PRESSURE EFFECTS IN INTERMETALLIC URANIUM COMPOUNDS*

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High-pressure experiments are reported on various series of ferromagnetic intermetallic uranium compounds. Pressure effects in these compounds are compared with the results of high-pressure studies on 3d and 4f metals in order to establish the itinerant or localised nature of ferromagnetism in these compounds. Special attention is devoted to the equiatomic UPT compound in which complex magnetic phenomena are observed, including pressure-induced hysteretic effects.

1. Introduction

Pressure effects on the magnetic properties of various intermetallic uranium compounds have been discussed in several previous publications [1–3]. High-pressure experiments on the spontaneous magnetisation near zero temperature yield, in general, different results for d and f metal systems. Pressure effects in the ferromagnetic d metals are mostly negative and become especially large for materials in which ferromagnetism is weak. The negative pressure effects are directly connected in these metals with the positive magneto-volume relation: the formation of magnetic moments is accompanied by a relatively large increase of the atomic volume and vice versa. First-principle, spin-polarised band calculations on the pure elements Fe, Co and Ni result in values for the spontaneous magnetic moment and its pressure derivative that do agree satisfactorily with the experimentally observed values, see table I. For the weakly ferromagnetic intermetallic compound Ni_3Al good agreement between experiment and electronic structure calculations was also obtained. In order to make a fair comparison between the experimental and calculated results in this latter case we have to deduce the properties of the perfectly ordered Ni_3Al compound from experiments on necessarily imperfectly ordered materials. These problems are also encountered in the analysis of some intermetallic uranium compounds (e.g. UNi_2).

In the above given examples of 3d metallic magnetism, the zero temperature properties can satisfactorily be described in the Stoner theory for itinerant-electron magnetism. As an example of the effect of pressure on a 4f metal we refer to experiments on Gd at 4.2 K, from which an almost zero value for the relative pressure dependence of the spontaneous magnetisation is derived in the pressure interval 0–4 kbar. In ferrimagnetic Er_6Fe_{23}, a compound in which the erbium and iron sublattice moments nearly compensate, the dominant pressure effect of the iron sublattice magnetisation is nicely reflected in a decrease of the net magnetic moment below and an increase of this moment above the compensation temperature [9].

With these differences between 3d and 4f metallic magnetism in mind we started a study of pressure effects in ferromagnetic intermetallic uranium compounds. It is well known that the 5f electrons in the first half of the actinide series are less localised than the 4f electrons in the corresponding 4f series. In discussing the transition from band states to localised states, the relevant parameters are the bandwidth (W), that represents the hopping energy of the 5f electrons between the actinide ions, and the intra-atomic Coulomb repulsion (U) between the 5f electrons. For U much smaller than W we are in the limit

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Table I
Calculated and experimental values for the relative pressure dependence of the spontaneous magnetisation near zero temperature (σ_0) for some ferromagnetic metals

Remarks		$\partial \ln \sigma_0/\partial p$ (Mbar^{-1})		Ref.
		Exp.	Calc.	
Fe		−0.29	−0.43	[4, 5]
Co		−0.26	−0.25	[4, 5]
Ni		−0.23	−0.18	[4, 5]
Ni$_3$Al	as measured	−8.7		[6]
	perfectly ordered	−5.3	−8.5	[6, 7]
Gd		0 ± 0.1	−	[8]

of itinerant behaviour, whereas for $U \simeq W$ a transition to localised electron states may occur. By increasing the interatomic distances between the actinide ions in suitably choosen compounds this transition is likely to occur. An interesting question is whether magnetic order in, for instance, uranium compounds is restricted to those compounds in which this localisation is realised.

2. Pressure effects in intermetallic uranium compounds

High-pressure experiments have been performed on various series of intermetallic uranium compounds: the Laves phase com-

pounds UX_2 ($X =$ Fe, Co, Ni), uranium–platinum compounds and some ferromagnetic compounds of uranium with gallium and germanium. In addition a few experiments will be reported on U_3P_4 and U_3As_4.

