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INVITED PAPER

ELECTRONIC AND MAGNETIC PROPERTIES OF URANIUM–PLATINUM INTERMETALLIC COMPOUNDS

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A review is presented of specific heat, high-field magnetisation, resistivity, high-temperature susceptibility and neutron scattering experiments on various uranium–platinum compounds. Spin-fluctuation contributions are found to be present in the low-temperature specific heat of UPt_2, UPt_3 and UPt_5; long-range magnetic order is only observed for UPt. Recent results of neutron scattering experiments on UPt and UPt_3 are discussed. The magnetic structure of UPt is still puzzling. Antiferromagnetic correlations in UPt_3 are most likely to be found along the *b*-axis in the hexagonal plane.

1. Introduction

Interest in the magnetism and superconductivity of the uranium–platinum compounds started with the early work of Matthias et al. [1] in 1969 on UPt that was followed by an extended study of Huber et al. [2] in 1975 of the pressure effects on the magnetic properties of this compound. Subsequent studies by Frings and Franse [3] in 1985 revealed a competition between ferro- and antiferromagnetism and a close relation between structural and magnetic properties. Magnetism of UPt is of an interesting nature; its study, however, is hampered by the cumbersome metallurgical properties of this peritectoidal compound that is formed by a solid-state reaction between U and UPt_2. Lawson et al. [4] recently made an attempt to deduce the magnetic structure of UPt from neutron diffraction measurements. In this paper we shall present additional information from neutron diffraction studies performed in the high-flux reactor of the ILL in Grenoble.

The most prominent member of this series of compounds, however, is UPt_3, a congruently melting compound that can rather easily be prepared as a bulk single crystal. Interest in the thermal and magnetic properties of this compound started with the publication of specific-heat and susceptibility data in 1983 by Frings et al. [5,6] in which the large value of 420 mJ/mol K^2 was reported for the electronic coefficient γ and in which an interpretation of the low-temperature specific heat in terms of spin fluctuations was mentioned. The publication of a superconducting transition in UPt_3 in 1984 by Stewart et al. [7] largely intensified the activity in the study of this compound and of the heavy-fermion superconductors in general. The combination of large spin-fluctuation contributions to the specific heat and the occurrence of superconductivity is so unusual that suggestions for pair bonding of the electrons in the superconducting state otherwise than by electron–phonon interactions are frequently heard. An extensive study of UPt_3 has recently been finished by De Visser [8]. Inelastic-neutron-scattering experiments by Aeppli et al. [9] suggest antiferromagnetic correlations between spins in adjacent planes of this hexagonal material. Experiments by Frings et al. [10], however, put some question marks concerning this conclusion.

The remaining two compounds, UPt_2 and UPt_5, seem less exiting at first sight. A thorough investigation of these systems, however, certainly will help in improving the understanding of the other two compounds.

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2. Structure and electronic properties

A survey of the crystallographic data of the uranium–platinum compounds is presented in table 1. Since nearest uranium–uranium distances, d_{U-U}, range from 3.61 Å in UPt up to 5.25 Å in UPt_5, one expects an increasing localisation of the uranium 5f electrons with increasing platinum content and, as a consequence, a gradual change from itinerant-electron behaviour to localised magnetism. Ferromagnetism, possibly of an itinerant nature, is observed for UPt, superconductivity for UPt_3, whereas UPt_2 and UPt_5 do not order at all.

The electronic properties of these compounds will be discussed on the basis of specific heat, magnetisation, resistivity and susceptibility experiments. Specific heat data on this series of uranium–platinum compounds have previously been reported by Frings et al. [5]. In subsequent papers by Frings and Franse [3] and by De Visser et al. [11], the specific heat data of UPt and UPt_3 have been discussed, respectively. In the present paper we shall concentrate on the specific-heat results for UPt_2 and UPt_5. Details of the specific-heat data are shown in fig. 1 in a plot of

