

Magnetism in the Actinides

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Abstract

Magnetism involving $5f$ electrons in the actinides exhibits a bewildering diversity that is difficult to fit within any conventional framework. In this article I review briefly some of the significant work that has been performed during the last 5 years. From itinerant $5f$ systems such as UFe_2 , to heavy-fermions exhibiting non-Fermi-liquid behaviour such as $(\text{U},\text{Y})\text{Pd}_3$, to quasi-localized materials such as NpBi , to fully localized compounds such as UPd_3 , the magnetism continues to provide both richness and surprises. Neutron scattering, especially inelastic scattering, provides the surest method to help define the “state of hybridization” in these compounds. Heavy-fermion superconductivity remains the most difficult aspect to understand. I argue that the communities working on both “conventional” actinides and heavy-fermion compounds would benefit from greater contact with each other.

1 Introduction

Characteristically, the title for my talk was chosen by Allan Mackintosh without consulting me. I say characteristically because every time we talked about $5f$ magnetism he was searching for a framework into which he could put my remarks. Being one of the pioneers in establishing a framework, and a highly successful one as the elegant book by Jens Jensen and him (Jensen and Mackintosh, 1991) shows, for $4f$ magnetism, he felt (even insisted) that we must find the framework for $5f$ magnetism. He recognized many years ago, of course, that it was not the same as that for the lanthanides, but his orderly mind refused to accept what appears to be a great heap of unconnected facts in $5f$ magnetism. Thus, I shall accept that challenge, difficult though it is.

One of the principal techniques for elucidating the magnetic properties of compounds in both the $4f$ and $5f$ series is neutron scattering. The results for $4f$ systems, with the exception of Ce and some other materials that exhibit intermediate valent behaviour, are for the main part understood (Jensen and Mackintosh, 1991). The framework of localized moments interacting with each other through the conduction electrons and subject to the crystal-electric fields (CEF) from the

surrounding ions, explains not only the neutron results, but also almost all the bulk property measurements. Of course, neutrons are never the first technique to be applied to a system, especially the actinides, and they have never, and will never, discover new heavy-fermion compounds, for example. In the end, however, until the neutron scattering results can be placed in a framework, the materials are not understood. The reason for this in magnetism is simple. The neutrons couple to magnetic moments so they can give us the magnetic structures, which is an important manifestation of the ground state, and the energy scale of neutron spectroscopy is from 1 to 100 meV, thus allowing information about the excited states to be extracted. Given the narrow bandwidths (as opposed to the many eV of the transition-metal compounds) of f electrons, whether they be $4f$ or $5f$, this is exactly the energy range of importance to learn about the ground and first excited states.

Some start has been made in establishing such a framework in the recent reviews in the Rare Earth Handbook series (Lander, 1993; Holland-Moritz and Lander, 1994; Aeppli and Broholm, 1994). I shall not repeat information already discussed, which represent the situation in ~ 1992 , and refer to these chapters rather than the original references to save space, but without any intention to slight the original authors!

Before starting with the neutron experiments, it is worth mentioning the “arrival” of x-ray resonant scattering into the study of the magnetism of the actinides (Isaacs et al., 1989, 1990). This technique is a very exciting one, and one with great promise for the future, both from the scattering and the dichroism aspects (Lander, 1996). So far, the scattering technique has added to our knowledge about the coherent lengths in magnetically ordered compounds (Isaacs et al., 1990), about the nature of phase transitions (for example, the presence (Langridge et al., 1994a,b; Watson et al., 1996a), or absence (Nuttall et al., 1995), of “two length scales” in the development of the critical correlations just above the ordering temperature), and on the details of the magnetic ordering processes (Langridge et al., 1994c; Perry et al., 1996). Most of these discoveries are a consequence of the better (than neutrons) q -space resolution of the x-ray technique. No new structures have yet been discovered by x-rays, but the small samples that can be used in x-ray experiments should allow diffraction studies of the heavier ($> \text{Am}$) actinides, and also the examination of thin films and multilayers. In dichroism, the first experiments have been reported (Collins et al., 1995), but, again, the element specificity and the information on the electron states (Tang et al., 1992) have not been exploited yet to any appreciable extent. Recently, the first measurement of surface antiferromagnetism has been reported (Watson et al., 1996b,c) with grazing-incidence x-rays on a polished sample of UO_2 . This is an important new frontier, but it addresses questions of surface rather than of actinide physics. Inelastic magnetic scattering using the

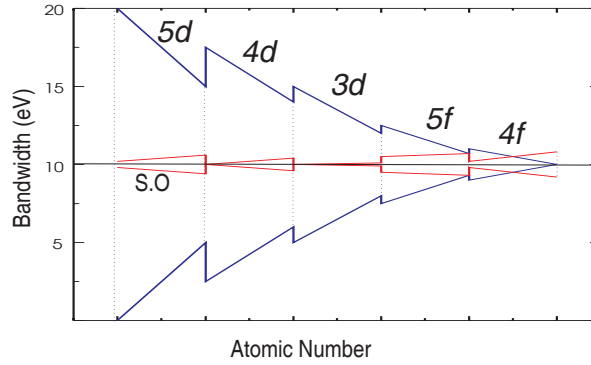


Figure 1. A schematic of the bandwidth, W , and spin-orbit splitting, Δ_{so} , for the d and f series elements. (Taken from Lander, 1993)

strong resonances is another subject that has not been explored very much (Ice et al., 1993).

We shall, no doubt, hear more from this competitive (or complementary would probably be a better word) microscopic technique in actinide research, but at the moment the surest information on the physics of actinides is still coming from neutron scattering experiments.

2 Band $5f$ electrons

Figure 1 shows the energy scale of two of the most important interactions in the magnetism of the various electron series (Lander et al., 1991). In the actinides it may be seen that the spin-orbit and bandwidths are of comparable magnitude. This is one of the fundamental reasons that the model I discussed earlier is so difficult to characterize. The $5f$ electrons fit neither into the schemes devised for the d -transition metals, where the spin-orbit interaction is a small perturbation on the bandwidth parameter, nor into those applicable to the rare earths, where the reverse is true. We find that actinides have characteristics of both series.

To illustrate this point I start with a compound that can surely be best described by the band approach, UFe_2 . This compound has the cubic fcc Laves phase structure, and some years ago extensive calculations of the properties by the single-electron band-structure approach, including spin-orbit coupling and orbital polarization, showed that the main properties could be understood if the $5f$ electrons were treated as band electrons (Brooks et al., 1988). This paper even went so far as to predict an unusual form factor for the U $5f$ -electrons in this material

associated with the cancellation of the orbital and spin contributions to the U magnetic moment. This was experimentally verified (Wulff et al., 1989; Lebeck et al., 1989), although the magnitudes of the individual contributions to the moment at the uranium site were smaller than the calculations suggested.

