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Chapter 11
EPILOGUE

This thesis basically consists of two relatively separate parts. Below, the lines of argument are represented, in a bird's eye view, for each part separately. We start with the first part.

A relatively new interesting class of materials is formed by the heavy-fermion compounds. Their chemical composition always involves a dense periodic arrangement of actinide or lanthanides atoms embedded in a metallic host. The essential feature of the actinide/lanthanides magnetic atoms is their narrow not-completely filled f shell. Arrangements of magnetic ions in metallic hosts are also found in more "common" systems: e.g. magnetic systems (where magnetic ions are also arranged densely periodic) or Kondo systems (dealing with the situation of a magnetic ion embedded in a metallic host). It is, therefore, not surprising that heavy-fermion compounds share experimental features with these systems. Some of the features are even exhibited in a more extreme sense than by the "original" systems. This includes the name-giving property, the apparent heavy electron mass.

At the lowest temperature a new state of matter sets in. Among other features, this reveals itself as an enhancement of the linear term of the temperature dependence of the specific heat. This is, generally, interpreted as an enhancement of the apparent effective mass. A similar feature is found in Kondo systems (in terms of the concentration of magnetic ions involved, Kondo systems can be considered diluted). The features observed in Kondo systems are adequately traced back to the particular nature of the interactions between the (in this case) f states of the magnetic ion and the conduction states. Only therein the enhancement of the effective mass is smaller.

The enhancement of the apparent effective mass associated with the creation of the heavy-fermion behaviour is generally interpreted as the introduction/formation of many low-energy excitations (as heavy-fermion behaviour starts by lowering the temperature, suddenly much more energy per degree Kelvin can be stored in the electronic part of the system than in the absence of that behaviour). In terms of densities of states a pronounced narrow peak is formed at the chemical potential. For the Kondo effect, this peak is generally referred to as the Abrikosov-Suhl resonance. Heavy-fermion behaviour appears to have similar features, even more pronounced. This seems, at least heuristically, to be a correct description.

For the Abrikosov-Suhl resonance a theoretical description exists. In this

thesis, this description is formulated in terms of Friedel's sum rule. That approach cannot straightforwardly be adapted for the case of a dense and periodic arrangement of magnetic ions, as is the case in heavy-fermion systems. An intriguing "Gedanken" experiment is proposed. Imagine the situation where a piece of heavy-fermion material is embedded in a metallic host. In this case, again, a transformation from a non-magnetic impurity in a Fermi-liquid to a magnetic impurity in a Fermi gas can be performed. Again, Friedel.s sum rule should hold at sufficiently large distances.

From the previous presentation the suggestion could rise as if the heavy-fermion behaviour is just some turboform of the Kondo effect. This is far from what we would like to suggest.

The effective mass enhancement in Kondo systems is attributed to, what can, loosely speaking, be seen as associated to the low-energy excitations involved in an effective "screening" of the f-electron spin of the magnetic ion by the spins of the conduction electrons. Similar mechanisms cannot straightforwardly be adapted to the case of heavy-fermion systems. This is for fundamental reasons. There are simply not sufficient conduction electrons present and too many conduction states have interactions with too many magnetic-ion f states simultaneously (a state can only be in singlet formation with one other state at a time). The result must be some form of interaction between the magnetic ions which must be magnetic of origin. But what the nature is of these magnetic interactions is not unambiguously established.

A similar dense and periodic arrangement of magnetic ions is found in more "classical" magnetic systems. It is, therefore, not surprising that heavy-fermion systems share features with this form of magnetic system, as there are: the retrieved large magnetic moment (with ordering) at sufficiently high temperatures where heavy-fermion behaviour is suppressed and, in some sense, the high effective Grüneisen parameter (expressing a vastly enhanced strain dependence of various properties such as energy levels, characteristic temperatures, characteristic fields etc.) observed in the presence heavy-fermion behaviour.

The observation that heavy-fermion behaviour is some form of compromise between Kondo interactions and magnetic interactions does not do justice to the problem. Kondo interactions and magnetic interactions seem to be competing tendencies in these systems. We argued that the Kondo screening seems to destroy the magnetic interactions, whereas the latter seems to suppress the Kondo screening. An effect we observed is that the spin of a magnetic ion can also be "screened" by the spins of surrounding magnetic ions.

