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# Modulated magnetic structures in $UPd_2Ge_2$

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Neutron diffraction study of polycrystalline $UPd_2Ge_2$ compound with the tetragonal body centered $ThCr_2Si_2$-type crystal structure shows successive modulated magnetic phases below $T_N \simeq 135$ K. For $T \leq 80$ K, the propagation wave-vector **k** is locked to the commensurate value $\mathbf{k}=(0,0,k_z=3/4)$; for $T>80$ K $k_z$ becomes incommensurate varying with temperature from 0.75 to ~ 0.717 at 130 K. For $T<50$ K, the magnetic structure is well approximated by a squared modulation; above 50 K it transforms continuously up to 95 K where it becomes purely sinusoidal. Below $T_N$, the uranium magnetic moments are always parallel to the tetragonal c-axis.

## 1. Introduction

In the last decade an extensive amount of research work has been dedicated to a series of ternary intermetallic $MT_2X_2$ compounds, where M is a lanthanide or actinide, T is a transition metal and X is a group III, IV, or V element (B, Al, Si, Ge, P, As, Sb).

The tetragonal $ThCr_2Si_2$-type compound $UPd_2Ge_2$ is antiferromagnetic below 140 K. The magnetic moment ordering in $UPd_2Ge_2$ is represented by a static longitudinal wave propagating along the c-axis of the tetragonal crystal lattice with the wavevector $k=(0,0,0.748(10))$. The type of the magnetic structure does not change in the temperature region 4.2 K - $T_N$. [1]

Magnetic measurements performed by various authors give different results. In paper [2] below $T_N=140$ K the magnetization curves have a complicated character as a function of temperature and magnetic field. At T=4.2 K the magnetization increases with increase of the magnetic field; for a constant applied field (H=1 T) two broad maxima are observed in the temperature regions: 20-50 K and 50-80 K. Tien et al. [3] indicated $T_N=140$ K and additionally magnetic state changes near 50 K and 70 K whereas Duh et al. [4] indicated changes of the magnetic state at 20 K and 80 K.

In order to clarify these contradictions we have decided to make an extensive study of $UPd_2Ge_2$ as a function of temperature collecting better - resolution neutron data.

## 2. Experiment and results

Experiments were carried out on polycrystalline samples, as reported in the previous paper [1]. AC magnetic susceptibility $\chi_{ac}$ measurements were carried out by the mutual inductance method at frequency 122 Hz of alternating magnetic field $H_{exc}$. The neutron diffraction data were obtained with the neutron powder diffractometer G4.1 at the Orphée reactor (Laboratoire Léon Brillouin, Saclay) at an incident neutron wavelength of 2.426 Å. All the recorded neutron diagrams were obtained in increasing temperature from 1.4 K to 143 K except the two ones collected at 122 K and 91 K in decreasing temperature. Neutron scattering lengths were taken from the Sears work [5] and $U^{3+}$ form factor was calculated in the dipolar approximation with $<j_o>$ and $<j_2>$ taken from Freeman et al. [6]. Neutron data have been analyzed with the Rietveld-type Fullprof program [7].

In fig. 1 we show AC magnetic susceptibility $\chi(T)$ and reciprocal magnetic susceptibility $\chi^{-1}$ (T) respectively. Above 200 K the reciprocal magnetic susceptibility obeys the Curie-Weiss law. Near T=175 K a broad maximum is observed for $\chi$ (T). Below 100 K two maxima exist at 70 K and 83 K respectively, together with a small anomaly near 25 K.

