



Pressure effects on magnetism in the uranium and neptunium monopnictides

D. Braithwaite^{a,*}, A. Demuer^a, I.N. Goncharenko^{b,c}, V. Ichas^d, J.-M. Mignot^b, J. Rebizant^d,
J.C. Spirlet^d, O. Vogt^e, S. Zwirner^d

^aDépartement de Recherche Fondamentale sur la Matière Condensée, SPSMS/LCP, CEA/Grenoble, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

^bLaboratoire Léon Brillouin, CEA-CNRS, CEA/Saclay, 91191 Gif sur Yvette, France

^cRussian Research Centre 'Kurchatov Institute', 123182 Moscow, Russia

^dEuropean Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D 76125, Karlsruhe, Germany

^eLaboratorium für Festkörperphysik, E.T.H., CH-8093 Zürich, Switzerland

Abstract

The magnetic properties of the cubic NaCl uranium and neptunium monopnictides (UX, NpX; X=N, P, As, Sb, Bi) have been widely studied at ambient pressure. Properties ranging from itinerant to localized magnetism, and a variety of ordered magnetic structures have been observed. In particular the profusion of non-collinear double-*k* or triple-*k* structures is a consequence of strongly anisotropic exchange interactions. The application of pressure is a clean way of continuously varying the lattice parameter, and the exchange interactions, from one compound to another. A number of studies have been performed using different high pressure techniques. Some of the effects of pressure can be understood in a simple picture of a continuous variation of the lattice parameter, but some highly anomalous effects are also found which are discussed in relation to the possible nature of the magnetic interactions. © 1998 Elsevier Science S.A.

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1. Introduction

The magnetic properties of the cubic NaCl uranium and neptunium monopnictides (UX, NpX; X=N, P, As, Sb, Bi) have been the subject of numerous studies for over 20 years now [1]. Their magnetic structures were originally thought to be the simple type I antiferromagnet kind consisting of a stacking of (100) ferromagnetic planes with the moment perpendicular to the planes. However a series of experiments by Rossat-Mignod et al. [2] showed that the real structures are more complicated. Most of these compounds have a non-collinear double-*k* or triple-*k* magnetic structure, and many of them display more than one structure at different temperatures (Table 1). The very existence of these non-collinear structures is proof that the magnetic interactions are not simple, and must be highly anisotropic. However the exact nature of these interactions is not fully understood. In order to gain further insight into which kind of mechanism plays the main role one must be able to vary some parameter. Chemical substitution to

create solid solutions intermediately between two compounds is one possibility, but in this case it is always difficult to differentiate the various effects such as changing lattice parameter and changing the nature of the ligand. The introduction of disorder and defects is also undesirable. The application of external pressure is a much cleaner way of continuously varying the lattice parameter and so studying the effect of volume changes on the magnetic properties.

2. Magnetic interactions in actinide compounds

Compared to the rare earth compounds, the main differences to consider in the uranium and neptunium monopnictides is the greater spatial extension of the 5f-orbitals compared to the 4f-states, and the proximity of the 5f states to the Fermi energy. The first point means that the direct overlap of the 5f-orbitals of adjacent actinide atoms can play a role as first pointed out by Hill [3]. When the An–An distance becomes less than a critical value called the Hill limit, the 5f electrons are delocalized and no magnetic order occurs. In the traditional Hill plot, the

*Corresponding author. Tel.: +33 47 6884411; fax: +33 47 6885096; e-mail: dbraithwaite@cea.fr

Table 1

Ordering temperatures, magnetic structures, and volume dependence of ordering temperatures and magnetic moment when known for all the uranium and neptunium mononictides

	Ordering temperatures (K) [1]	Magnetic structures [1]	a (Å)	dT_N/dP (K/GPa)	$d \ln T_n / d \ln V$	$d \ln \mu / d \ln V$
UN	53	Type I $1k$	4.890	−4.9	19 [20]	19 [20]
UP	122	Type I $1k$	5.589	−1.3 [15]	1.1	—
	22	Type I $2k$				—
UAs	127	Type I $1k$	5.779	2.6 [15]	−2.0	—
	62	Type IA $2k$				—
USb	215	Type I $3k$	6.191	−17 [12]	4.9	—
UBi	285	Type I ($3k$?)	6.364	—	—	—
NpN	87	Ferro	4.897	—	—	—
NpP	130	incomm. $3k$	5.615	—	—	—
	74	$1k$ $3+$, $3-$				—
NpAs	173	incomm. $1k$	5.838	−3.0 [11]	1.3	0.8 [16]
	154	$1k$ $4+$, $4-$				—
	138	Type I $3k$				—
NpSb	200	Type I $3k$	6.254	−11.5 [11]	3.1	0.4 [11]
NpBi	193	Type I $3k$	6.438	−1.05 [11]	0.7	—

References are shown.