Table 1
Some crystallographic parameters of uranium–platinum alloys

Compound	Structure	d_{U-U} (10^{-10} m)	Molar volume (10^{-5} m^3/mol f.u.)
UPt	orthorhombic (CrB)	3.61	26.61
UPt_2	orthorhombic ($InNi_2$)	3.81	33.62
UPt_3	hexagonal $MgCd_3$)	4.12	42.43
UPt_5	cubic ($AuBe_5$)	5.25	61.53

c/T vs. T^2 for temperatures below 10 K. As for UPt_3, the specific heat of UPt_2 and UPt_5 shows a very weak field dependence, especially in the temperature region where upturns in the c/T vs. T^2 plots are observed. The absence of any significant field effect proofs that these low-temperature deviations from a straight line in the c/T vs. T^2 plot are not due to impurity contributions. The upturn in the low-temperature specific heat of UPt_3 can successfully be described by an additional $T^3 \ln(T/T^*)$ term. A similar analysis has also been applied to the data of UPt_2 and UPt_5, resulting in values for the specific-heat parameters as presented in table 2. To further evaluate the specific-heat data, fits have been made in the

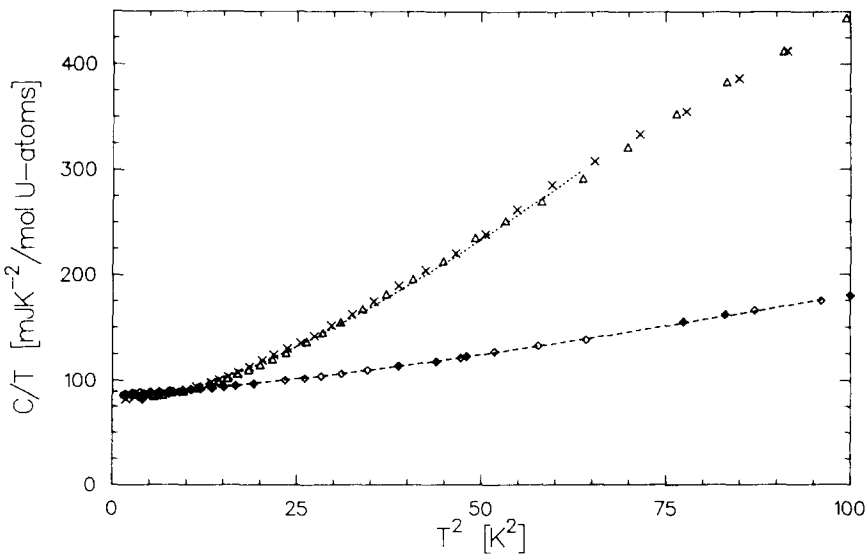

Fig. 1. Low-temperature specific heat of UPt_2 (◇, ◆) and UPt_5 (△, ×) plotted as c/T vs. T^2 in zero magnetic field and in an applied field of 5 T, respectively. The broken and dotted curves represent the fit of the zero-field data resulting in the parameters as listed in table 2.

Table 2
Specific-heat data of UPt_2 and UPt_5; c/T fitted to $\gamma + \beta^* T^2 + \delta T^2 \ln T$ (c in mJK^{-1}/mol f.u., T in K); T^* is defined by $\beta^* = \beta - \delta \ln T^*$; β is evaluated from a fit of the specific heat data to $c/T = \gamma + \beta T^2$ in the higher-temperature range

Compound	Temperature range	γ	β^*	δ	β	T^*
UPt_2	1.3–10 K	89 (1)	−0.4(3)	0.6(1)	1.03	10
UPt_5	1.3–4.8 K	95.0 (6)	−5.2(2)	4.1(1)	4.2	10
	1.3–8 K	92 (1)	−4.0(2)	3.5(1)	4.2	10

temperature interval between 5 and 10 K to the expression $c = \gamma T + \beta T^3$ in order to deduce values for the phonon coefficient β. These β values result in values for the Debye temperature of 177 and 140 K for UPt_2 and UPt_5, respectively. The characteristic temperature T^* amounts to 10 K in both systems.