The neutron diffraction pattern recorded and refined at $T>T_N$ (T=143 K, fig. 2a) confirms that $UPd_2Ge_2$ has the tetragonal $ThCr_2Si_2$-type structure with I4/mmm space group ($R_N$=2.2%) and atoms in the

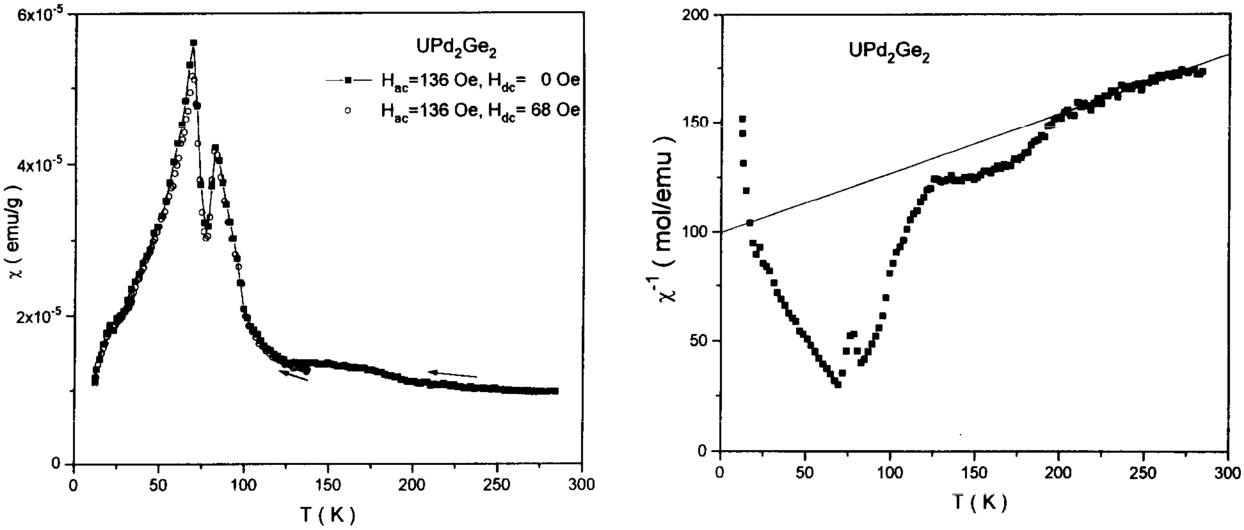


Fig. 1. Temperature dependence of the ac magnetic susceptibility and reciprocal susceptibility of $UPd_2Ge_2$.

following crystallographic positions: U in 2(a): 0,0,0; Pd in 4(d): 0,1/2,1/4; 1/2,0,1/4; Ge in 4(e): 0,0,z; 0,0,-z. The refined germanium position parameter z is 0.3816(2) at 143 K and remains constant down to the lowest temperature 1.4 K.

The thermal variation of the refined $UPd_2Ge_2$ lattice parameters a and c is displayed in fig. 3; we can clearly notice an anomaly on the a parameter near 25 K.

At the lowest temperature 1.4 K a fairly large number of magnetic peaks can be seen on the recorded neutron diffraction pattern (fig. 2b); the position of the most intense of them can be indexed with a propagation vector $\mathbf{k}=(0,0,k_z)$ with $k_z=0.750(1)$ i.e $k_z=3/4$, in agreemant with the previous neutron data [1]; but due to a better resolution we can also observe small supplementary magnetic peaks which can be indexed as high order satellites of the propagation vector $\mathbf{k}=(0,0,3/4)$.