Recently, we studied the dynamics of UFe_2 with a large single crystal and neutron inelastic scattering (Paolasini et al., 1996a,b). Following the extensive work on the isostructural Laves phases of the rare earths, we would expect three modes at low energy. However, only one mode, involving the Fe spins only was found. Some data from an experiment with full polarization analysis at the Institut Laue Langevin (ILL) are shown in Fig. 2. Exhaustive searches were made for the two other modes, but without success. That the “crystal-field like” mode of the U moment in the molecular field of the Fe moments was not observed is not a surprise – this is an itinerant system. More of a surprise was our inability to find the low-energy acoustic mode involving both the U and Fe spins. Elementary spin-wave theory tells us that this mode must be present, but it is probably strongly damped, perhaps by the strong coupling to the single-particle (Stoner) modes, or because of the unusual coupling of the spin and orbital moments on the uranium site.

The dispersion of the Fe only mode in UFe_2 was found to very steep. Figure 3 shows a plot of the energy of the excitation as a function of q^2 . In a ferromagnetic the spin wave energies (E) for small q may be written as $E = E_0 + Dq^2$, where E_0 is the spin-wave gap, and the slope of the line gives the value of D , the spin-wave stiffness. The gap in UFe_2 is small, consistent with the small overall anisotropy of this material, but the D values are even bigger than found in pure Fe. In linear spin-wave theory D can be taken to be a measure of the direct exchange and does not have a strong T dependence, so by this analogy we would expect UFe_2 to have an ordering temperature even greater (or at least similar to) that found in pure Fe. That is not the case, T_C of UFe_2 is a low value of 165 K. Diluting Fe with U (if that is a justifiable way to consider the Laves phase compound UFe_2) has then had two important effects:

1. To increase the direct exchange interactions between the Fe spins, thus suggesting that high Curie temperature materials with uranium can be made.
2. To increase the temperature dependence of D (see the values in the figure caption), which, put another way, indicates that linear spin-wave theory is no longer applicable because of the strength of the higher-order interactions.

More studies are planned on UFe_2 . At the moment the spin-wave energies of the Fe mode have not been observed much above ~ 7 meV, and certainly extending this in energy may give more information on whether the single-particle modes play an important role in this itinerant system.

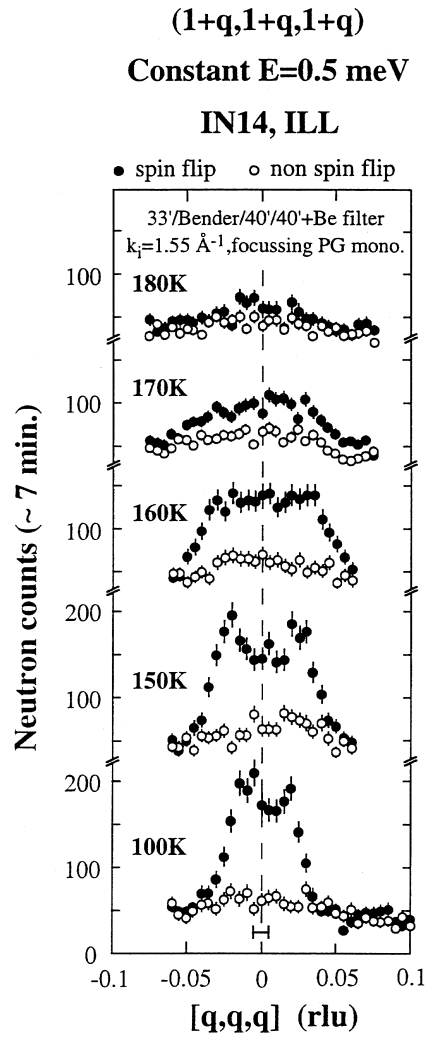


Figure 2. Data taken on UFe_2 single crystal near the (111) zone center and with full polarization analysis using the IN14 triple-axis spectrometer at the Institut Laue Langevin, Grenoble. The incident neutron wavevector is 1.55 \AA^{-1} . A horizontal field of 1 T was used to saturate the sample along a $\langle 111 \rangle$ direction. The energy transfer is 0.5 meV in neutron energy loss. The instrumental resolution in q -space is shown as a horizontal bar in the lower panel. Solid points are spin flip (magnetic) and open points are non-spin-flip (non magnetic). (Taken from Paolasini et al., 1996a,b)

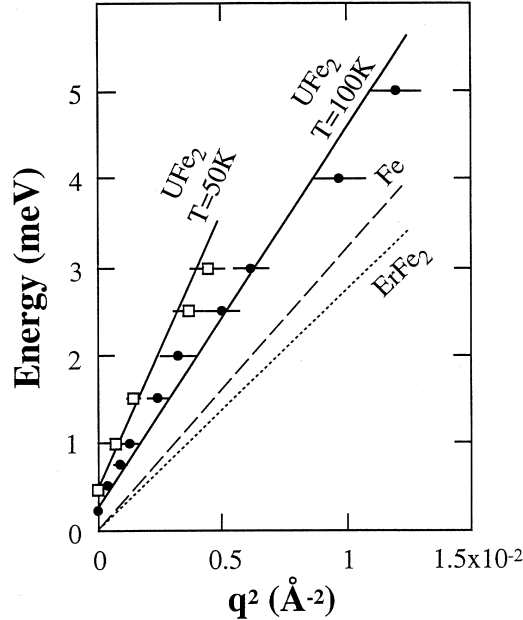


Figure 3. Analysis of the low- q region for various materials. Dashed line is best fit for pure Fe giving $D = 325(10) \text{ meV}^{-2}$. The dotted curve represent $D = 280 \text{ meV}^{-2}$ as found for ErFe_2 at 295 K; note that a large gap E_0 has been suppressed in this plot. The two solid lines are fits to UFe_2 at 100 and 50 K giving values of $D = 440(30)$ and $630(50) \text{ meV}^{-2}$, respectively. (Taken from Paolasini et al., 1996a,b)

Of course, many of the actinide compounds that can be described as band systems (including the light actinide elements) do not order magnetically because the Stoner criterion is not fulfilled. Compounds with Fe, Co, and Ni are an exception because there is strong exchange involving the d electrons that drives the magnetic ordering. Other examples of band systems include the 1:1:1 compounds, such as URhAl and URuAl . In these compounds polarized neutrons (Lander, 1993) have shown that an important characteristic is that the d electrons on one of the Rh (or Ru) atoms are strongly polarized, and give $\sim 30\%$ of the total moment (Paixão et al., 1993). This means that the hybridization involves a planar interaction (this plane being perpendicular to the easy direction of magnetization) and gives a possible explanation of the large bulk anisotropy found in these materials. Unlike the itinerant system UFe_2 , these 1:1:1 itinerant systems exhibit a large anisotropy that must originate from the large orbital moment of the $5f$ electrons. Understanding

the dynamics of such systems is clearly the next step after the experiments on UFe_2 (at least as far as band-like systems are concerned) and we have attempted such experiments on URhAl . No low-energy spin waves were found. Experiments at the ISIS spallation source (Hiess et al., 1996b) show a wide magnetic contribution centered around ~ 90 meV, see Fig. 4. There is little theoretical framework within which to interpret spectra of this sort; we can speculate that the magnetic contribution arises from the mixed $5f-4d$ band from the hybridization of the U and Rh electrons. If this can be considered as the spin-wave gap, see above, then it corresponds to an anisotropy field of ~ 700 T, which is clearly beyond the reach of laboratory magnetic fields, and represents a quite new mechanism of anisotropy.