— indicates no experimental values available.

ordering temperature is displayed vs. An–An distance and generally increases with increasing distance, though many exceptions can be found. It is now well known that this model is oversimplified, and that to explain the properties of compounds where the An–An distance is well above the Hill limit, other mechanisms must be considered.

The usual form of indirect RKKY interaction [4] via the conduction electrons found in metallic compounds cannot be applied directly here as the situation is further complicated by the particular band structure of the actinide mononictides. These are mostly semi-metals, having few carriers (electrons and holes) which lie in well-defined pockets of the Fermi surface. It seems now well established that the most important interactions are due to the proximity of the 5f-states to the Fermi energy, and involve mixing of the 5f orbitals either with the conduction band (d-f mixing) [5] or with the p-states of the ligand (p-f mixing) [6] to mediate the interaction in a way similar to the usual RKKY interaction, but with strongly anisotropic and non-linear interactions.

High pressure experiments can to some extent distinguish between the different interactions. In a simple Hill description, the interaction should depend only on the An–An distance and be relatively insensitive to the nature of the ligand. This would mean that for a whole family of pnictides of uranium or neptunium, the magnetic properties should be pure volume effects, and that applying enough pressure on a compound with large An–An spacing should eventually reproduce all the other compounds with smaller spacing. As the decrease in the ordering temperature is governed in this case by the progressive delocalization of the 5f electrons, there should also be a direct correlation between the decrease of the ordering temperature and the magnetic moment with pressure [7]. In the opposite extreme with localized moments and RKKY interaction, the magnetic moment should be insensitive to pressure. In

this case the interaction will usually increase with pressure and the ordering temperature should rise, although competition with Kondo compensation may cause the opposite effect. Finally when mixing effects are important the situation becomes extremely complicated as the 5f electrons play a role both as almost localized moments, and by mixing with the d or p states as transmitters of the interaction. Basically pressure will bring the 5f states closer to the Fermi energy and so increase mixing effects and the interaction strength. However, simultaneously this promotion of f-electrons to the conduction band will decrease the magnetic moment, so reduce the interaction strength [8]. The ordering temperature can either increase or decrease depending on which effect dominates. To summarize, it is virtually impossible to determine the magnetic interactions in play from the variation of the ordering temperature with pressure alone. If on the other hand this information can be compared with the change in the magnetic moment, the field of possible mechanisms can be at least narrowed down considerably.

3. High pressure techniques and magnetism

From the previous paragraph it is clear that if we wish to investigate the effect of pressure on the magnetic order of the different compounds, we must be able to modify the lattice parameter by at least the difference in lattice parameter between two neighbouring compounds. The effect of pressure on the structural data (compressibilities and structural transitions) of all actinide mononictides at room temperature is well documented [9]. These compounds have compressibilities of the order of 100 GPa which means that a pressure of 10 GPa produces a change of lattice parameter of about 3% which is roughly the difference between two compounds. With high pressure

techniques able to reach almost 30 GPa we might therefore hope to be able to sweep the whole family with one experiment. However nothing is ever quite so easy and most of the compounds undergo a structural transition from the NaCl to a more compact phase (CsCl or similar) at a lower pressure. The nature of this transition and the possible magnetic properties of the high pressure phase is a whole subject in itself, but which we will not treat in this paper. Usually the NaCl phase of one compound is stable over a wide enough pressure range to at least approach the lattice parameters of its neighbour.

Surprisingly perhaps, as regards a study of magnetic properties under pressure, one quantity which is very rarely measured is magnetization! At least in the pressure range we are investigating here ($P > 2$ GPa) the constraints on sample volume and accessibility of the different kinds of high pressure cells make this measurement very difficult.