The absence of any $00l^{\pm}$ and $00l^{+3}$ magnetic Bragg

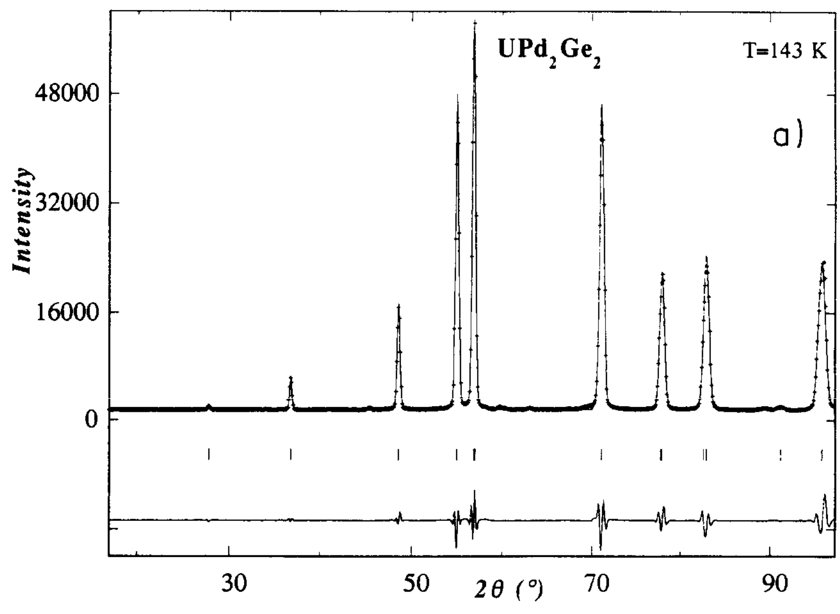


Fig. 2. *Continued on p. 925.*

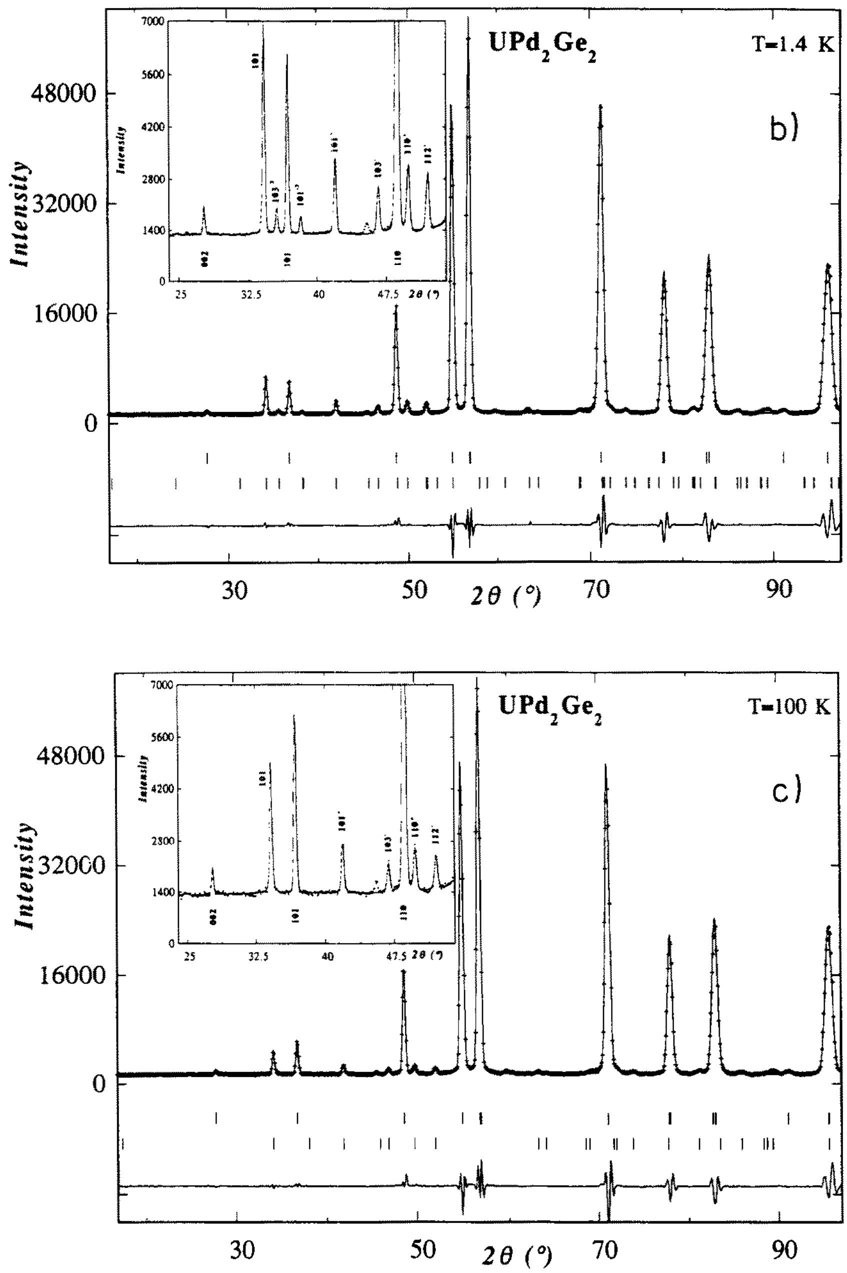


Fig. 2. Observed and calculated neutron diffraction patterns for $UPd_2Ge_2$ ($\lambda$=2.426 Å) at T=143 K (paramagnetic region - fig. 2a), T=100 K (longitudunal sinusoidal magnetic structure - fig. 2c) and T=1.4 K (longitudinal «squared» magnetic structure - fig. 2b). For each of these diagrams, the symbols represent the observed points, the solid lines the calculated profile and the difference between observed and calculated profiles. The ticks correspond to $2\theta_{hkl}$ Bragg positions, either of nuclear (upper ticks) and/or magnetic (lower ticks) origin. The inerts at 1.4 K and 100 K enlarger the neutron counts in the $24^0$ - $54^0$ $2\theta$ range.