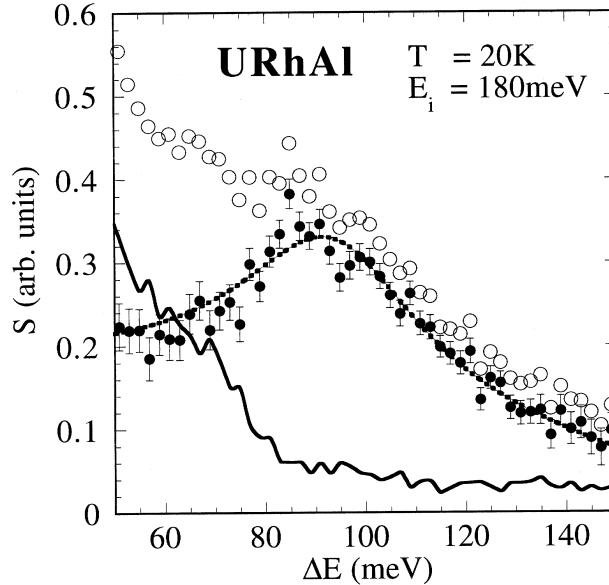


Figure 4. Results of experiments with $E_i = 180$ meV and $T = 20$ K on URhAl . Open circles are data from the low-angle detectors, the solid line the data from the high-angle detectors. The closed circles are the difference. The broken line gives a fit to a Lorentzian centered at $94(5)$ meV and with a $\Gamma/2 = 22(3)$ meV. The broken line is asymmetric because the uranium form factor changes appreciably over this range of energy transfer because of the variation in Q . A sloping background is also required to give a good fit. This could either be magnetic or from multiphonon contributions. (Taken from Hiess et al., 1996b)

3 Heavy-fermion compounds and the non-Fermi-liquid state

The correlations that develop, particularly at low temperature, in heavy-Fermion (HF) compounds continue to be at the center of much research in condensed-matter science. The understanding of such compounds falls outside the scope of the conventional band-structure approach as their most important feature are the correlation effects, which are neglected in single-electron theory. A more complete discussion of all the neutron experiments performed on single crystals of HF compounds up to ~ 1992 can be found in Aeppli and Broholm (1994).

3.1 Two new HF superconductors

Two new superconducting HF compounds have been found recently, UP_2Al_3 and UNi_2Al_3 (Geibel et al., 1991; Krimmel et al., 1992), both which exhibit magnetic order and then become superconducting at a lower temperature. UPd_2Al_3 is the most studied, and has a surprisingly large moment of $0.85 \mu_B$. The magnetic structure consists of a simple arrangement of alternating $+ - + -$ sheets of ferromagnetic planes stacked along the hexagonal c -axis. The wavevector is $q = (0, 0, 1/2)$, and the magnetic moments lie in the basal plane. Experiments on single crystals have shown that the moments probably lie along the a -axis (Kita et al., 1994; Paolasini et al., 1994). No sign of any incommensurate component has been found, unlike the case of UNi_2Al_3 , in which the magnetic ordering is more complicated and the ordered moment is smaller (Schröder et al., 1994). UPd_2Al_3 becomes superconducting at ~ 2 K. Although the ordered magnetic structure seems well established of the UPd_2Al_3 , the presence (if any) of an interaction between the magnetism and superconductivity has been more difficult to find (Petersen et al., 1994; Sato et al., 1996), and this is an area of considerable current activity. Clearly on the scale of the superconducting temperature $T_C \sim 2$ K, one might expect effects at the energy scale of less than 1 meV.

On a different energy scale is the question of whether UPd_2Al_3 might exhibit crystal-field (CF) levels, which have been deduced from bulk-property measurements (Böhm et al., 1993; Grauel et al., 1992). Recently, Krimmel et al. (1996) have reported on a series of experiments at the HET spectrometer at the ISIS spallation source. We reproduce a key figure from their paper in Fig. 5. It is important to realize that these data have been corrected for the phonon contribution, which have definite peaks in them, so that given these uncertainties it seems safe to make the statement that there is really no hard evidence for CF levels in this material. Of course, there are CF interactions in all these uranium materials. However, the crucial point about the neutron spectroscopy is that it shows that the CF levels

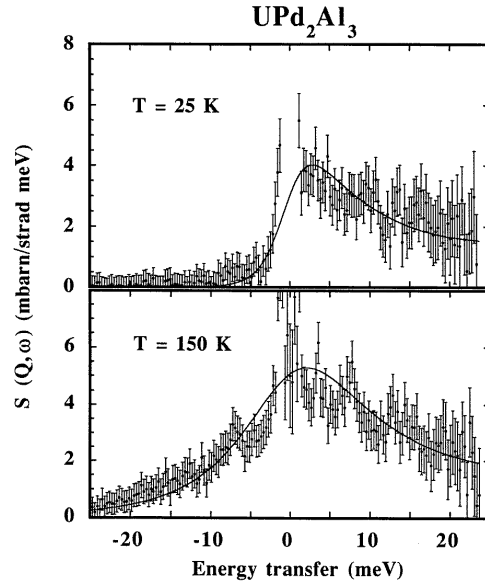


Figure 5. Corrected spectra of UPd_2Al_3 with an incident neutron energy of $E_i = 25$ meV showing the magnetic intensity at $T = 25$ K and $T = 150$ K. The data are fitted (solid lines) by two Lorentzians, one centered at $E = 0$ (quasielastic scattering) and $\Gamma/2 = 2.5$ meV at 25 K, and 5.7 meV at 150 K, and the other Lorentzian centered at 23.4 meV with $\Gamma/2 \sim 5$ meV, and thus being inelastic in origin. The detailed balance factor is included in the fit. (The FWHM of the Lorentzians is Γ , consistent with the nomenclature in Holland-Moritz and Lander (1994); figure taken from Krimmel et al. (1996)

are broadened, perhaps changed substantially, and the rare-earth model does not work. The values of $\Gamma/2$ (~ 3 meV at 25 K and ~ 6 meV at 150 K) in UPd_2Al_3 are rather small for uranium compounds, see Table 5 of Holland-Moritz and Lander (1994) where one can see that the values of $\Gamma/2$ for uranium compounds range between 5 and 15 meV. Indeed one is tempted by the data of Fig. 5 to try just one Lorentzian of a larger width ($\Gamma/2$ at least 8 meV at 25 K) and it is unfortunate that the authors do not show how such a fit looks.