It is, therefore, not surprising that heavy-fermion systems also have properties which cannot be associated to either the Kondo or the magnetic interactions. Heavy-fermion systems generally have a Wilson ratio (the enhancement of the specific heat versus the enhancement of the susceptibility) unequal to two (as it should be for Kondo systems) and sometimes an extremely small, but essentially non-zero magnetic moment. Suggestions have been made that these small moments are rapidly

fluctuating in time. This could explain why these moments are detected in neutron experiments but not in μSR experiments.

To deal with "competing tendencies", heavy-fermion behaviour is often considered to occur close to a quantum-critical point. The phenomena near that critical point bare resemblance to thermodynamic phase transitions. This time, the important parameters is not an external macroscopic quantity like the temperature, but rather the interaction-parameter strength. With the help of a scaling Ansatz, critical exponents and their mutual relationships can be established. These parameters are then experimentally accessible. An alternative interpretation is in terms of the double channel Kondo problem.

Although this is a highly legitimate (and successful) approach, in this thesis the emphasis is on the microscopic nature of the many-body states responsible for heavy-fermion behaviour.

In a certain manner, heavy-fermion systems do not form a "class of materials" in the strictest sense of the word as for example the "classical" BCS superconductors do. For BCS superconductivity two properties are of importance: the Meissner effect and the zero resistivity. Both properties have to be compared to the normal (metallic) state of matter. Heavy-fermion behaviour is more characterized by its eclectic collection of properties and it has to be compared to magnetic states or Kondo states, on top of which it seems to prevail. For instance, by gradually replacing Ce by La in $CeRu_2Si_2$ the properties of $(Ce,La)Ru_2Si_2$ shift from heavy-fermion behaviour to Kondo behaviour. There are no clean-cut boundaries. It is more as if heavy-fermion behaviour forms a no-man's land in parameter space between various regions in which different types of behaviour prevail: magnetism, Kondo behaviour, etc..

After serious deliberation, the properties we believe to be the most characteristic for heavy-fermion behaviour are: the apparent high effective mass, the high Grüneisen parameter and the small, but essentially non-zero, magnetic moment.

We started with a detailed inspection of existing theories. In particular, the Kondo effect and the magnetic interactions were closely examined. This is for various reasons. Why the Kondo theory cannot be straightforwardly adapted to the situation of heavy-fermion systems? Is it possible to understand the conflict between Kondo and magnetic interactions in heavy-fermion systems? As the standard Hamiltonian to deal with heavy-fermion systems we chose the Periodic-Anderson Hamiltonian. For the diluted regime we introduced the Anderson Hamiltonian. The concept of an effective Hamiltonian was introduced and it was demonstrated how under the restriction that each f state stays integer occupied, for the case of a diluted concentration of magnetic ions, the Kondo Hamiltonian is retrieved from the Anderson Hamiltonian. We also discussed the "Kondo-versus-RKKY approach", in which case for the magnetic interactions interactions of the RKKY type are chosen. The pro's and con 's of that approach were discussed. Among other observations, we pointed out that under the same restrictions used to derive the Kondo Hamiltonian from the Anderson Hamiltonian one can derive an effective Hamiltonian from the Periodic-Anderson Hamiltonian

in which in the lowest term the "Kondo-lattice Hamiltonian" is recognized. In higher order terms, interactions of the RKKY form can indeed be recognized. But to understand why only these parts of the higher order terms prevail one must make use of the fact that a quantum critical point exists.

Eventually, we introduced a different effective Hamiltonian for the Periodic-Anderson Hamiltonian. It consists of three terms; for the conduction states a straightforward conduction-band Hamiltonian, a Hamiltonian for the f states in which the a Hubbard Hamiltonian can be recognized and an interaction term between the f and conduction states. The latter has the form:

$$\Delta H_{\text{eff. cond-f states}} \equiv - \sum_{\{\mathbf{k},\mathbf{q}\},\{\sigma,\rho\}} I_{\{\mathbf{k},\mathbf{q}\}}^{\{\sigma,\rho\}} \left[c_{\mathbf{k},\sigma}^{\dagger} f_{\mathbf{q}\rho}^{\dagger} \right] \left[f_{\mathbf{k},\sigma} c_{\mathbf{q}\rho} \right]$$

with:

$$\mathbf{s}_{\mathbf{k},\mathbf{q}} \equiv \frac{1}{2} \begin{pmatrix} c_{\mathbf{k}\uparrow}^{\dagger} c_{\mathbf{q}\downarrow} + c_{\mathbf{k}\downarrow}^{\dagger} c_{\mathbf{q}\uparrow} \\ -\mathrm{i} \left(c_{\mathbf{k}\uparrow}^{\dagger} c_{\mathbf{q}\downarrow} - c_{\mathbf{k}\downarrow}^{\dagger} c_{\mathbf{q}\uparrow} \right) \\ c_{\mathbf{k}\uparrow}^{\dagger} c_{\mathbf{q}\uparrow} - c_{\mathbf{k}\downarrow}^{\dagger} c_{\mathbf{q}\downarrow} \end{pmatrix}, \quad \mathbf{S}_{\mathbf{k},\mathbf{q}} \equiv \frac{1}{2} \begin{pmatrix} f_{\mathbf{k}\uparrow}^{\dagger} f_{\mathbf{q}\downarrow} + f_{\mathbf{k}\downarrow}^{\dagger} f_{\mathbf{q}\uparrow} \\ -\mathrm{i} \left(f_{\mathbf{k}\uparrow}^{\dagger} f_{\mathbf{q}\downarrow} - f_{\mathbf{k}\downarrow}^{\dagger} f_{\mathbf{q}\uparrow} \right) \\ f_{\mathbf{k}\uparrow}^{\dagger} f_{\mathbf{q}\uparrow} - f_{\mathbf{k}\downarrow}^{\dagger} f_{\mathbf{q}\downarrow} \end{pmatrix}$$

Notice that $\mathbf{s}_{\mathbf{k},\mathbf{k}}$ and $\mathbf{S}_{\mathbf{k},\mathbf{k}}$ are the standard spin-vector operator definitions for the conduction and f state with quasi-momentum $\mathbf{k}$, respectively. For special choices of $I_{\{\mathbf{k},\mathbf{q}\}}^{\{\sigma,\rho\}}$, the Hamiltonian $\Delta H_{\text{eff. cond-f states}}$ reduces to the Kondo or the Kondo-lattice Hamiltonian. For heavy-fermion systems resembling Kondo systems, $I_{\{\mathbf{k},\mathbf{q}\}}^{\{\sigma,\rho\}}$ is non-zero for small values of $|\mathbf{k}-\mathbf{q}|$. If a wider range of $\mathbf{k}$ and $\mathbf{q}$ values is allowed, a description in terms of itinerant f states is better applicable (as it seems to be the case for UPt_3).

It is this term we hold responsible for the low-energy excitations that are typical for heavy-fermion behaviour.

It is the Hubbard term in this effective Hamiltonian we hold responsible for the magnetic ordering. In the case of half filling it is known that the Hubbard Hamiltonian effectively reduces to an Hamiltonian for an Heisenberg antiferromagnet. In heavy-fermion systems we have slightly less than half filling, in which case holes propagate through the antiferromagnetic ordered lattice of magnetic ions leaving trails of magnetic frustrations behind.

This approach indicates why generally all heavy-fermion compounds order antiferromagnetically and not ferromagnetically. To order ferromagnetically a strong spin-orbit coupling is needed (as in our small molecules).

We considered rather simple molecules, so that eigenstates and energy spectra can be readily generated, to study several microscopic features of many-body states that we expect to occur in heavy-fermion systems. E.g. we studied the effects of conduction-electron states shared by two f states both for the situation where an

inadequate number of conduction states/electrons is present to form singlets with each f state/electron individually and where an adequate number is present to do so. Also the effects of altering the number of electrons present in the system on the energy spectrum is studied. This is of interest because the differences between such spectra form the single quasi-particle spectra as determined in an XPS or BIS experiment. Another subject of interest is the effect on the correlation between sites when a surplus of symmetry operators is present.

A detailed study is made of what we called "particle-hole excitations". As such excitatons exist also ground states exist where conduction and f states are arranged in triplets in stead of singlets.

In the final part of the second chapter we studied the effects of a fictitious field, enforcing the magnetic ions to order either ferromagnetically or antiferromagnetically. Among other features, an energy scaling relation between characteristic field and characteristic temperature is retrieved.

In the second part of this thesis, high-field dilatation experiments on the $U(Pt_{1-x}Pd_x)_3$ compounds are performed. UPt_3 serves as a Drosopilae for the heavy-fermion compounds. UPt_3 has all the properties characteristic for heavy-fermion behaviour in its extremest form. By replacing Pt by Pd its properties can be altered in a controlled fashion. Dilatation experiments are an excellent tool to study heavy-fermion behaviour. The creation or suppression of heavy-fermion behaviour as a result of field or temperature changes is accompanied by large changes in the molar volume (a result of the high Grüneisen parameter).