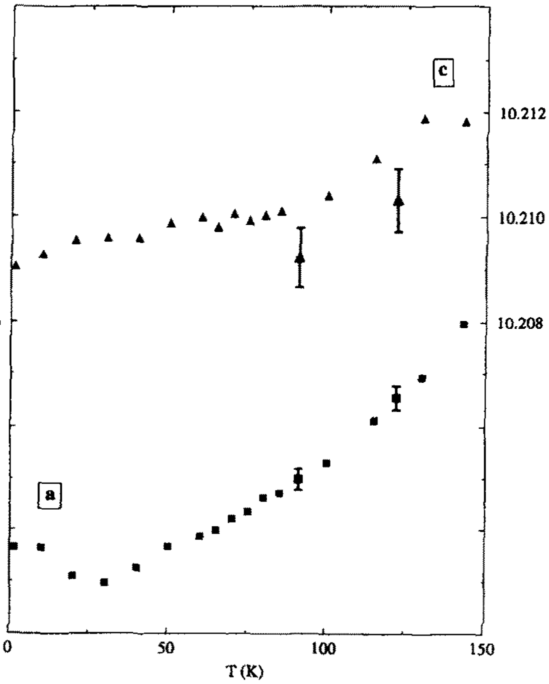


Fig. 3. Temperature dependence of the $UPd_2Ge_2$ lattice constants a and c.

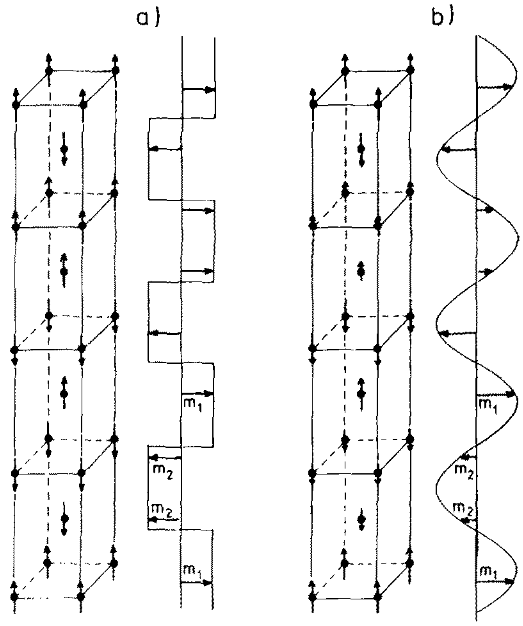


Fig. 4. Modulated magnetic structures of $UPd_2Ge_2$: (a) square at low temperature ($T \leq 50$ K) and (b) sine modulated in the 95 K - 135 K T region for the sake of simplicity a commensurate wave vector has been used in each case ((k=3/4$\bar{_c}$*).

peak implies that the uranium magnetic moments at T=1.4 K are parallel to the tetragonal c-axis. The existence of high order ( >1) satellites clearly indicates that the $UPd_2Ge_2$ magnetic structure at T=1.4 K is not purely sinusoidal. The obtained magnetic structure is shown in Figure 4.