One of the more intriguing theories about UPd_2Al_3 and its superconductivity is that there are two electron systems that are relevant, both involving $5f$ electrons. The first gives the ordered moment, the normal behaviour for the susceptibility, the CF level structure, and the second $5f$ electron system is relevant for the superconductivity at ~ 2 K (Caspary et al., 1993; Feyerherm et al., 1994). Corroborating

evidence for this idea comes from the polarized-neutron study (Paolasini et al., 1993) of single crystals. In this work the most interesting results were that the ratio of the orbital to spin orbital moments (μ_L/μ_S) was somewhat below the free-ion value, and that there is an appreciable positive conduction-electron polarization. Normally in U compounds (and in all compounds with the lighter actinides) there is a negative conduction-electron polarization (Lander, 1993), so that the situation in UPd₂Al₃ is unusual. In contrast to the studies cited earlier on URhAl and URuAl, no induced moment is found on the Pd site in UPd₂Al₃. Certainly, this material is a long way from the band 5*f* electrons discussed in the Introduction above.

3.2 New experiments on HF systems

3.2.1 UPt₃

A key question in the superconductivity of the HF compounds is whether it is of the *s*- or *d*-wave form. UPt₃ is perhaps the most-studied compound, and increasing evidence suggests that the superconductivity is unconventional (i.e. not of the *s*-wave form) (Fisk and Aeppli, 1993). Related to this question is how the magnetic ordering found in UPt₃ (Aeppli et al., 1988) interacts with the superconductivity. The earlier experiments (Aeppli and Broholm, 1994) had shown that the amplitude of the magnetic moment appeared to be reduced when UPt₃ becomes superconducting, however, it was also possible that there was a change in the magnetic structure that went unobserved in the early work. The AF state of UPt₃ has therefore been re-examined (Isaacs et al., 1995) with both neutron and resonant x-ray techniques. This study finds that the correlations in the AF state of UPt₃ are definitely smaller than in a classic long-range ordered materials and range from ~ 300 to ~ 500 Å, as was found also for URu₂Si₂. Furthermore, there is definitely a slight reduction in the ordered moment when the material becomes superconducting, but neither a change in the direction of the moment nor a different magnetic structure. The intensities reduce by about 10% when $T < T_C$. This is important as it shows a coupling between magnetism and superconductivity. Further than that takes us into the realm of the newest theories for *d*-wave superconductivity.

The inelastic response for UPt₃ has been measured and consists of at least two energy scales. At the highest energy, corresponding to a $\Gamma/2 \sim 9$ meV, each U moment is correlated antiferromagnetically with its six nearest neighbours (Aeppli and Broholm, 1994). On a smaller energy scale (longer time scale) of $\Gamma/2 \sim 0.2$ meV another characteristic response has been found (Aeppli and Broholm, 1994), and this has been examined in some detail recently by Bernhoeft and Lonzarich (1995) especially as a function of q at low q . The main result is that in this region of q -space the form of the function $\chi''(q, \omega)$ cannot be understood in terms of a single-

pole model with a wavevector-independent relaxation spectrum. The response at very low energies, which is associated with the quasiparticles that establish the HF state, accounts for about 20% of χ'' , with the remainder coming in the higher-energy region. Unfortunately, there is no theory yet that attempts to account for the two energy scales observed in UPt₃, UBe₁₃, and USn₃ (Holland-Moritz and Lander, 1994) so it is not easy to make further remarks.

3.2.2 URu₂Si₂

In this material the major question is also related to the co-existence of superconductivity and magnetism. There are two major problems to reconcile in URu₂Si₂ and they derive from the fact that in the ordered state an interpretation of the intensity of the magnetic Bragg peaks indicates that the ordered magnetic moment is only $0.04 \mu_B$. However, there is a large jump in the specific heat at T_N and this is an order of magnitude greater than can be accounted for by the mean-field ordering of such a weak magnetic moment. The second problem is that in the neutron inelastic spectrum there is a gap in the energy spectrum, and the longitudinal fluctuations across this gap have matrix elements that correspond to a moment of $\sim 1.2 \mu_B$, and yet the final ordered moment, as we have seen, is much smaller. These difficulties have led to suggestions that the real order parameter may be much more complex, and has not yet been found. In the last 3 years a number of theoretical papers have been published following this idea, and at least 2 experimental papers published (Walker et al., 1993; Mason et al., 1995) trying to establish whether any of these theories can be verified. Unfortunately, the experiments have failed to find any indication that the ordering is anything other than simple dipole. The mystery remains.

3.2.3 UBe₁₃ and NpBe₁₃

UBe₁₃ is a superconductor at about 0.9 K and, so far, is the only HF superconductor in which no magnetic ordering or magnetic correlations have been found. That in itself is odd, and weakens attempts to build consistent theories for these materials. Hiess and collaborators (Hiess et al., 1996a,b) have recently performed experiments on NpBe₁₃ that sheds some light on the problem of the magnetic response function in metal-Be₁₃ compounds. Some of the data from this study, performed on both a polycrystalline sample and a small (~ 1 mg) single crystal, are shown in Fig. 6. By using the Mössbauer (on ²³⁷Np) and neutron techniques they were able to establish the interesting magnetic structure for the Np atoms shown in Fig. 7. The data clearly show that the ordering wavevector is $q = \langle \frac{1}{3}, 0, 0 \rangle$ in this cubic system, and this is the same wavevector that is found for the lanthanide-Be₁₃ compounds. It is unusual to find any similarity between magnetic structures of