The easiest way of following the evolution of magnetic properties, especially the ordering temperature, is by electrical resistivity measurements under pressure. Indeed if we measure the resistivity versus temperature, the magnetic ordering temperature will usually appear as an accident in the curve. This can be for two reasons: in a metallic sample the disappearance of electronic scattering by spin fluctuations will produce a sharp decrease in resistivity in the ordered state. On the other hand in a semi-metal the resistivity is partially governed by the low carrier density. The onset of magnetic order can modify the band structure and cause a decrease in the number of carriers and so increase the resistivity in the ordered state. This is quite spectacular in the neptunium pnictides with the triple- k magnetic structure which show semi-conducting behaviour at low temperature [10]. Many devices have been developed using the Bridgman technique with sintered diamond or tungsten carbide anvils, with steatite as a pressure transmitting medium to provide quasi-hydrostatic pressure. These routinely allow resistivity measurements up to 28 GPa. This kind of measurement is relatively easy on uranium compounds. The process of mounting pressure cells with active materials and measuring at low temperature is tedious and complicated, but has been carried out successfully for several years now in the 'Institute for Transuranium Elements' in Karlsruhe [11]. Resistivity measurements under pressure have now been performed on NpAs, NpSb, NpBi [12], USb [13], and UAs (which will be presented here). The drawback of resistivity measurements is that they can usually only follow the evolution of features well known at ambient pressure. Normally the different magnetic structures, their ordering temperatures, and the corresponding features in the resistivity of the compound being studied are known, and these can then be followed under pressure. On the other hand if a new magnetic phase appears, or if a magnetic structure changes under pressure, not much information on the new phase can be obtained from the resistivity. Similarly, although the variation of the ordering temperature can be obtained,

we would like to correlate it to the magnetic moment which resistivity cannot provide. As bulk magnetization measurements are not available we must turn to microscopic probes for the extra information.

Elastic neutron diffraction is a powerful technique which can provide information on ordering temperatures, magnetic structures, and the ordered moment. Until recently the relatively large volume of sample necessary limited this technique to pressures below about 3 GPa. Such a study has been carried out on UN [14]. However, a technique using sapphire anvils has been developed by a collaboration between the 'Kurchatov Institute' in Moscow and the 'Laboratoire Léon Brillouin' in Saclay which can generate pressures up to 10 GPa [15]. A systematic study on the uranium mononictides has been carried out [16]. The same technique could in principle be applied to the neptunium mononictides, but the safety aspects have so far prevented any experiments on active samples.

Mössbauer spectroscopy is another microscopic probe, particularly well adapted for the ^{237}Np ion [17], which can be performed under pressure. A Bridgman type cell, similar to the kind used for resistivity, but with larger sample volume has been set up in ITU in collaboration with the Mössbauer group of the University of Munich and has been used successfully for several years [18]. Mössbauer spectroscopy provides several parameters, the most important for us here being the hyperfine field B_{hf} which gives a measurement of the ordered moment. This can be measured as a function of temperature and so provide the ordering temperature. It does not give any direct information on the magnetic structure, though if a change of the orientation of the moments occurs it often causes a change in the ordered moment. Mössbauer studies under pressure have been carried out on NpAs [17] and NpSb [12]. Unfortunately the Mössbauer technique is not possible under pressure on uranium. The relevant parameters from all these experiments are summarized in Table 1. Let us now see how these techniques can be combined through the study of two examples, uranium monoarsenide and neptunium monoantimonide.

3.1. Uranium monoarsenide

At ambient pressure UAs orders in the antiferromagnetic type I single- k ($k=(1,0,0)$) structure at 127 K with the moments along the $\langle 1,0,0 \rangle$. It undergoes a transition at 62 K to an AF IA double- k structure ($k=(1/2,0,0)$) with a reorientation of the moments along the $\langle 1,1,0 \rangle$ direction. The first high pressure study on UAs was performed by neutron diffraction at the LLB [19]. Some results are shown in Fig. 1. The AF IA phase could not be observed directly but was seen from the disappearance of the intensity of the peaks associated with the type I structure. However at a pressure of 5 GPa the situation was found to have changed. A magnetic transition was still found to occur at around 50 K but the low temperature phase was