Two values of magnetic moments ($m_1$, $m_2$) are necessary to describe this magnetic structure (sequence $m_1$, $m_2$, $m_2$, $m_1$, $-m_1$, $-m_2$, $-m_2$, $-m_1$), with $m_1 = m_2$ in the case of a pure «squared» structure. This description ($m_1$, $m_2$) is equivalent to the wave vector description, which provides two parameters, $M_1$ and $M_3$ (see figure 7a) directly connected to the «first» and «third» order satellites intensities. Let us notice however that for the commensurate **k**=3/4**c***  magnetic structure, neither «first» nor «third» order satellites are pure Bragg peaks: the $n^{th}$ order is in that case always contaminated with $n+8n'^{th}$ orders ($n' \geq 0$, $n' \leq 0$).

The relationhips between $M_1$, $M_3$ and $m_1$, $m_2$ are the following:

$$m_1 = M_1 \sin\Phi - M_3 \cos\Phi$$
$$m_2 = M_1 \cos\Phi + M_3 \sin\Phi$$

with $\Phi = 2\pi \mathbf{k}.1/4\mathbf{c}$. These relationships are valid whatever the commensurability (**k**=3/4**c***) or incommensurability character of the magnetic wave vector **k**. For incommensurate **k** however these relationships need $M_3=0$ (pure sinusoidal case).

At T=1.4 K, we got $M_1$=3.04(6) $\mu_B$, $M_3$=1.15(8) $\mu_B$; with $R_N$=2.1% and $R_M$=4.3%. These points are shown in figure 7a, and the magnetic moments $m_1$ and $m_2$ in Figure 7b.

When temperature increases from 1.4 K to 50 K, the propagation vector remains locked to the commensurate value k=(0,0,3/4) (fig. 5) and the high order harmonics peaks remain quasi constant (fig. 6): the proposed "squared" magnetic modulation at 1.4 K is thus still valid up to 50 K with just a slight decreasing of the magnetic moments on the uranium atoms (fig. 7b).

From 50 K to 80 K as $k_z$ is still locked, the high-order harmonics peaks decrease quite rapidly (fig. 6), and correspondingly the $M_3$ magnetic component (fig. 7a); the magnetic structure varies continuously from the "squared" modulation to a more sinusoidal one.

At 80 K, $k_z$ abruptly decreases from 0.75 becoming incommensurate and varying with temperature down to $k_z$=0.717(5) at 130 K (fig. 5); some high-order harmonics are still present up to (95-100) K (fig. 7a, 7b).

Above 95 K as the $k_z$ component still decreases the modulation becomes purely sinusoidal with the disappearing of the high-order harmonics (fig. 7b). At 100 K for example (fig. 2c) we obtained $k_z$=0.7302(17) and a purely sinusoidal modulation whose amplitude is 2.49(8) $\mu_B$, with $R_N$=2.2 %, $R_M$=4.9 %.

The temperature evolution of the main magnetic reflections $101^-$ and $101^+$ (fig. 6) gives a Néel temperature $T_N \simeq 135$ K. The magnetic structure models below 50 K and above 95 K are displayed on fig. 4.