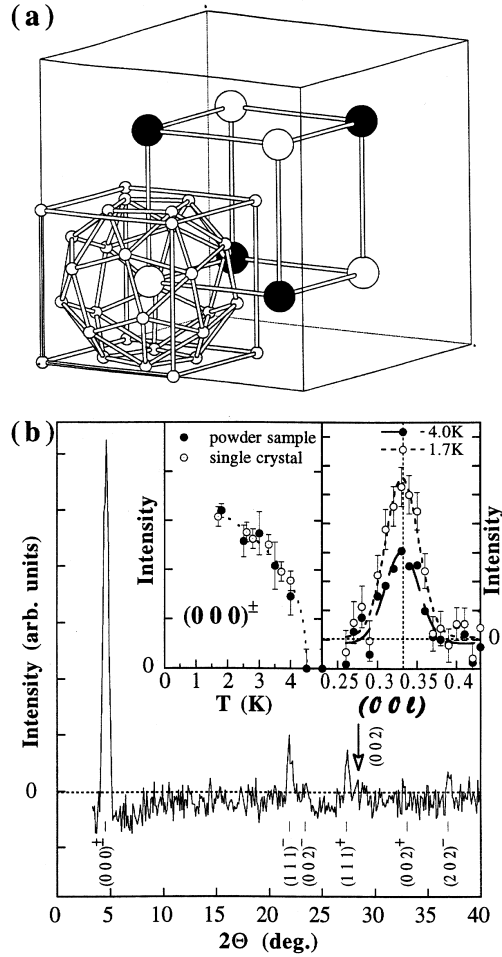


Figure 6. (a) Chemical structure of the MBe_{13} compounds. The two different Bravais lattices of the M atoms are shown as black and open spheres. Each M atom is surrounded by a polyhedron of 24 Be atoms (smaller gray spheres) at a distance of 3.0 Å. The nearest M–M distance is $a_0/2 = 5.12$ Å. (b) The main figure shows the low-angle part of the difference pattern $I(T = 1.5 \text{ K}) - I(T = 10 \text{ K})$ obtained from the polycrystalline sample. The magnetic reflections are indexed and the position of the nuclear (002) peak marked. The insets show (left) the intensity of the $(000)^\pm$ satellite as a function of temperature, and (right) the intensities from the single crystal as a function of wavevector at two different temperatures. (Taken from Hiess et al., 1996a)

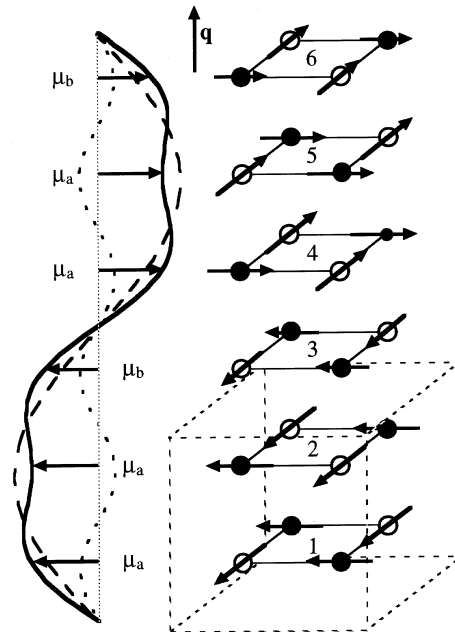


Figure 7. The magnetic structure of NpBe₁₃. On the left hand-side are shown the wave forms of the modulations for one Bravais lattice. The long-dashed line is the ($p = 1$) first and the short-dashed the ($p = 3$) third harmonic. They combine together to give the modulation shown by the solid line, which is the envelope describing the magnitudes of the magnetic moments. On the right-hand side are shown three chemical unit cells (the first outlined). The moments are perpendicular to the propagation direction, and the two sublattices (see Fig. 6a) have their moments perpendicular to each other. (Taken from Hiess et al., 1996a)

chemically isostructural lanthanide and actinide compounds because the magnitude of the interactions are normally quite different in the two series. However, the conduction-electron response, which is an important parameter in defining the ordering wavevector, comes in these compounds primarily from the Be electrons so that it is not too surprising that the ordering wavevector is a general property of MBe₁₃ systems, provided that the metal ions have a valence of three. So this suggests where to begin the search for such correlations in UBe₁₃. The magnetic structures of the lanthanide–Be₁₃ are, however, quite different from that found in NpBe₁₃. The lanthanide–Be₁₃ follow a helical arrangement (Becker et al., 1985), with all the moments in a plane perpendicular to the propagation direction (see Fig.

7) ferromagnetically aligned and simply turning from plane to plane. In NpBe_{13} the arrangement is such that both a ferro and an antiferro component exist. The most likely structure is shown in Fig. 7. An interesting aspect of this structure is that each Np moment is surrounded by 6 moments that are perpendicular to the initial one. Thus, the direct exchange term $\mathbf{J} \cdot \mathbf{J}$ is actually zero. The NpBe_{13} structure does not appear to “square” down to 1.5 K. This probably indicates the importance of the Kondo effect in stabilizing an oscillatory component of the moment – a similar situation has been found in NpRu_2Si_2 (Bonnisseau et al., 1988). Both of these compounds have large terms in the specific heat and are thus heavy fermions, although there is no indication (yet) that they are superconductors. It would be interesting to extend the diffraction study of this compound down to lower temperatures.

3.3 The non-Fermi liquid state

Over the last several years increasing evidence has pointed to the fact that in many electronic systems the thermodynamic, magnetic, and transport properties are not adequately described by conventional Fermi-liquid (FL) theory. One of the most important predictions of the latter theory, is that at low temperature the specific heat can be written $C = \gamma T + AT^3 + \dots$, so that as $T \rightarrow 0$ the quantity C/T should tend to a constant, the so-called Sommerfeld coefficient, that gives the electronic contribution to the specific heat. This theory is based on the assumption that the quasiparticles, which in the HF compounds consist of states involving both the f and conduction electrons, are only weakly interacting. In many respects the FL theory is found to work for the heavy-fermions, although when the measurements are extended to very low temperatures, important deviations are found from FL theory. A similar situation is found in the layered superconductors, and this has given rise to many experiments trying to shed further light on this intriguing problem. UBe_{13} is one of the systems that do not obey FL theory (Ramirez et al., 1994), as are compounds based on the solid solutions $\text{U}_x\text{Y}_{1-x}\text{Pd}_3$ and $\text{UCu}_{5-x}\text{Pd}_x$.

Neutrons give important information on the development of the non-FL ground state and some rather interesting experiments have been done on the compound UCu_4Pd (Aronson et al., 1995). Some of the data is shown in Fig. 8. The most striking property of Fig. 8(a) is the temperature independence of the data. Because of detailed balance considerations, this constant signal means that the imaginary part of the dynamic susceptibility, $\chi''(\omega, T)$, must have a special form. $S(\omega)$ and $\chi''(\omega, T)$ are related by $S(\omega) = [n(\omega) + 1]\chi''(\omega, T)$, where $n(\omega) + 1$ is the thermal occupation factor (Holland-Moritz and Lander, 1994). Since for $T \gg \omega$, $[n(\omega) + 1] \sim T/\omega$, then $\chi''(\omega, T) \sim (\omega/T)G(\omega)$ and for $T \ll \omega$, $[n(\omega) + 1] \sim 1$, $\chi''(\omega, T) \sim G(\omega)$.