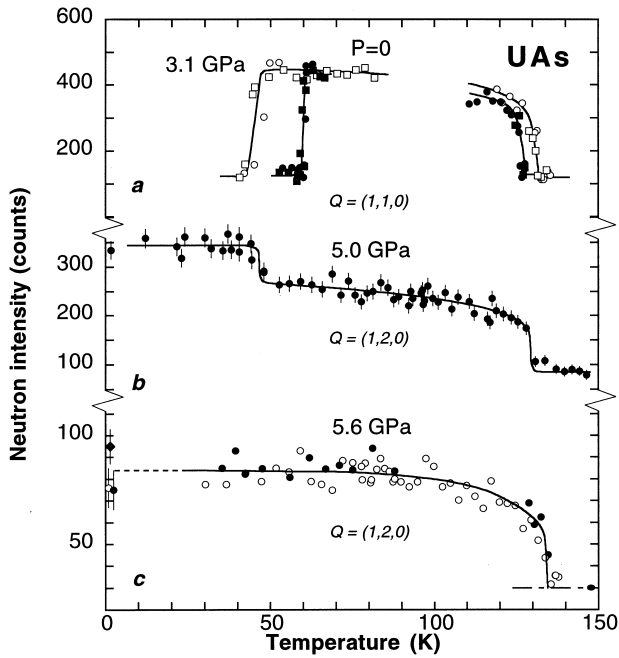


Fig. 1. Temperature dependence of the intensities of elastic neutron magnetic reflections in UAs for three different pressures (from [15]).

now type I too. At even higher pressures no step in the intensity as a function of temperature was found, suggesting that the low temperature transition no longer existed, though this was only speculation as changes in intensity between two type I structures arise mainly from changes of domain populations. Because of this uncertainty a resistivity study under pressure has been carried out. The resistance vs. temperature curves for selected pressures are shown in Fig. 2. The two transition tempera-

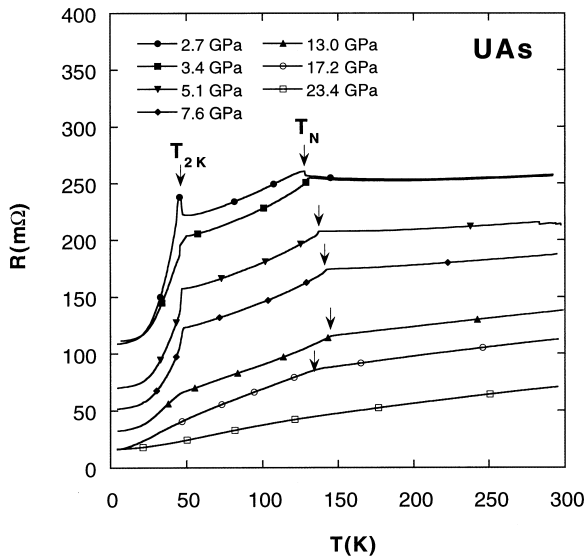


Fig. 2. Resistance vs. temperature curves for UAs at selected pressures from 2.7 to 23.4 GPa. Arrows show the Néel temperature and the transition to the low temperature phase which clearly exists at over 7 GPa and probably also at 13 GPa.

tures are clearly visible and can be followed with pressure. The information from the neutron diffraction and resistivity measurements are summarized in the phase diagram in Fig. 3. The first striking result is that the low temperature transition persists at pressures much higher than seen from the neutron data and that its critical temperature hardly changes. The second is that the Néel temperature which increases with pressure at low pressures, goes through a maximum at about 14 GPa and then starts to decrease. This behaviour will be discussed further in the last section.

3.2. Neptunium monoantimonide

At first sight NpSb seems comparatively simple. It orders at 200 K in the AF type I triple-*k* structure, which retains the cubic symmetry of the lattice. At ambient pressure the onset of the triple-*k* structure produces a huge increase in the resistivity which becomes almost semi-conducting at low temperature. A high pressure resistivity study [20] showed that between 2.3 and 2.7 GPa this increase disappears and instead a sharp decrease of the resistivity is observed at what is presumably still the magnetic ordering temperature (Fig. 4). In the absence of any other information this effect was tentatively attributed to a magnetic transition to a new structure. It was also suggested that the strong decrease in the ordering temperature with pressure could be due to delocalization effects because of the large spatial extension of the 5*f* orbitals. In order to verify these points a Mössbauer spectroscopy study has been performed to provide information on the change of the ordered moment with pressure. This is shown in Fig. 5. Contrary to what was expected, no step in