High-pressure data for the magnetic parameters of the Laves phase compounds are collected in table II and compared with experimental results for two weakly ferromagnetic d-metal compounds Ni$_3$Al and ZrZn$_2$. Pressure effects in the ferromagnetic U(Fe, Co)$_2$ compounds are large and of comparable magnitude as those observed in Ni$_3$Al and ZrZn$_2$. Two additional arguments are in favour of a description of ferromagnetism in terms of an itinerant-electron model for the U(Fe, Co)$_2$ compounds:
– values for the logarithmic pressure derivatives of the spontaneous magnetic moment near zero temperature and the Curie temperature are almost identical;
– the logarithmic pressure derivative of the spontaneous magnetic moment diverges for values of the spontaneous magnetic moment approaching to zero.

The pressure derivatives of the magnetic parameters of the compound UNi$_2$ clearly fall outside the systematic trends present in the U(Fe, Co)$_2$ compounds. That observation led to an interpretation of ferromagnetism in UNi$_2$ in terms of defects in the atomic structure [1, 2].

Magnetic order in uranium–platinum com-

Table II
Magnetic parameters and their pressure derivatives for some Laves phase uranium compounds. For comparison the corresponding data for Ni$_3$Al and ZrZn$_2$ are also presented

	T_C (K)	σ_0 (A m^2/mol fu)	$\partial \ln T_C/\partial p$ (Mbar^{-1})	$\partial \ln \sigma_0/\partial p$ (Mbar^{-1})	Ref.
U(Fe$_{1-x}$Co$_x$)$_2$					
x = 0	160	6.2	−3.2	−4.8	[1]
x = 0.1	127	4.7	−4.8	−6.0	[1]
x = 0.2	87	3.0	−9.0	−8.9	[1]
x = 0.3	24	0.76	−37	−44	[1]
UNi$_2$	27	0.29	−6.7	−10	[1]
Ni$_3$Al	43	1.32	−11.6	−8.7	[6]
ZrZn$_2$	27	0.72	−50	−44	[10]

pounds (UPt, UPt₂, UPt₃, UPt₅) only occurs in case of UPt [11]. The type of magnetic order in this latter compound turns out to be rather complex and extremely sensitive to the application of pressures of a few kbars. In the following section we shall present a more detailed account of pressure-induced magnetic transitions and hysteretic effects in UPt. The absence of magnetic order in the remaining uranium–platinum compounds suggests that localisation of the 5f electrons is prevented by hybridisation with the 5d electron states of platinum. Even without this localisation, ferromagnetism can be expected due to the large density of states at the Fermi level as derived from specific heat [9] and XPS [12] measurements.

Ferromagnetic order with extremely large magnetic anisotropies is found in the compounds UGa₂ [14], UGe₂ and U₃Ge₄. UGe₂ has been studied under high pressures on polycrystalline as well as on single-crystalline samples [3]. The high-pressure results around T_C have been obtained for a polycrystalline sample, see Table III. These results probably do not differ much from results on single-crystalline samples. The opposite is true for the pressure effect on the spontaneous magnetic moment at 4.2 K. The saturation moment itself and the magnetic anisotropy both can be influenced by the applied pressures. The value of −6.8 Mbar⁻¹ for the relative pressure dependence of the spontaneous magnetic moment, reported for a polycrystalline UGe₂ sample, should be considered with caution.

Preliminary experiments on a single-crystalline sample result in a value of −2.4 Mbar⁻¹ for this quantity.

Finally we report on high-pressure results for the spontaneous magnetisation of U₃P₄ and U₃As₄ at 4.2 K. These pressure effects are almost zero in contrast to the relatively large pressure shift in T_C that was derived for U₃P₄ from resistivity measurements under pressure [15].