The low-temperature properties of the uranium–platinum compounds have further been in-

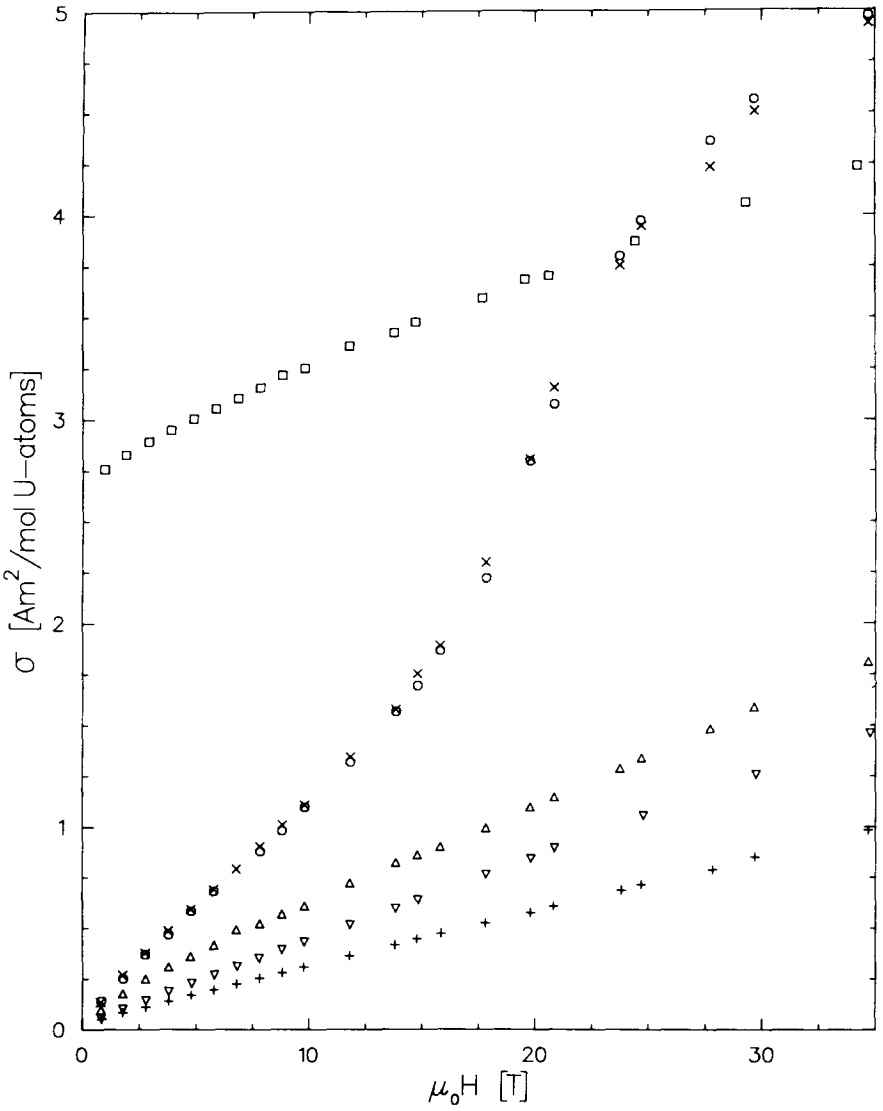

Fig. 2. Magnetisation curves of uranium–platinum compounds at 4.2 K: UPt (□), UPt_2 (▽), UPt_3 (*a*-axis (×), *b*-axis (○), *c*-axis (△)) and UPt_5 (+).

vestigated in high-field magnetisation studies up to 35 T and in resistivity measurements down to 1.4 K. The results of the magnetisation measurements at 4.2 K are presented in fig. 2. Values for the spontaneous magnetic moment (UPt) and for the initial (UPt_2, UPt_3 and UPt_5) or the differential (UPt) susceptibility are listed in table 3. The electrical resistivity of polycrystalline samples of UPt_2, UPt_3 and UPt_5 is shown in fig. 3 for temperatures below 10 K. A double logarithmic plot for UPt_2 and UPt_5 indicates a quadratic temperature dependence for both compounds with values for the coefficient of the term quadratic in temperature of 0.09 and 0.01 $\mu\Omega$ cm K^{-2}, respectively. This coefficient is considerably smaller for these two compounds than the values reported for UPt_3 (1.6 along the *a*- and *b*-directions, 0.7 along the hexagonal *c*-axis). An overall picture of the resistivity of the uranium–platinum compounds for temperatures below 300 K is shown in figs. 4a and b. The magnetic ordering of UPt is clearly indicated by the abrupt change in slope at 27 K. Values for the RRR's amount to 3.5, 14 and 5.6 for UPt, UPt_2 and UPt_5, respectively. Considerably higher values have been obtained for monocrystalline UPt_3 samples [13].