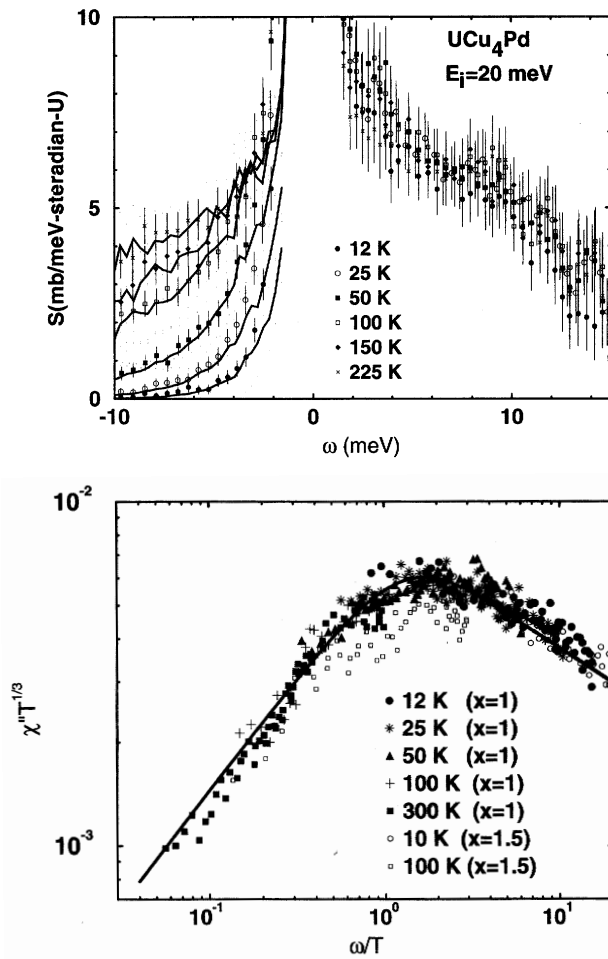


Figure 8. (a) $S(\omega)$ of UCu_4Pd at fixed temperatures ranging from 12 to 225 K. The incident energy is 20 meV. Solid lines for energy gain (left-hand side) are calculated from the energy loss part of the neutron spectrum by the detailed balance factor. (b) A plot of $\chi'' T^{1/3}$ against ω/T showing almost universal scaling properties for compounds $\text{UCu}_{5-x}\text{Pd}_x$ ($x = 1$ and 1.5). Data with $\omega > 25$ meV are not included. Solid line: $\chi''(\omega, T) T^{1/3} \sim (T/\omega)^{1/3} \tanh(\omega/1.2T)$. (Taken from Aronson et al., 1995)

For energies below a characteristic energy ω^* it is found that $G(\omega) \sim \omega^{-1/3}$, and this idea is at the basis for the representation of the data in Fig. 8(b). The major result of this study is that the magnetic response depends only on temperature, rather than depending on some characteristic energy – usually associated with the Kondo temperature. The inference from these results is that there is a divergence at $T = 0$, a so-called quantum phase transition.

A rather similar situation of a non-FL ground state has been found in the solid solution $U_xY_{1-x}Pd_3$ (Seaman et al., 1991, 1992; Andraka and Tsvelik, 1991). At low uranium concentration ($x < 0.2$) these compounds were thought to be spin glasses. Since these materials are related to UPd_3 , which I shall discuss later, there has been an expectation that they exhibit sharp crystal-field transitions between different states. In fact, as shown by McEwen et al. (1995a), the picture is more complex. Whereas for $x = 0.45$, crystal-fields can be readily seen, they get much more difficult to observe when the uranium concentration is reduced (and this is not simply a dilution effect) as they become much broader in energy space. Initially, the bulk property measurements were interpreted in terms of the quadrupolar Kondo effect (Cox, 1987, 1988a,b). This theory, which has also been applied to UBe_{13} (see Ramirez et al., 1994), requires that the ground state be non-magnetic. In particular, for a non-Kramers ion such as U^{4+} there exists the crystal-field state Γ_3 that meets these requirements. Although the work of McEwen et al. (1995a) firmly established CF transitions at ~ 5 and ~ 36 meV in both the $x = 0.2$ and 0.45 samples, these measurements were not able to determine the ground state. More recently, experiments by Dai et al. (1995) have shown that there is a substantial amount of quasielastic scattering in both the $x = 0.45$ and 0.2 samples and this is inconsistent with the non-magnetic doublet Γ_3 as the ground state, but rather point to the triplet Γ_5 being the ground state. They did not consider any possible $5f^3$ CF configurations. In addition, and perhaps quite surprising considering the number of people who have studied these samples, they found that the $x = 0.45$ sample orders magnetically with a simple doubling of the unit cell. The magnetic structure is identical to that found in UPd_4 , which also has the same $AuCu_3$ structure, and the ordered moments of both compounds are $\sim 0.7 \mu_B$. Interestingly, the muon experiments (Wu et al., 1994) had already indicated that the $x = 0.4$ system contained a magnetic moment, but in the absence of direct diffraction evidence for its long-range order, there was a belief that the compound was a spin glass. This study by Dai et al. (1995) went on to observe elastic magnetic correlations in the $x = 0.2$ sample at the same reciprocal-lattice vector as the ordering was found in the $x = 0.45$ sample, so that the $x = 0.2$ material is certainly close to a magnetic instability. Furthermore, fluctuations were still seen at $E = 0$ meV in the $x = 0.2$ sample, so that the CF scheme is probably the same for both values of x , although the scattering is much reduced in the $x = 0.2$ sample, in agreement with the finding

of McEwen et al. (1995a). This study by Dai et al. (1995) is a good example of how a careful neutron study can change completely the ideas about the physics of a certain material.

4 The progression towards localized $5f$ electrons

The discussion about how to define localized $5f$ electrons has been one that has been at the center of actinide research for many years. In many respects the answer depends on the measuring technique. As far as neutron scattering is concerned the answer is relatively simple: the $5f$ electrons can be described as localized when sharp and clear CF excitations can be seen with neutron spectroscopy. This is a definition that follows the framework of defining compounds containing the lanthanide elements, and has the advantage of simplicity. Most compounds containing lanthanides exhibit sharp, or relatively sharp, CF transitions; compounds containing cerium being the one notable exception (Holland-Moritz and Lander, 1994). Unfortunately, the only metallic actinide compound (so far) that has been found to fit readily into this classification is UPd₃. We do not include here a discussion of the oxides, which are without doubt localized, even though they exhibit many unusual properties (Holland-Moritz and Lander, 1994).