Concerning the magnetic properties of the $U(Pt_{1-x}Pd_x)_3$ compounds we used an alternative approach to the more common Kondo-versus-RKKY interpretation.

We argued that unlike as for the single-ion case for the periodic magnetic-ion case $\Delta n_f \neq 0$ (the deviations from integer filling of each f orbital) is an important property. In general terms, by allowing the peak in the density of states related to the itinerant f-states to have an energy equal to the chemical potential, instead of an energy much smaller than the chemical potential, the system will be able to form low-energy correlated many-body states. Some room in phase space must be created to allow for these new excitations to occur. For this the f-band is slightly depopulated. In terms of the hybridization-peak-at-the-Fermi-level description just introduced it is Δn_f which determines at which energy the chemical potential is found within this peak. It will not be surprising that the effective mass is a function of Δn_f.

We even argued that the size of the extremely small but essential non-zero magnetic moment is also a function of Δn_f. For this purpose we adapted the Stoner theory to be applied to particular hybridization-style shaped bandstructures (each bandstructure corresponding to one particular type of antiferromagnetic ordering). Such an interpretation could be made to agree with the notion that the small magnetic moment is a rapidly fluctuating moment (so that it is only detectable by some experimental techniques).

We explained the observation of a maximum in the Néeel temperature versus

Pd doping in terms of sizes of orbitals and a super-exchange mechanism.

Some heavy-fermion systems resemble Kondo systems, while others seem better describable in terms of a renormalized hybridization peak. The system we considered, UPt_3, belongs to the latter class. The empirical notion concerning the shape of the peak in the density of states at the Fermi level, typical for heavy-fermion behaviour, is that it is shaped as if a dispersionless f-style band is hybridized with a broad conduction-style band. Phenomenologically, concerning the shape of the peak in the density of states, many-body interactions should have two mayor effects. *A priori*, as $(\mu - \epsilon_f) \gg |T|$ (the energy associated with the bare f state of the magnetic ion is well below the chemical potential) such a hybridization peak would not be detectable in a thermodynamic experiment. $(\mu - \epsilon_f)$ Should effectively be renormalized so that the resulting peak is found at the chemical potential. To accommodate for the experimentally detected large effective masses (associated with the shape of the peak) the ligand-hybridization should be approximately ten times smaller as is estimated by means of an overlap integral.

For UPt_3, the shape of this hybridization-style peak seems to be in agreement with the temperature and angular dependence of the observed de Haas van Alphen oscillations [1]. But we took it a step further. We assumed the relative strain dependencies of various energy levels within this peak to be as if it would be such a (renormalized) hybridization peak and as if all strain dependence stems from the volume dependence of the ligand-hybridization strength.

We argued that this is consistent with the observation of a broad shoulder in the size of the low-temperature effective mass versus temperature (as deduced from high-field specific heat data) for UPt_3 at $B^* \approx 20$ T while its relative strain dependence displays a sharp cusp (determined from a combination of high-field specific heat and high-field thermal-expansion data).

In this heuristic picture the effect of introducing an external field is primarily to shift this hybridization peak to lower energies with respect to the chemical potential. The characteristic-field strength, B^*, is then associated with the field needed to shift the peak completely below the Fermi energy. At the lowest temperatures, it is no longer detectable in a thermodynamic experiment. As the peak is shifted below the chemical potential, large local moments start to be created.

For $B \gtrsim B^*$ the peak is still present only at energies smaller than the chemical potential. At the lowest temperatures, thermodynamic data are not affected by that peak but, as temperature is increased, it starts to be, again, included within the temperature window $k_B T$ of the chemical potential. We coined the phrase "re-entrant heavy-fermion behaviour".

In dilatation experiments, heavy-fermion behaviour reveals itself as a valley in a three-dimensional plot of the length versus temperature and field. So, in case of re-entrant heavy-fermion behaviour we run for increasing temperatures into the valley as opposed to out of the valley for "regular" heavy-fermion behaviour. This implies

that for the "regular" heavy-fermion behaviour we expect a positive sign for the thermal-expansion coefficient, while for the "re-entrant heavy-fermion behaviour" that sign should be negative.