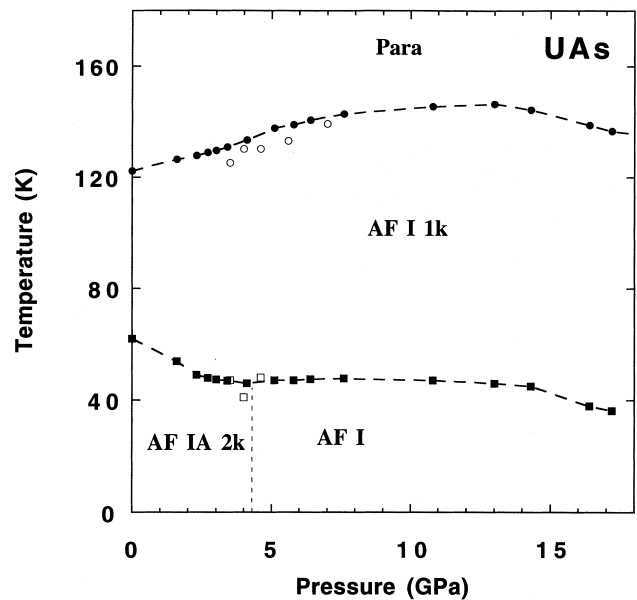


Fig. 3. Magnetic phase diagram of UAs. The temperatures are taken from both resistivity measurement (full symbols) and neutron diffraction measurement (open symbols). The different structures are deduced from neutron diffraction [15].

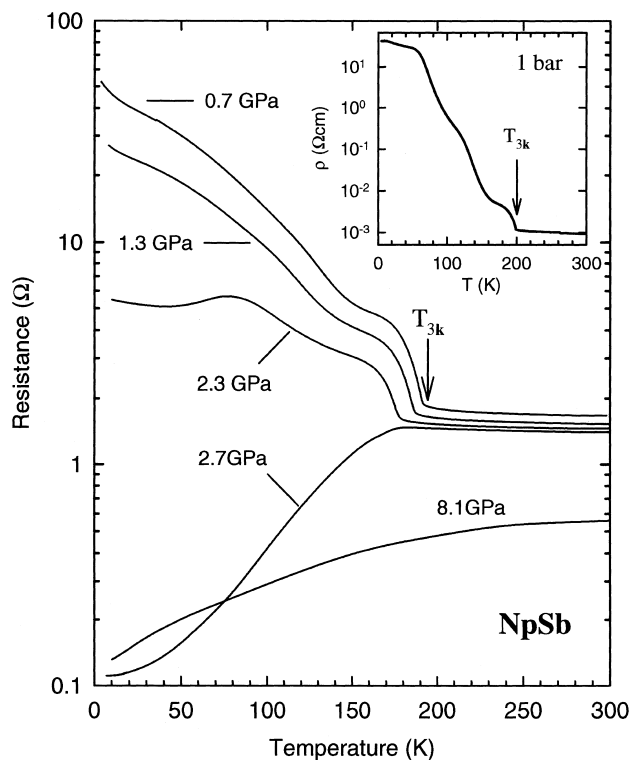


Fig. 4. Resistance vs. temperature curves for NpSb (adapted from [19]). The inset shows ambient pressure resistivity of a similar crystal. Note logarithmic scale for resistance.

the magnetic moment was found between 2 and 3 GPa. Although the Mössbauer technique does not give direct access to the magnetic structure, in most cases where a reorientation of the moments is known to occur with temperature (UP, UAs, NpAs), the ordered moment is also found to change [1]. From both theoretical considerations [21] and comparison with other compounds [12] it still seems likely that pressure can destabilize the $3k$ phase and favour collinear structures. However so far there is still no direct proof of this. Furthermore the Mössbauer experiment showed that although the ordered moment does decrease slightly with pressure, this is not sufficient to explain the strong decrease of T_N through delocalization effects, and some other explanation must be sought.

4. General behaviour of ordering temperatures with pressure

In Fig. 6 we show the effect of pressure, converted into the change in lattice parameter, on the ordering temperature for all the uranium and neptunium mononictides for which this data is known. With the exception of NpN which is a ferromagnet, all the others order antiferromagnetically. NpP and NpAs order with incommensurate $3k$ and $1k$ structures, respectively. The others order with a type I either $1k$ (UN, UP, UAs) or $3k$ (USb, NpSb, NpBi).