4.1 Compounds with the NaCl crystal structure

Certainly the most studied examples of compounds in this class are those with the NaCl crystal structure and comprising the mononictides and monochalcogenides. However, there are a number of exceptions. The most notable are the first member of this series, UN, which is itinerant (Holland-Moritz and Lander, 1994), and the Pu-chalcogenides, which are still the subject of much debate, and have been proposed as showing intermediate-valent behaviour (Wachter et al., 1991). However, with these caveats, the remainder of the compounds, e.g. USb, UTe, NpAs, NpBi, NpTe, PuSb, may be regarded as quasi-localized. Although they do not, for the most part, exhibit CF excitations, relatively sharp excitations involving the uranium moments have been found in most of them. A recent review (Lander et al., 1995) has focused on these compounds so that I will not repeat what is written there. Experiment and theory are in modest agreement; the latter having to include a considerable amount of hybridization between the $5f$ and conduction-electron states. Recently, Bourdarot and colleagues (Bourdarot et al., 1995) have succeeded in seeing sharply defined spin-wave modes in NpBi, but an experiment on an equally good single crystal of NpTe failed to find any excitation. The localization is certainly more important for the pnictides (N, P, As, Sb, and Bi) than for the chalcogenides (S, Se, and Te), and there is always a trend for more localization as one proceeds to

heavier actinides or anions. The failure, so far, to find excitations in a material like NpTe would seem to be contrary to the above rules since excitations have been measured in UTe (Lander et al., 1995). However, if we are approaching an intermediate valent behaviour in the Pu-chalcogenides, then the Np-chalcogenides may exhibit precursor effects.

The last few years have seen a number of new studies of the phase diagrams of the AnX compounds, both with neutrons and with resonant x-rays (Lander, 1996). With neutrons two different types of investigations merit discussion. A significant study of the NpX compounds with elastic neutron scattering has been performed by Bourdarot (1994) as part of his thesis work at the Centre d'Etudes Nuclaires, Grenoble; unfortunately, most of this remains unpublished. A new capability has been developed at the Laboratoire Leon Brillouin, Saclay, to look at single crystals at low temperature and high pressures up to 8 GPa. Initial studies have performed on UAs and USb (Goncharenko et al., 1994; Braithwaite et al., 1996), and are very promising in trying to understand the development of the complex magnetic structures (Lander and Bulet, 1995) as a function of pressure, and thus give information on changes in hybridization as a function of volume.

4.2 Compounds with the AuCu₃ structure

The UX₃ compounds have been of interest for many years and a full discussion of their properties, as known so far, may be found in the chapters of the Vol. 17 and 19 of the Rare Earth Handbook (Lander, 1993; Holland-Moritz and Lander, 1994; Aeppli and Broholm, 1994). In these compounds, as in the NaCl series, the 5*f* hybridization with the conduction electrons and the anion *p* states is critical in determining the magnetic properties. Like the NaCl compounds they exhibit increased hybridization for the lighter anions. UGa₃ is classified as a band antiferromagnet, UGe₃ as a band paramagnet, USn₃ as a spin-fluctuation system, and UPb₃ close to a localized antiferromagnet. Recently, an effort in the Cadarache Laboratories of the CEA has led to the production of a number of single crystals of the NpX₃ compounds, and provided the opportunity for neutron experiments to extend our knowledge of the systematics into the Np series. This work is not yet complete, but initial reports are summarized by Sanchez et al. (1993), with brief details on NpAl₃ (Oddou et al., 1994), NpGa₃ (Bouillet et al., 1993), NpIn₃ (Colineau et al., 1995), and NpSn₃ (Charvolin et al., 1994). Large enough single crystals of NpSn₃ are now available for inelastic neutron experiments, and these will be performed at the ILL shortly. At the moment it is clear that the Np samples are more "magnetic" than their uranium analogues, which is consistent with our general picture that, for an isostructural series, the hybridization reduces as one substitutes a heavier actinide.

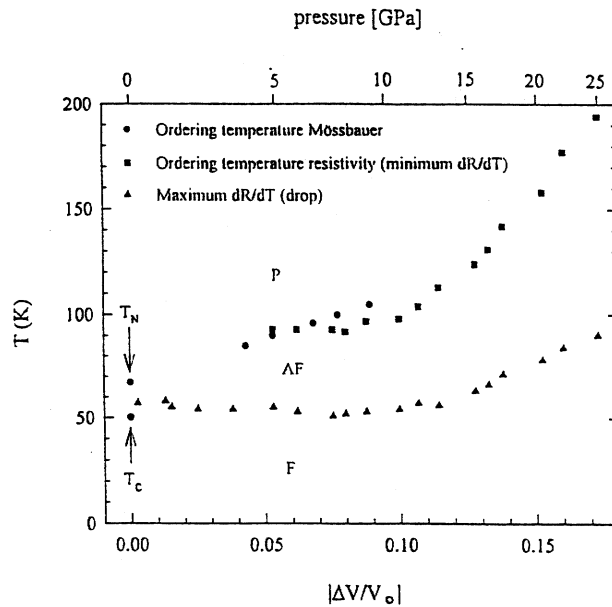


Figure 9. The ordering temperature deduced from Mössbauer spectroscopy (circles) and from resistance measurements (squares) versus volume reduction (pressure on the top scale) for NpGa_3 . The maximum of the derivative dR/dT of the low-temperature drop in resistance is also plotted (triangles). The phase diagram, P = paramagnetic, AF = antiferromagnetic, and F = ferromagnetic is proposed. (Taken from Zwirner et al., 1996)

Within the AnX_3 compounds a rather complete experiment (except for the use of neutrons) has been performed on NpGa_3 under pressure (Zwirner et al., 1996). We reproduce from this study the tentative phase diagram under pressure in Fig. 9. Perhaps the most startling aspect of this phase diagram is the dramatic increase in the ordering temperature T_N as a function of pressure above 10 GPa. The increase has been confirmed directly by Mössbauer spectroscopy up to this pressure, but the technique is not easily applicable above 10 GPa, and T_N is taken from a change of slope seen in the resistivity. The authors explain their many measurements by assuming that the Np $5f$ -electrons are initially only weakly hybridized at ambient pressure, and the increase in T_N may be ascribed to the increase of exchange as the atoms are pushed closer together. This is consistent with a decrease in both the isomer shift and the quadrupole interaction as measured by the Mössbauer technique with applied pressure. Of course, at higher pressures the hybridization should start