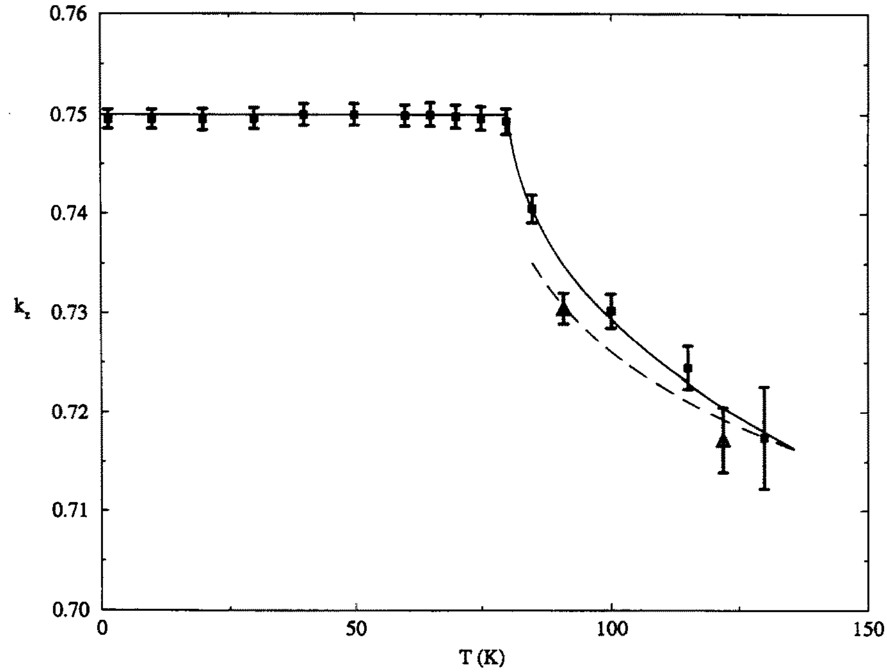


Fig. 5. Temperature dependence of $k_z$. $\mathbf{k}=(0\ 0\ k_z)$ is the $UPd_2Ge_2$ magnetic structure wave vector. The continuous and broken lines in this figure correspond to increasing and decreasing temperature respectively.

Finally we can also notice on fig. 5 that the locking (or commensurate - incommensurate) transition at 80 K has a first order character which is reflected in hysteresis effects for the $k_z$ and c thermal variations.

### 3. Symmetry analysis

The magnetic representation for the I4/mmm ($D_{4h}^{17}$) symmetry group and 2(a) positions of magnetic atoms and for $\mathbf{k}=(0,0,k_z)$ can be presented as direct sum of two irreducible representations: one dimensional $\tau_2$ and two dimensional $\tau_5$. The calculated magnetic modes are given in Table 1.

The best agreement with the experimental data gives the modulated magnetic structure with moments along the z-axis, which belongs to the one-dimensional irreducible representation $\tau_2$, two arms of $\mathbf{k}$ vector star $\{k_{10}\}$ and mixing coefficients getting the order parameter p=(c,-c):

$$S_{1+t}=2ce_z\cos(\mathbf{kt})$$
$$S_{2+t}=2ce_z\cos(\pi\mu+\mathbf{kt})$$

Below 80 K $k_z$=0.75 and the magnetic structure becomes commensurate with the crystal lattice, and magnetic cell becomes 4-times larger then crystal cell.

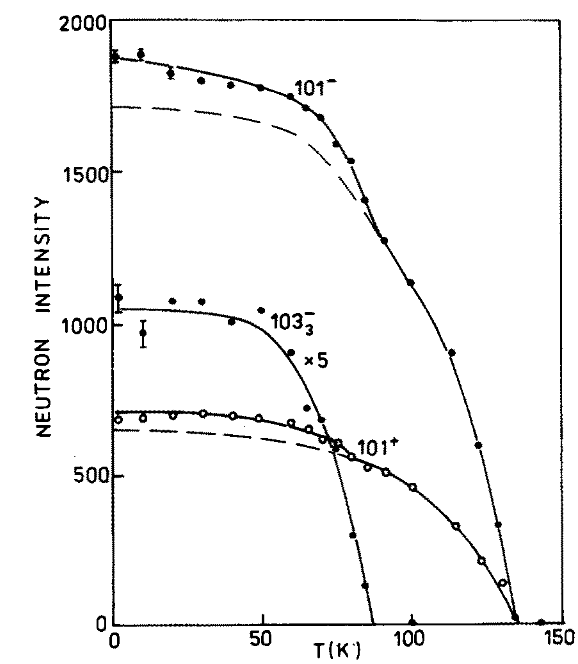


Fig. 6. $UPd_2Ge_2$: temperature dependence of $101^-$, $101^+$ and $103^{3-}$ magnetic Bragg peaks intensities.