Table 3
Values for the effective magnetic moment μ_{eff} (μ_B/f.u.), for the spontaneous magnetic moment σ_0 (μ_B/f.u.), for the (differential) magnetic susceptibility at 4.2 K $\chi_{4.2}$ ($10^{-9}m^3$/mol f.u.), for the coefficient of the electronic term in the specific heat γ (mJK^{-2}/mol f.u.) and for the ratio $\chi_{4.2}/\chi(\gamma)$, where $\chi(\gamma)$ is given by: $\chi(\gamma) = 3\mu_0\mu_B^2\gamma/\pi^2k_B^2$

Compound	μ_{eff}	σ_0	$\chi_{4.2}$	γ	$\chi_{4.2}/\chi(\gamma)$
UPt	3.5	0.5 [a], 0.9 [b]	45	115	2.5
UPt_2	3.5		51	89	3.3
UPt_3	2.8		103 [c]	422	1.9
UPt_5	4.3		34	95	2.0

[a] From bulk-magnetisation measurements on a polycrystalline sample.
[b] From neutron-diffraction measurements.
[c] For polycrystalline material.

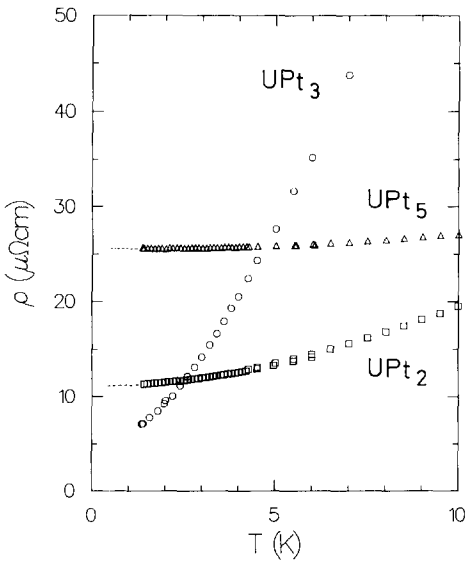

Fig. 3. Electrical resistivity of polycrystalline UPt_2 (□), UPt_3 (○) and UPt_5 (△) below 10 K; the dashed lines represent data taken in a ^{3}He cryostat down to 300 mK.

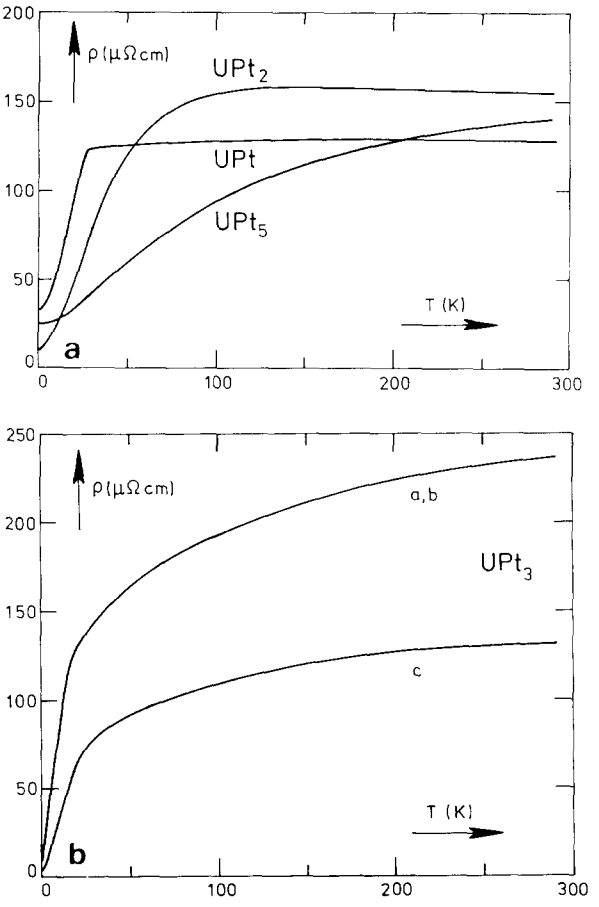

Fig. 4. Electrical resistivity vs temperature for UPt, UPt_2 and UPt_5 (a) and for monocrystalline UPt_3 along different crystallographic directions (b).

