obtained with a better statistics, as reflected by the uncertainties on M_U.

The temperature dependence of the uranium magnetic moment is displayed in Fig. 6, giving an ordering temperature $T_N \leq 31$ K, which is smaller than the Néel temperature determined by the magnetic susceptibility and specific heat measurements [4–6].

4. Discussion

Neutron studies performed on U_2Ni_2Sn [8], U_2Ni_2In (this study), U_2Pd_2Sn [9,10] and U_2Pd_2In (Ref. [10], this study] show that three different types of magnetic structures have been obtained for the so far investigated 2:2:1 compounds.

This neutron powder diffraction study of the magnetic structures of U_2Ni_2In and U_2Pd_2In intermetallics shows that the uranium magnetic moments in U_2Ni_2In and U_2Pd_2In are perpendicular to the **c**-axis and form an arrangement either described as the $\mathbf{k} = (0, 0, 1/2)$ Γ_3-model for U_2Ni_2In [8] or as the $\mathbf{k} = (0, 0, 0)$ Γ_8-model for U_2Pd_2In (Fig. 4). A characteristic feature of these two magnetic moment arrangements is that the U sites have their moments directed along the C_{2v}-axis, the easy directions predicted by the crystal field theory [8].

In the equiatomic uranium intermetallic compounds UTM, the U magnetic moments almost invariably lie in a direction perpendicular to the shortest U–U link [13]. This empirical rule is observed here for U_2Ni_2In (d_1(U–U) = c < d_2(U–U) = $2\sqrt{2}\, x_U a$); the situation is less evident for U_2Pd_2In, where at $T = 53$ K these two distances are equal. A precise determination, with high resolution neutron powder diffraction, of the thermal variation of the crystal parameters a, c and x_U would be necessary to conclude definitively on the validity of this 'distance' rule in U_2Pd_2In.

The uranium magnetic moment at $T = 1.5$ K is equal to 0.85 μ_B in U_2Ni_2In and 1.55 μ_B in U_2Pd_2In. These values are both lower than $g_J J = 3.27$ μ_B expected for the U^{3+} free ion magnetic moment, but compare to 1.05 μ_B and 2.0 μ_B obtained in U_2Ni_2Sn [8] and U_2Pd_2Sn [10], respectively. As in other uranium intermetallic compounds [14,15], these values for the uranium magnetic moment are due to 5f–5f and/or 5f–ligand states overlap.

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