We argued that one of the effects of Pd doping in the $U(Pt_{1-x}Pd_x)_3$ compounds is similar to applying magnetic fields. It shifts the peak to lower energies. We argued that 10 % of Pd doping corresponds to applying an external field of $B^* \approx 20$ T.

The above interpretation provided an explanation for the sign reversal of the thermal-expansion coefficients measured along the a, b-axes and c-axis in $U(Pt_{0.9}Pd_{0.1})_3$ as compared to UPt_3 and all other $U(Pt_{1-x}Pd_x)_3$ compounds with $x < 0.1$.

We could demonstrate that all thermal-expansion curves for $U(Pt_{0.9}Pd_{0.1})_3$ obtained at various field are basically of one universal shape if they are renormalized with respect to their extremum. This can be taken as an indication of re-entrant heavy-fermion behaviour.

Comparing high-field thermal-expansion data for $U(Pt_{0.9}Pd_{0.1})_3$ there seems to be an off set of approximately 4 T between the thermal-expansion data obtained along the a- and along the b-axis. We interpreted this as the presence of an extra internal field resulting from the creation of the local moments. For both axes, the minimum that is observed at (T_{ext}) in the thermal-expansion coefficient ($\alpha_{min}(T_{ext})$) versus the temperature shifts linearly with T_{ext} as obtained for various field strengths. The lines for the a- and b-axis intersect for $\alpha_{min}(T_{ext}) = 0$ and $T_{ext} < 0$. This can be taken as a further indication for re-entrant heavy-fermion behaviour. Besides, the features observed on UPt_3 in fields $B > 20$ T (as the effective mass, thermal expansion etc.) resemble very much the features as observed on $U(Pt_{0.9}Pd_{0.1})_3$ for $B > 0$ T.

Furthermore, in our interpretation the presence of antiferromagnetic ordering is expected to further stabilize heavy-fermion behaviour (they are not interpreted as two opposing tendencies as in the "Kondo-versus-RKKY approach"). This is also what we observed in the measurements on $U(Pt_{0.95}Pd_{0.05})_3$. For temperatures smaller than the Néeel temperature all surface thermal-expansion curves for the (a, b)-plane scale. They can be shown to be identical with respect to a temperature normalized by the relevant Néeel temperature.

We also could study the effects of the presence of domains on dilatation measurements. The concept of a "dislocking field" is introduced.

As Pd is introduced to the $U(Pt_{1-x}Pd_x)_3$ at low concentrations ($x \approx 0.02$) local moments start to be created. Further increase of the Pd concentration will make the long-range antiferromagnetic ordering more pronounced (the Néeel temperature increases) only to reach its maximum for $x = 0.05$. At a further increase of the Pd concentration, the long-range antiferromagnetic ordering is depressed. We assume that as we increase Pd concentration the f states turn more and more localized. This notion is inspired by observations made in doping experiments of Pt and Pd in Au. It is basically the ligand-atom orbital which becomes effectively smaller. We interpreted the occurrence of an optimum in the Néeel temperature versus Pd concentration in

terms of a super-exchange mechanism. Between two magnetic ions a ligand atom is situated with its degenerate ligand orbital. There must be sufficient room between the two magnetic orbitals to shift the two degenerate versions of the orbital with respect to one another so that a sufficient polarization is introduced in the overlap region with the f orbital . On the other hand the magnetic ions must be sufficiently close to the ligand atom so that their respective orbitals have sufficient overlap.

It became clear that the c-axis response in $U(Pt_{1-x}Pd_x)_3$ is large and not directly related to the heavy-fermion state. In UPt_3 the c-axis thermal-expansion curves are even not magnetic field dependent. Applying a field exceeding B^* has no mentionable effect on the shape of these curves. No feature is present which can be associated with the characteristic temperature. On the other hand the size of the thermal expansion is considerable.

At first glance, one could argue that the thermal expansion curves along the c-axis for $U(Pt_{0.95}Pd_{0.05})_3$ and $U(Pt_{0.9}Pd_{0.1})_3$ result from some elastic deformation of the crystal. Extensive studies, however, demonstrate that this could not be the case. The origin of the large c-axis response is still mired. We interpret the thermal expansion phenomena in $U(Pt_{1-x}Pd_x)_3$ as resulting from sheets of heavy-fermion behaviour in the (a, b)-planes coupled to one another by mechanisms yet to be identified.

D.I.W.

11.1 References

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