In addition to the low-temperature studies of specific heat, magnetisation and resistivity, high-temperature susceptibility measurements have been performed on the uranium–platinum compounds for temperatures up to 1000 K. The susceptibility data are presented in fig. 5 in a plot of χ^{-1} vs. T. All compounds approximate a Curie–Weiss behaviour at higher temperatures. With an exception of UPt_2, however, pronounced curvatures are observed. Values for the effective moments have been deduced from the slopes of the χ^{-1} vs. T curves at the highest temperatures. The results are collected in table 3. The effective moments for UPt and UPt_2 are within an L–S coupling scheme compatible with a $5f^2$ or $5f^3$ configuration. UPt_3 has an effective moment in between $5f^2$, $5f^3$ and $5f^1$, $5f^4$ configurations. The effective moment for UPt_5, however, cannot be accounted for by a particular 5f configuration. Moreover, the value for the paramagnetic Curie temperature is unreasonably large and negative for this latter compound. For that reason we conclude that in UPt_5 a large (temperature-independent) Pauli contribution to the susceptibility

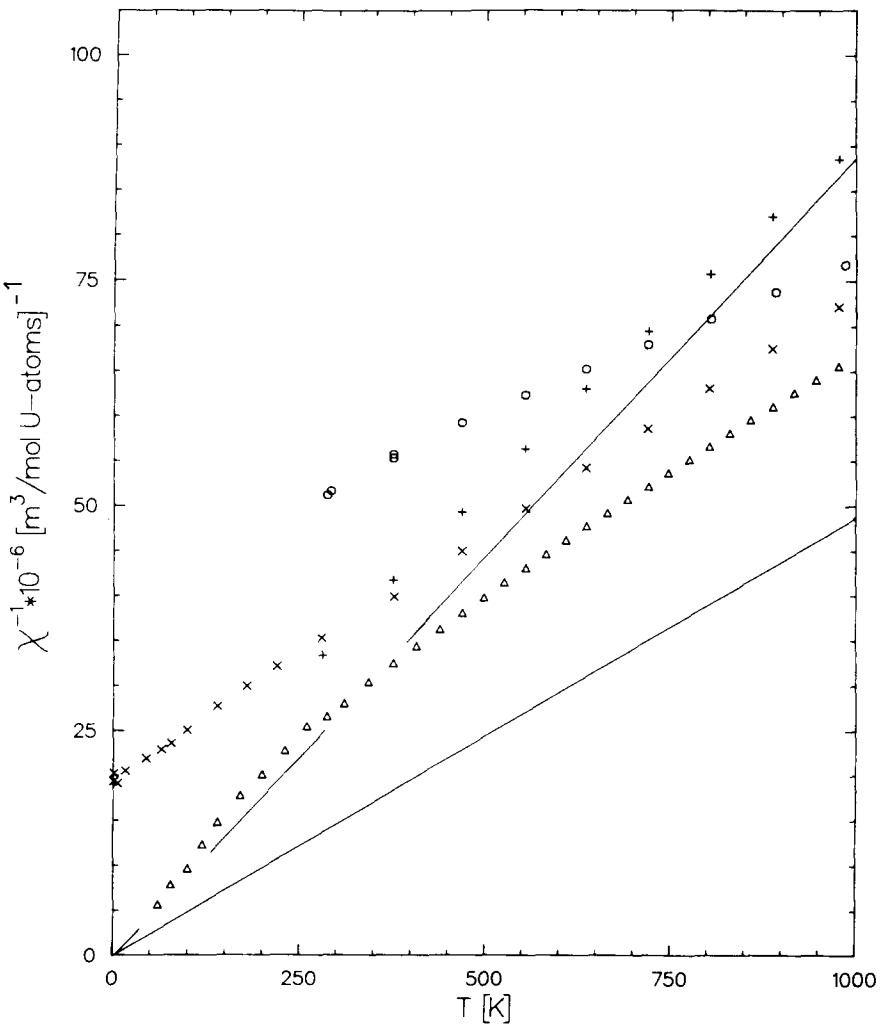

Fig. 5. Inverse susceptibility of uranium–platinum compounds below 1000 K: UPt (△), UPt_2 (×), UPt_3 (+) and UPt_5 (○); full lines represent the Curie behaviour for a $5f^3$ ($3.62\mu_B$) and a $5f^4$ ($2.68\mu_B$) configuration.