### 4. Discussion

Apart the previously observed antiferromagnetic - paramagnetic transition at $T_N \sim 135$ K, our neutron investigation on $UPd_2Ge_2$ has revealed: first a main

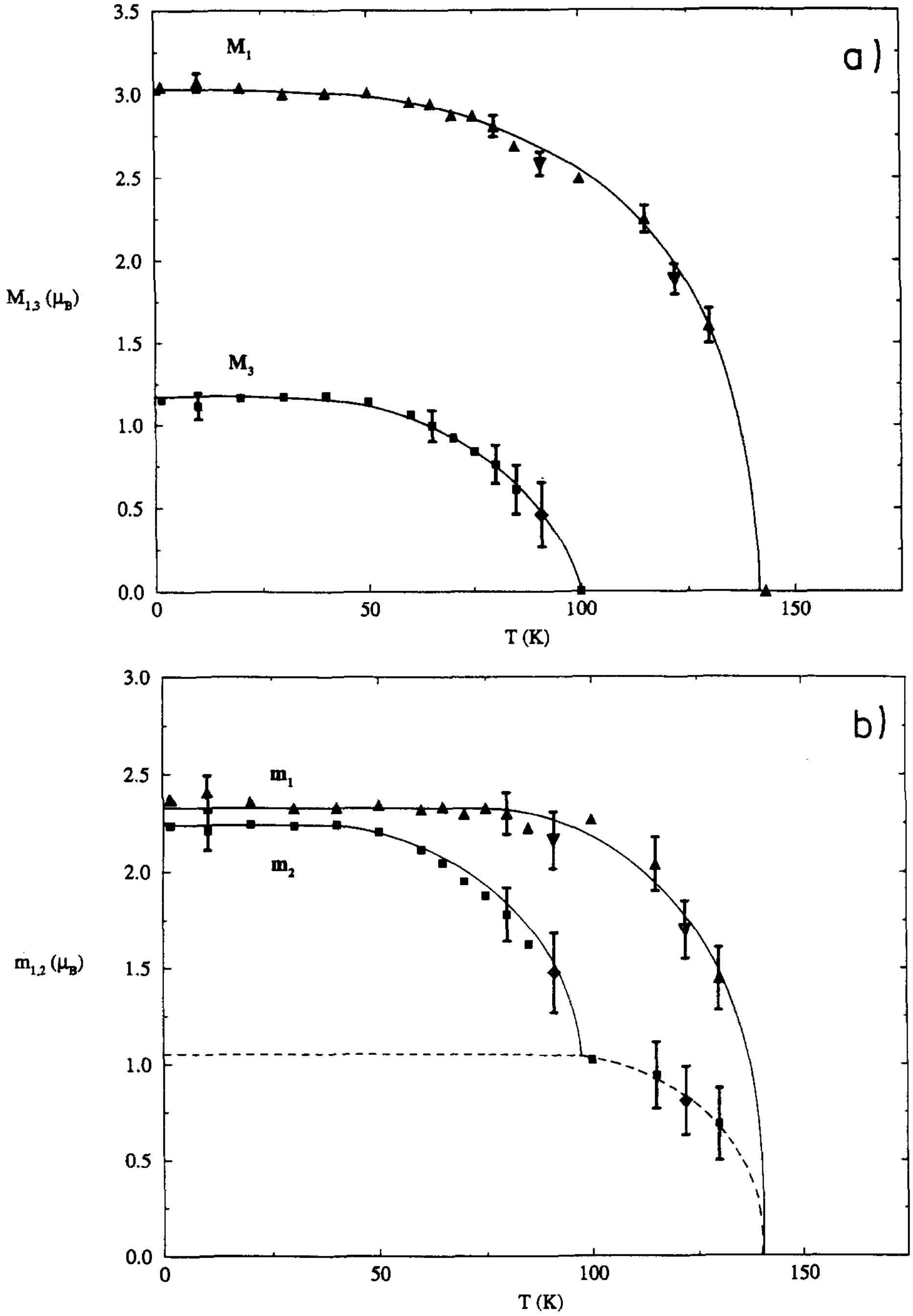


Fig. 7a. $UPd_2Ge_2$: temperature dependence of the $M_1$ and $M_3$ magnetic parameters. The filled and open symbols correspond to increasing and decreasing temperature respectively.