These high-pressure data on UGa₂, UGe₂, U₃Ge₄, U₃P₄ and U₃As₄ are compared in table III with the high-pressure results for pure gadolinium. In conclusion we note that high-pressure experiments point to an itinerant type of magnetism in U(Fe, Co)₂ compounds, whereas for UGe₂, U₃P₄ and U₃As₄ a localised type of magnetism is suggested.

3. Anomalous pressure effects in UPt

Magnetic order in the equiatomic compound UPt is a complex phenomenon. Thermal expansion, ac susceptibility and specific heat measurements reveal an additional transition of magnetic origin near 18.5 K, well below the transition to the paramagnetic state near 27 K [17]. This additional transition is depressed by applying hydrostatic pressures of a few kbars, as will be shown below. At releasing pressures at low temperatures this second transition does not show up again, unless the sample is annealed up to room temperature in between. The bulk magnetisation at 4.2 K is strongly dependent on

Table III
Magnetic parameters and their pressure derivatives for some compounds of uranium with gallium, germanium, phosphorus and arsenic. For comparison the corresponding data for gadolinium are also presented

	T_C (K)	σ_0 (A m²/mol fu)	$\partial \ln T_C/\partial p$ (Mbar⁻¹)	$\partial \ln \sigma_0/\partial p$ (Mbar⁻¹)	Ref.
UGa₂	120	–	1.8	–	[1]
UGe₂	52	8.0	−24	−2.4	[1, 3]
U₃Ge₄	91	–	−2.6	–	[1]
U₃P₄	138	23	−14	0 ± 3	[15], this work
U₃As₄	198	31	–	−1 ± 1	this work
Gd	294	42.6	−5	0 ± 0.1	[16, 8]

pressure [13]. Magnetisation curves under pressures of a few kbars show a magnetic transition between 2 and 4 T, the transition field being roughly independent of pressure. Before giving a detailed description of these results we shall first specify our samples, since sample preparation methods and magnetic properties are sometimes closely related in the uranium compounds.

The intermetallic compound UPt is formed below 961°C by a solid state reaction between UPt$_2$ and a solid solution of γU + 4.3 at% Pt [18]. In our case, uranium (2N8) and platinum (4N) are arc-melted in a stoichiometric ratio in a titanium-gettered argon atmosphere. After remelting the sample several times, the final melt is casted into a water-cooled copper crucible. Material losses during melting and casting were negligible. The quenched sample is subsequently wrapped in tantalum foil and annealed, together with a small piece of metallic uranium, in an evacuated silica tube at 900°C for a period of 10–14 days.

Debije-Scherrer exposures at room temperature and at 4.2 K on the annealed samples show the presence of the desired UPt phase with an orthorhombic CrB-type of structure. A few additional weak lines could be due to metallic uranium. We have to realise that the peritectoid route by which the samples are prepared produces a lot of defects, including short-range concentration gradients and does not allow the growth of single crystals from the melt. Possibilities for growing single crystals by the chemical transport method are under study now.

Magnetisation measurements at low temperatures on UPt samples of different melts show the same overall characteristics:

– a magnetic moment per cell between 0.4 and 0.45 μ_B;

– saturation of the magnetisation is not reached in fields up to 35 T;

– a magnetic ordering temperature of about 27 K;

– a strong depression of the bulk magnetisation at 4.2 K with pressure;

– a metamagnetic transition at 4.2 K under pressure between 2 and 4 T.

One of the samples (a cylinder of 10 mm length and 6 mm diameter) has extensively been in-

vestigated in magnetisation, magnetostriction, specific heat, thermal expansion, neutron diffraction and neutron depolarisation measurements. Although these neutron experiments have not yet been finished, we shall use in this paper some preliminary results.

