Application of the underscreened Kondo lattice model to neptunium compounds

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Abstract. The coexistence of Kondo effect and ferromagnetic order has been observed in many uranium and neptunium compounds such as UTe or \textit{Np\textsubscript{2}PdGa\textsubscript{3}}. This coexistence can be described within the underscreened Anderson lattice model with two \textit{f}-electrons and \textit{S} = 1\textsubscript{spins on each site. After performing the Schrieffer-Wolff transformation on this model, we have obtained an effective Hamiltonian with a \textit{f}-band term in addition to the Kondo interaction for \textit{S} = 1\textsubscript{spins. The results indicate a coexistence of Kondo effect and ferromagnetic order, with different relative values of the Kondo \textit{T}\textsubscript{K} and Curie \textit{T}\textsubscript{C} temperatures. We emphasize here especially the case \textit{T}\textsubscript{K} < \textit{T}\textsubscript{C} where there is a Kondo behavior below \textit{T}\textsubscript{C} and a clear decrease of the magnetization below \textit{T}\textsubscript{K}. Such a behavior has been observed in the magnetization curves of \textit{NpNiSi\textsubscript{2}} at low temperatures.

1. Introduction

It is now well established that cerium and uranium compounds have a different Kondo behavior. First, in the case of cerium and ytterbium systems, the Kondo effect and the magnetic order are provided by the \textit{s} – \textit{f} exchange interaction between the localized \textit{S} = 1/2 spins of the 4\textit{f}-electrons and the conduction electrons. As the conduction electrons may completely screen the local magnetic moment, there is a strong competition between the Kondo effect and the magnetic ordering, which has given the well known Doniach diagram \cite{1} and relatively small Néel or Curie temperatures, typically of order 5-10 K. On the other hand, uranium and neptunium compounds, like UTe \cite{2} or \textit{Np\textsubscript{2}PdGa\textsubscript{3}} \cite{3}, have larger localized spins, as for example \textit{S} = 1; these spins are partially screened (underscreened) by the conduction electrons and it results a coexistence between the underscreened Kondo effect and a ferromagnetic ordering, yielding relatively large Curie temperatures \textit{T}\textsubscript{C} of order 50-100 K. Moreover, the 5\textit{f} electrons in actinide compounds are less localized than the 4\textit{f} electrons in rare-earth systems.

We have recently developed the underscreened Kondo lattice model \cite{4,5}, where ferromagnetic order and Kondo behavior coexist, as observed in actinide compounds like UTe (with \textit{T}\textsubscript{C}=102 K) \cite{2} or UC\textsubscript{10.9}Sb\textsubscript{2} (with \textit{T}\textsubscript{C}=113 K) \cite{6}, but we extend the parameter space to include the case...
where $T_K < T_C$ that seems to be particularly suitable to describe the magnetization curves of neptunium compounds like NpNiSi$_2$ (with $T_C=51.5$ K) [7] or Np$_2$PdGa$_3$ (with $T_C=62.5$ K) [3].

2. The Underscreened Kondo Lattice model

Starting from the underscreened Anderson lattice model (UAL) with two $f$-electrons in different orbitals, we have recently derived an effective hamiltonian, using the Schrieffer-Wolff (SW) transformation [5]. We first briefly summarize the main results of ref. [5]: supposing that the two $f$-electrons are strongly coupled in the triplet $S = 1$ configuration through Hund’s rule. After performing the SW transformation, and keeping terms with $f$-operators in different sites (usually neglected), the effective hamiltonian is given by:

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + \sum_{i\sigma} E_0 n_{i\sigma} + J_K \sum_i s_i \cdot S_i + J_H \sum_{\langle ij \rangle} S_i \cdot S_j + H_f$$ (1)

In this hamiltonian, $\varepsilon_k$ is the energy of the conduction band, the second term of the Hamiltonian accounts for the energy $E_0$ of the two $5f$ localized electrons (the indices $\alpha = 1, 2$ correspond to the two $f$-orbitals) of the $5f^2$ configuration of the actinide atoms. In the third term $J_K > 0$ is the Kondo coupling (proportional to the square of the hybridization) between the localized spin $S_i$ and the spin $s_i$ of a conduction electron at the same site derived with the SW transformation. $J_H$ is an ad hoc interaction between nearest-neighbor spins [4, 5], which we consider as ferromagnetic ($J_H < 0$) and $H_f$ is the effective $f$-band term, which is also derived from the SW transformation. The presence of a finite $f$-band width improves the model which can, therefore, describe a small delocalization of the $5f$ electrons [5]. Finally, the intersite exchange is considered here as an independent parameter, though RKKY can also be obtained from the starting UAL.