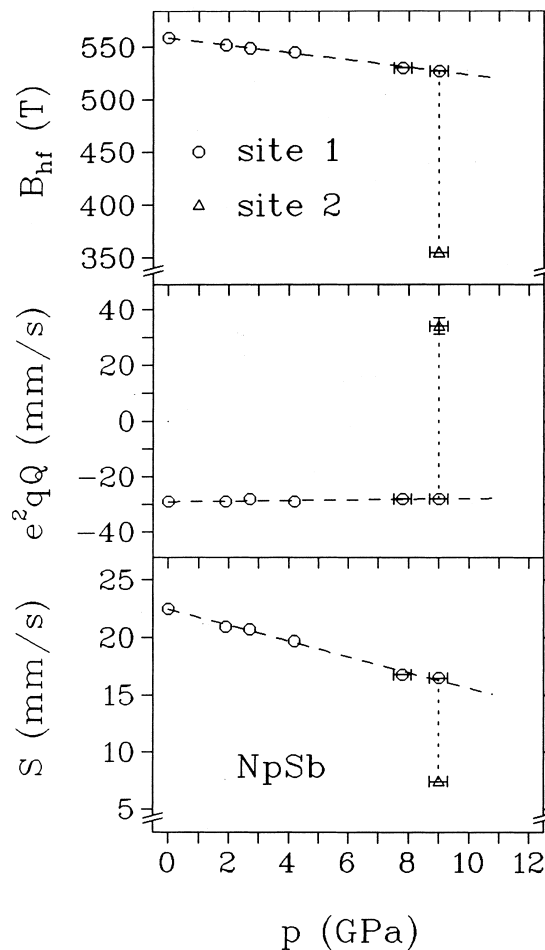


Fig. 5. Results from Mössbauer spectroscopy measurement under pressure on NpSb [11]. Graphs show the pressure dependence of the magnetic hyperfine field B_{hf} (proportional to the magnetic moment on the Np site), the coupling constant of the induced quadrupole interaction $E2qQ$, and the isomer shift S relative to $NpAl_2$. At the highest pressure the existence of two Np sites implies that the expected structural transition has started and that the high pressure phase is also magnetic.

The structure of UBi is not known but it is type I, perhaps also $3k$.

The behaviour of UN is probably the best understood. It has the smallest lattice parameter and a very reduced moment ($0.75 \mu_B$) putting it in the family of itinerant magnets. Furthermore an experiment up to 3 GPa has shown that the decrease in T_N is correlated to the decrease in the magnetic moment [22]. For UN it is likely then that a simple description based on direct $5f$ - $5f$ overlap is sufficient. However it seems clear that this simple description cannot be extended to the other compounds.

The case of UAs is also special as T_N initially increases with pressure, then decreases above 13 GPa. The most probable explanation for this behaviour is a competition between increasing hybridization, therefore increasing exchange, and weakening of the moment due to delocalization. Recently the pressure dependences of the Curie temperatures of the ferromagnetic uranium chalcogenides

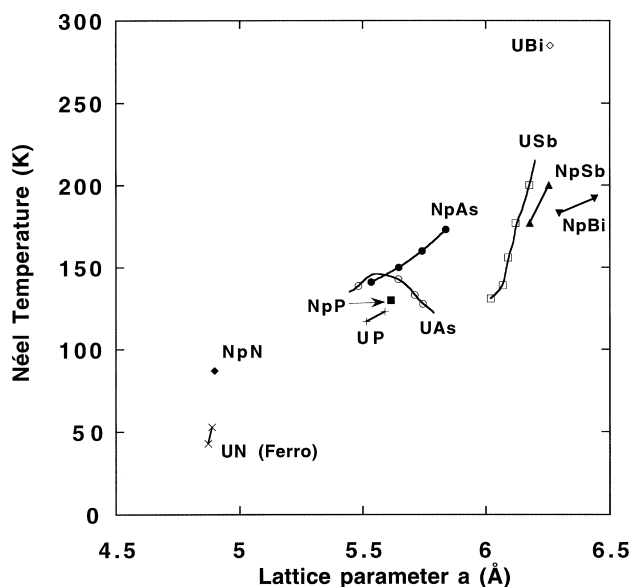


Fig. 6. Evolution of the ordering temperatures with lattice parameter for all the uranium and neptunium monopnictides.