Neutron diffraction studies at the ILL (Grenoble) point to a magnetic moment per uranium atom at 4.2 K of (0.78 ± 0.1) μ_B, directed along the c-axis. This value does not seem to be reduced considerably by applying pressure of 5 kbar. In bulk magnetisation measurements on the same sample a magnetic moment is found equivalent to (0.4–0.45) μ_B per uranium atom, indicating a strong uniaxial magnetic anisotropy. In subsequent experiments, high magnetic field measurements were performed on a different UPt sample before and after powdering (particle diameter between 10 and 40 μm). The magnetisation of the powdered sample exceeded that of the bulk sample by about 15%. In succeeding field runs the residual magnetisation at 1T slightly increased due to a further reorientation of a small fraction of the particles. From these experiments we conclude that the UPt crystallites are of the order or less than 10 μm. The magnetic moment at high fields approaches for the powdered sample a value of 0.8 μ_B per uranium atom, whereas no sign of saturation is found in the magnetisation curve. It means that the increase in magnetisation with increasing field cannot fully be explained by a rotation of magnetic moments towards the field direction. At least partly, this increase in magnetisation must be due to a susceptibility of the magnetic moments themselves. The combination of the high-field differential susceptibility and the specific heat data for UPt leads to a reasonable value for the Stoner enhancement factor of 2.5, see ref. [2].

In a previous publication we noticed a pronounced peak in the ac susceptibility at 18.5 K and only weak anomalies near the magnetic ordering temperature of about 27 K [17]. In samples of a second melt these anomalies appear to be much more pronounced, see fig. 1. By applying pressures of a few kbars the peak at 18.5 K disappears, whereas the peak at 27 K is suppressed and possibly shifted to somewhat lower temperatures. Releasing the pressure at
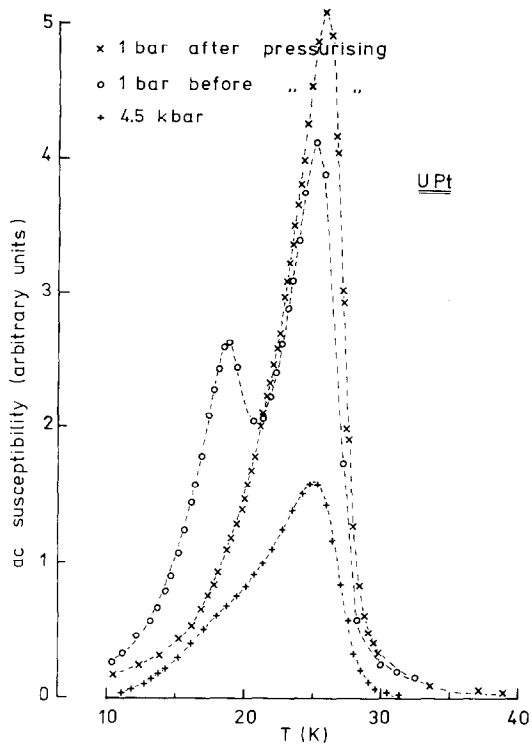
Fig. 1. The ac susceptibility of UPt as a function of temperature at different pressures. Pressure has been released at about 40 K.

low temperatures (about 40 K) the peak at 27 K is restored, whereas the peak at 18.5 K is still absent. By warming up to room temperature and cooling down again this peak re-appears. In summary we conclude that magnetic order in UPt is a complex phenomenon, very sensitive to external and internal stresses. A microscopic picture of the hysteretic phenomena is lacking at present.

4. Summary

High-pressure experiments have been performed on various series of uranium compounds. Pressure effects on Curie temperature and spontaneous magnetic moment near zero temperature are large and negative for the ferromagnetic $U(Fe, Co)_2$ Laves phase compounds, indicating itinerant-electron ferromagnetism in this system.

Pressure experiments suggest a localised type of magnetism for UGe_2, U_3P_4 and U_3As_4. The relative pressure dependence of the Curie temperature differs considerably from the relative pressure dependence of the magnetisation in two of these compounds, a result that is also valid for pure gadolinium, for instance.

Large pressure effects have been reported for UPt, a compound with a difficult metallurgical structure in which complex magnetic phenomena are found. Hysteretic effects induced by pressure variations at low temperature point to a close relation between the magnetic properties and the state of stress of the material.

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