exists. Summarising the information that can be deduced from these experiments we conclude that UPt, the compound with the smallest value for d_{U-U}, is the only compound in this series showing long-range magnetic order. Although in the remaining compounds the conditions for localised 5f behaviour are more favourable, no magnetic order is observed. These compounds are believed to exhibit spin fluctuation phenomena. The upturns in the low-temperature specific heat as well as the large temperature effects on the electrical resistivity point to such a type of description. It is not clear whether the observed temperature dependence of the susceptibility has to be attributed to more or less localised 5f moments or to relatively narrow 5f bands at the Fermi level. The fact that the observed values for μ_{eff} of UPt and UPt_2 correspond with calculated values for various 5f configurations ($5f^3$ and $5f^2$) tends to be in favour of a local-moment description of these two compounds. The negative values for the paramagnetic Curie temperature are too large (in particular for UPt_2 and UPt_5) to be ascribed to an antiferromagnetic interaction between uranium moments. They might be connected with a compensating type of interaction between the localised uranium moments and the conduction electrons. The absence of any type of magnetic order in UPt_2 and UPt_5 is consistent with such a picture. Another consequence of the interaction between the 5f electrons and the conduction electrons can be a strong d–f hybridisation by which the localised 5f character disappears.

Magnetic order is well established in UPt, although experiments reveal a complex magnetic structure in which ferro- and antiferromagnetic interactions compete. High-pressure measurements as well as neutron diffraction experiments point to a close relation between structural and magnetic properties. Some satellites in the neutron diffraction spectrum which show pronounced magnetic contributions below the magnetic ordering temperature, still partially exist at temperature far above this ordering temperature. Some of these results will be discussed in the final part of this paper. Although no long-range order is found in UPt_3, the high-field magnetisation measurements as well as the measurements on palladium substituted UPt_3 compounds [14] reveal a strong tendency to antiferromagnetism. The combination of superconductivity and these antiferromagnetic correlations is one of the exciting properties of this latter compound.

3. Neutron-scattering data

Detailed neutron diffraction measurements at the Grenoble High-Flux reactor on the powder diffractometer D1B were already mentioned in ref. [3]. At temperatures above 30 K the diffraction pattern of the orthorhombic CrB structure is observed, with, in addition, some yet unidentified but temperature independent intensities. Upon cooling below 30 K the intensity of several Bragg peaks slightly increases apart from new satellites that develop. It is known from magnetic measurements that UPt undergoes two magnetic phase transitions at 19 and at 27 K. Therefore, we subtracted the intensity in the non-ordered state (as measured at 30 K) from the intensities measured at 4 and at 20 K, see fig. 6. The magnetic intensities on the nuclear Bragg peaks as well as the magnetic satellites are clearly visible in this plot. A fit of the difference in intensity between 4 and 30 K for nine Bragg reflections (020, 110, 021, 111, 040, 131, 002, 151, 132 and 130) results in a value for the ferromagnetic component of the magnetic moment of $(0.9 \pm 0.1)\mu_B$ per uranium atom along the c-axis. This result is in clear contradiction with the conclusions of Lawson et al. [4] who state, on the basis of a temperature-independent intensity on the 020 reflection, that the ferromagnetic moment should be parallel to the b-axis. It emerges from our fit that the magnetic intensity on the 020 reflection is very weak due to the weak structure-factor of the uranium lattice at this position. The magnetic intensities can be divided into two groups, one group that disappears upon heating at 19 K (A, E, F, G and J) the other one at 27 K (B, C, D, H, I and K). It turns out to be difficult to identify a unique q-vector to account for the high- (B, D and K) and low- (A, E, F, G and H) temperature satellites. The q-vector of $(\frac{1}{2}, 0, \frac{1}{2})$ as proposed by Lawson et al. could account for some of the magnetic satellites (B, D, F and K). However, these intensities do not all have the