US, USe and UTe have been measured [23]. In USe and UTe the non-monotonous behaviour of the ordering temperature, quite similar to that of UAs, was attributed to this effect. The relatively symmetrical behaviour of the ordering temperature on the two sides of the maximum was taken as evidence against this behaviour being due to the competition between RKKY interaction and Kondo compensation as described by the Doniach model [24]. This would produce a precipitous drop of the ordering temperature with increasing exchange, as found in many cerium compounds. In an analysis of the effect of pressure in NpGa_3 , Zwirner et al. [25] also argued that in actinides the Doniach model is unlikely to apply, as in contrast to some cerium based compounds, the Kondo anomaly in the resistivity tends to be suppressed with pressure. Finally Sheng and Cooper [8] have now performed ab-initio calculations of the pressure-driven 5f itinerancy which successfully reproduce the behaviour of the uranium monochalcogenides. According to this model, at the highest pressures where NpAs and UAs have been measured delocalization effects should start to dominate. However, as for the same lattice parameter the ordering temperatures of UAs and UP, as well as those of NpAs and NpP are different, delocalization cannot be only from direct 5f-5f overlap but must be at least partly through hybridization with the ligand. We would also expect that the decrease of the moment with pressure should be enhanced but unfortunately this information is not available because the Mössbauer experiment is limited to 10 GPa. In order to check this, a measurement on NpP would be interesting, as well as possibly an extension to higher pressures of the study of UP.

The remaining compounds have the largest lattice parameters and should therefore tend towards localised

magnetism. In this context the very large negative pressure dependence of the ordering temperatures of USb and NpSb is rather surprising. The magnetic moment in NpSb is almost pressure independent which is normally the signature of a localized magnet. It is likely that the same is true of USb although there is no precise determination of the variation of the moment. To try to understand this behaviour we assume the ordering temperature to be given by an RKKY type expression [26]:

$$T_{ord} = \chi_c J_{5f-c}^2 \mu(\mu + 1)$$

where χ_c is the conduction band susceptibility, μ is the magnetic moment, and J_{5f-c} is the exchange integral between the 5f electrons and the conduction electrons, which can include mixing effects. Ichas et al. [12] showed that in NpAs the measured reduction of μ is insufficient to compensate for the expected increase of J_{5f-c} . In NpSb this is even more true as the ordered moment hardly changes with pressure and cannot explain the decrease of T_N , which is stronger than in NpAs, even if J_{5f-c} is constant. As the exchange integral can hardly be expected to decrease with pressure it was suggested that it is the conduction band susceptibility which decreases. At first view it may seem surprising that χ_c should decrease with pressure as in all these compounds the resistivity in the paramagnetic state decreases, indicating an enhancement of the carrier density. However we should remember that we are dealing with semi-metals where the carriers occupy certain well-defined pockets of the Fermi surface. The conduction band susceptibility may therefore display strong peaks for certain directions in k -space, which could be weakened by pressure due to changes in the Fermi surface. It is interesting to note that this effect is strongest in the triple- k structures where nesting effects are probably important [21]. Kasuya [27] suggested that the results of USb could be explained by a transition to a non-rigid $3k$ structure with unequal components. This might explain the decrease in the conduction band susceptibility and might be applicable to NpSb too. Because of the difficulties in handling, no high pressure data is available on UBi. However, taking into account the high value of T_N at ambient pressure, it seems likely that the ordering temperature will also decrease strongly with pressure, but this should be checked experimentally as on the contrary in NpBi T_N decreases much slower with pressure than in NpSb.

5. Conclusions

There now exists quite a wealth of data on the uranium and neptunium monopnictides from resistivity measurements, Mössbauer spectroscopy and neutron diffraction. From the combination of resistivity and neutron scattering the phase diagrams of most uranium compounds are now

known. On the neptunium compounds resistivity and Mössbauer measurements make it possible to compare the variation of the ordering temperatures with the change of the magnetic moment. To some extent pressure can change the An–An spacing to fill in the gaps between the compounds. We find that the variations of the ordering temperatures cannot be reduced to a simple volume effect, which would be the case if direct 5f–5f overlaps were dominant, but depend quite strongly on the nature of the ligand. It also appears that there is a correlation between the pressure dependence of the ordering temperature and the type of magnetic structure. The triple- k compounds USb and NpSb show very strong negative pressure dependences of their Néel temperatures with pressure in spite of large lattice parameters and otherwise almost localized behaviour. This cannot be easily explained by a simple model and we speculate that a decrease of the conduction band susceptibility, which is perhaps particularly enhanced for certain directions in k -space due to the band structure and nesting effects, is responsible for this behaviour.

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