to increase, and this must eventually lead to a $5f$ band that is too wide to fulfill the Stoner criterion, and thus a reduction of the ordering temperature. Such an effect of observing first a dramatic increasing in T_C and then, with further pressure, a reduction, occurs in UTe (Link et al., 1992). Theory (Cooper et al., 1994) and experiment are in reasonable accord for UTe, and the extent of hybridization required is consistent also with the neutron inelastic measurements and the observation of broadened spin waves (Holland-Moritz and Lander, 1994). Other pressure studies have been reported on NpSb (Amanowicz et al., 1994), and are in preparation for NpAs (Ichas et al., 1996). As the studies of UTe and NpGa₃ illustrate, the use of pressure gives a considerable amount of new information. These are hard experiments with neutrons. The higher pressures can only be obtained with samples almost too small to be useful for neutron scattering. It is an area that in future may be exploited by using the resonant x-ray technique, except that this too has its disadvantages. At the resonant energy of ~ 4 keV photons are strongly absorbed, and it will require great ingenuity to make a pressure cell inside a cryostat and still allow such photons to enter and diffract from the single crystals. However, the advantage is that the x-ray intensity from modern synchrotron sources is much greater than can ever be conceived with neutrons.

4.3 Localized $5f$ electrons in UPd₃

UPd₃ stands out as an extraordinary exception in the actinides (Holland-Moritz and Lander, 1994) as it clearly can be described starting from a localized $5f^2$ configuration. Crystal fields were first observed many years ago and much of the work at Chalk River National Laboratories is published in Buyers and Holden (1985). The structure of this material is not cubic AuCu₃ as discussed in the last section, but rather has the double hexagonal close-packed structure in which there are two different sites for the uranium ions.

In the last few years the transitions at low temperature have been examined in more detail by McEwen and his colleagues and the theory has been worked out by Walker and colleagues. Steigenberger et al. (1992) and McEwen et al. (1993, 1995b) have reported both inelastic and elastic neutron scattering. Two transitions take place at low temperature; the first at $T_1 \sim 6.7$ K involves the ordering of the quadrupoles of the uranium ions; the second at $T_2 \sim 4.5$ K involves magnetic ordering with a very small magnetic moment. The superlattice reflections that appear on cooling at T_1 arise from the modulated ionic displacements which accompany the quadrupolar modes: neutrons do not couple directly to the quadrupolar moments. This phase transition has been examined from a group theoretical point of view in a series of papers (Walker et al., 1994; Kappler et al., 1995; Luettmer-Strathman et al., 1995), and special attention has been given to the results of

experiments when a symmetry breaking field (either magnetic or uniaxial stress, for example) is applied. The combination of theory and experiment have now led to the triple- k quadrupole ordering given by Fig. 10. Quadrupolar ordering has also been observed in UO_2 (Lander, 1993), but occurs at the same temperature as the magnetic ordering. However, such orderings at higher temperatures than the magnetism are not confined to the actinides; they may be found for a number of lanthanide compounds (Morin and Schmitt, 1990). This work on UPd_3 illustrates the extreme complexity when the quadrupolar moments are the driving force for the phase transitions. Such quadrupole moments are large in f systems (Morin and Schmitt, 1990), and may significantly affect both the final magnetic structure as well as the nature of the transitions. That these quadrupolar effects have not (yet) been observed in systems such as UBe_{13} is only because there are other, more important, interactions involving the hybridized f -conduction-electron states in that material.

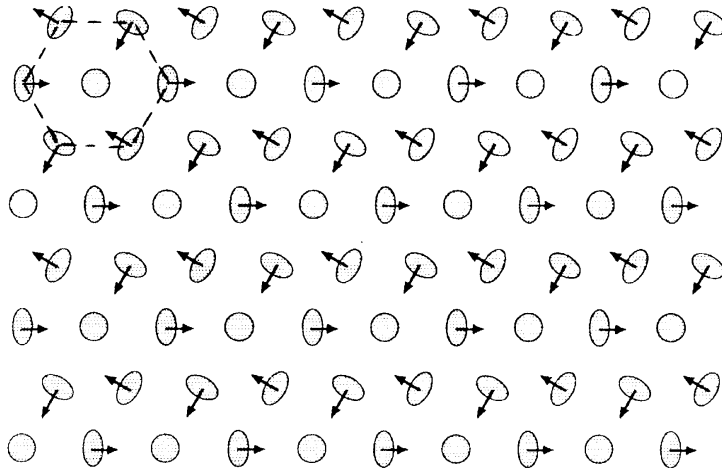


Figure 10. Basal plane projection of the antiferroquadrupolar structure on the cubic sites of UPd_3 below T_1 as described in the text. The unit cell of the structure is indicated. The ordering has the $3k$ symmetry. (Taken from McEwen et al., 1993, 1995b)

5 Discussion

A framework for the magnetism of the $5f$ electrons in the actinides still eludes us. A key parameter is the extent of hybridization, \mathfrak{F} . Unfortunately, this may take place either with the conduction-electron states (as, for example, dominates in most of the heavy fermions) or with the p - or d -states of neighbouring anions (as, for example, is believed to be the basic mechanism in the AnX_3 compounds), and it is difficult to distinguish which is the most important for any particular property that is being measured. Certainly introducing a single parameter \mathfrak{F} is too naive. However, what I have tried to show in this article is that if we start from the Jensen-Mackintosh (1991) picture of localized f electron behaviour, then the hybridization is zero (or very small) and this explains the magnetism of UPd_3 . With increasing \mathfrak{F} we come to the compounds of the form AnX and AnX_3 . A still further increase of \mathfrak{F} , especially with respect to the conduction-electron states, takes us to a magnetic instability and the possibility of the heavy-fermion state. Why some of these materials should be superconducting remains a mystery, but is believed to be due to the quasi-particles (involving hybridized $5f$ and conduction states) forming unconventional (i.e. non s -state) pairs at the lowest temperature (Aeppli and Broholm, 1994; Aeppli et al., 1988; Cox and Maple, 1995; Lonzarich, 1996). A further increase in \mathfrak{F} takes us to the truly itinerant $5f$ electron states, such as UN , UFe_2 , possibly UGa_3 , and allows the reduction of the orbital moment (Lander et al., 1991), and the understanding of the magnetism in terms of the local-density approximation (Johansson and Skriver, 1996; Brooks, 1996).

Many different factors determine where a particular actinide may fit into this loose framework. More work, both experiment and theory, lies ahead to attempt to make such a framework quantitative.

Acknowledgements

The tragic death of Allan Mackintosh in December 1995 was a loss not only of an exceptional human being, but it also deprived us of his great interest and inspiration in magnetism in general, and in that of f electrons in particular. By his example and by his enthusiasm he influenced my own research for more than 20 years; it is with much sadness that I dedicate this article to his memory. I am especially grateful to my students Luigi Paolasini and Arno Hiess for collaborations over the last 3 years.

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