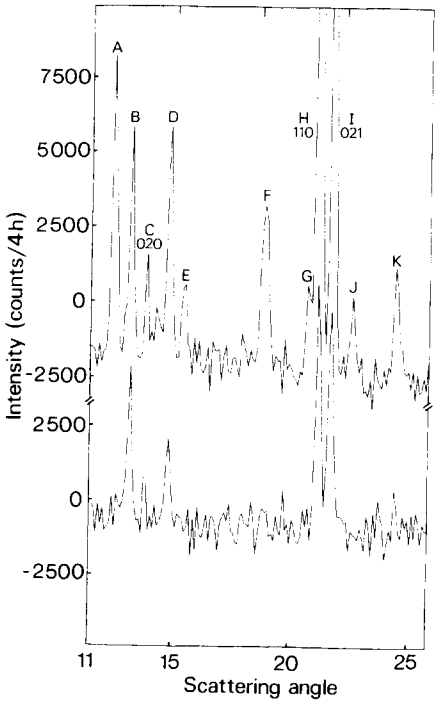

Fig. 6. Neutron-diffraction data for UPt; the intensity in the non-ordered state (as measured at 30 K) has been subtracted from the intensities measured at 4 K (upper curve) and 20 K (lower curve); the $|q|$-values (in Å^{-1} with $2\pi/a = 1.70845$, $2\pi/b = 0.58651$ and $2\pi/c = 1.43981$) for the different satellites are A: 1.059; B: 1.121; C (020): 1.173; D: 1.263; F: 1.615; G: 1.775; H (110): 1.806; I (021): 1.858; J: 1.932; K: 2.084; the maximum error in q is of the order of 0.008 Å^{-1}, the average error is about 0.003 Å^{-1}.

same temperature dependence which makes a description with one single q-vector questionable. Moreover, it turned out that the low-temperature satellites (B, D and K) decrease and the high-temperature satellites (A, E, F, G and H) increase in intensity upon application of hydrostatic pressures up to 5 kbar at 4.2 K. These results point to a pressure-induced transition from one magnetic structure to another one, in accordance with the high-pressure magnetisation measurements at 4.2 K. Finally we remark that even at room temperature small intensities, of the order of 10% of the low-temperature value, remain visible at the positions of the magnetic satellites.

Neutron experiments on the heavy-fermion superconductor UPt_3 reveal a weak magnetic scattering with a wide extension in q and energy space. The observation of magnetic intensities, demonstrating antiferromagnetic correlations along the c-direction was recently reported by Aeppli et al. [9]. The same scans as presented in the above-mentioned publication were performed at the ILL High-Flux reactor in Grenoble on INB and IN20, using unpolarised as well as polarised neutrons. This study [10] did not reveal such a pronounced q-dependence of the scattered intensity (i.e. maximum intensity for $q = (0, 0, 1)$ and $(0, 0, 3)$ and a minimum for $q = (0, 0, 2)$). It seems unlikely that the magnetic properties of the UPt_3 samples used in these neutron studies are different. Bulk measurements on polycrystalline and monocrystalline samples always yield identical results for the characteristic magnetic parameters. The antiferromagnetic correlations along the c-axis as reported by Aeppli et al. become even more puzzling in view of the recently reported antiferromagnetic order in UPt_3 with 5% Th [15] or Pd [16]. Antiferromagnetism is propagating along the b-axis (i.e. $q = (\frac{1}{2}, 0, 0)$) and not along the c-axis (i.e. $q = (0, 0, \frac{1}{2})$). Since the high-field magnetisation curves of UPt_3 and UPt_3 with 5% Pd differ only in the value of the "metamagnetic" transition field [17], we expect the magnetic character of these two systems to be rather similar. We suggest, for that reason, that antiferromagnetic correlations are more likely to be observed for UPt_3 along the b-axis.

Note added in the proof

Dommann et al. [18] recently reported a monoclinic structure for UIr that can be interpreted as a small distortion of the orthorhombic CrB structure. These authors suggested that similar distortion also may occur in UPt. The here-reported magnetic intensities that disappear at 27 K turn out to be at Bragg peak positions of a monoclinic structure. The small intensities that remain visible even at room temperature can now easily be understood as ordinary but very weak Bragg peaks. A preliminary analysis of our low temperature results within the monoclinic structure results in a (ferromagnetic) high-temperature phase with a moment of the order of 1 along the b axis. The satellites of the ordered low-temperature phase, however, could not yet be identified.

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