Fig. 7b. $UPd_2Ge_2$: temperature dependence of the $m_1$ and $m_2$ uranium magnetic moments. The filled and open symbols correspond to increasing and decreasing temperature respectively; the dashed line is the theoretical curve for $m_2$ variation in the case of a purely sinusoidal magnetic structure. A totally squared magnetic structure is characterized by $m_1 = m_2$.

**Table 1.** *Modes belonging to the $\tau_2$ and $\tau_5$ - representations of the I4/mmm ($D_{4h}^{17}$) group and* $\mathbf{k}_1=(0,0,k_z)$; $\mathbf{k}_2=-\mathbf{k}_1$ and 2(a) positions.

| | | | 1:(0,0,0) | 2:(0.5, 0.5, 0.5) |
|---|---|---|---|---|
| $\mathbf{k}_1$ | $\tau_2$ | $\Psi_1$ | (0, 0, 1) | (0, 0, $\exp(i\pi\mu)$) |
| | $\tau_5$ | $\Psi_1$<br>$\Psi_2$ | (1,-i, 0)<br>(1, i, 0) | ($\exp(i\pi\mu)$, $-i\exp(i\pi\mu)$, 0)<br>($\exp(i\pi\mu)$, $i\exp(i\pi\mu)$, 0) |
| $\mathbf{k}_2$ | $\tau_2$ | $\Psi_1$ | (0, 0,-1) | (0, 0, $-\exp(i\pi\mu)$) |
| | $\tau_5$ | $\Psi_2$<br>$\Psi_2$ | (1, i, 0)<br>(1,-i, 0) | ($\exp(-i\pi\mu)$, $i\exp(-i\pi\mu)$, 0)<br>($\exp(-i\pi\mu)$, $-i\exp(-i\pi\mu)$, 0) |

$\mu=k_z$

magnetic transition at 80 K between commensurate and incommensurate modulated structures; secondly two other characteristic transformation temperatures: T=50 K and T=95 K. Below 50 K the magnetic structure does not change and consists of a "squared" modulation; above 95 K the modulation is purely sinusoidal the $UPd_2Ge_2$ magnetic structure is intermediate between these two structures in the 50 K-95 K temperature range. Finally a small anomaly in the a parameter thermalvariation has been evidenced at 25 K but without any noticeably correlated change in the magnetic structure.

Comparing the magnetic susceptibily and magnetization measurements results oneside and NPD results on the other we can say that the neutron technique agrees with the $T_N$ value of 140 K; it is more difficult to ascribe precisely the anomalies noted on magnetic measurements to a magnetic transition or transformation observed with neutrons; a single crystal neutron study could only link more clearly the two types of measurements.

In all the magnetic phases observed in $UPd_2Ge_2$ the uranium magnetic moments are aligned along the tetragonal axis and are ordered in ferromagnetic (001) planes. This type of magnetic order exists if magnetic exchange is related to strong 5f - 6d hybridization and shortest U-U distances in the basal planes (equal to the lattice parameter a).

A transition between two magnetic phases is often observed in large number lanthanide and actinide $ThCr_2Si_2$-type compounds [9-11].

Oscillatory character of the magnetic ordering scheme observed in $UPd_2Ge_2$ suggests that magnetic interactions via conduction electrons postulated by the well-known theory of Ruderman-Kittel-Kasuya-Yoshida (RKKY) should be called for to explain the stability of the above structure. In the case of the lanthanide compounds the change of an incommensurate structure near $T_N$ towards a commensurate one at low temperatures is interpreted on the basis of the realistic mean field model which takes into account the periodic-exchange-field and crystal-field effects [12]. Because the crystal fields effects play the key role in understanding the magnetism of the $UT_2X_2$ ternaries [12], the model proposed by Gignoux and Schmitt may also explain [13] the observed change of the magnetic structure in $UPd_2Ge_2$.

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