We have previously studied the underscreened Kondo lattice model (UKL) which is similar to equation (1), but without the $f$-band term [4]. Coexistence of ferromagnetism and Kondo effect was already obtained in the UKL model, but inclusion of the last term in equation (1) gives a better description of the actinide compounds in which $5f$ electrons are not completely localized.

Because of the triplet state of the $5f$ electrons, the Kondo effect cannot lead to a complete screening of the localized $S = 1$ spins, and the ferromagnetic exchange between the partially screened spins may lead to the formation of a ferromagnetic order. In the present paper, we will study in detail the case where the Kondo temperature is smaller than the Curie temperature.

We have used the mean field approximation which has showed to be a very powerful tool to describe the competition between Kondo effect and magnetic ordering in the Kondo lattice [8, 9, 10]. In this approximation, the Kondo effect is described by the Kondo parameters:

$$\lambda_{\sigma} = \sum_{\alpha} \lambda^\alpha_{\sigma} = \sum_{\alpha} \langle c^\dagger_{i\alpha} f^\alpha_{i\sigma} \rangle$$ (2)

which couple conduction and $f$ electrons at the same site and that we assume site-independent, i.e. $\lambda_{\sigma} = \lambda_{i\sigma}$.

Moreover, in order to describe the magnetic properties of the system, we introduce also the magnetization operators for $f$- and $c$- electrons:

$$M_i^f = S_i^z = \frac{1}{2} (n^f_{i\uparrow} - n^f_{i\downarrow}) \quad \text{and} \quad M_i^c = \sigma_i^z = \frac{1}{2} (n^c_{i\uparrow} - n^c_{i\downarrow})$$

The ferromagnetic phase is described by non-zero values of $\langle M_i^f \rangle$ and $\langle m^c \rangle$, while non-zero $\lambda_{\sigma}$ describe the Kondo effect and the formation of the heavy-fermion state. In the ferromagnetic phase, $\lambda_{\sigma}$ depends on $\sigma$. The detailed calculations can be found in ref. [4, 5].
The last term of equation (1) is an effective 5f band, which is derived from the starting UAL model, within SW transformation. The half f-band width is spin-dependent and is given in mean field approximation by $W_f = A_\sigma$, where:

$$A_\sigma = -\frac{J_K P}{16} \left[ 7 + 3\langle\langle M_f^f\rangle^2 + 6\sigma\langle M_f^f\rangle \right].$$  \hspace{0.5cm} (3)

where $\sigma = \pm 1/2$.

The effective bandwidth depends on the Kondo coupling $J_K > 0$ and the f-magnetization. $P$ is here an adjustable parameter, which can be related to the parameters of the starting UAL model. This description has the advantage of describing the beginning of the delocalization of 5f electrons which are clearly less localized than the 4f electrons of rare-earths.

We have obtained a phase diagram giving the two temperatures $T_K$ and $T_C$ versus $J_K$ for fixed values of $J_H$. For small $J_K$ values, the Kondo temperature is zero and the Curie temperature increases slowly. At a critical value of $J_K$, $T_K$ increases rapidly and becomes larger than $T_C$. When $T_K$ and $T_C$ are of the same order of magnitude, the Curie temperature reaches a maximum [5].

This theoretical result can account for the experimental behavior of the Curie temperature $T_C$ of the monochalcogenide UTe under pressure, which is firstly increasing with pressure up to roughly 10 GPa and then decreases above this pressure [11, 12]. It is well known that pressure makes increase the Kondo coupling parameter $J_K$ in uranium compounds and our theoretical result can well explain the pressure dependence of the Curie temperature $T_C$ of UTe [5]. Thus, we propose that UTe can be described by the UAL with $T_K$ and $T_C$ of the same order of magnitude.

3. The case $T_K < T_C$: Comparison with experiments and conclusions

The case $T_K < T_C$ has been more recently studied and we present here briefly some results [13] showing that the $S = 1$ case is very different from what is obtained for the $S = 1/2$ Doniach diagram. The left panel of figure 1 shows the temperature dependence of the mean field parameters for this case. When decreasing the temperature below $T_C$, we can see that $M_f^f$ and $m^c$ increase with opposite signs (due to the positive sign of $J_K$), while the value of both $\lambda_\sigma$ remain zero below $T_C$. However, at a lower temperature corresponding to the Kondo temperature, the two $\lambda_\sigma$ become non zero, and there is a sudden drop of the magnetization parameters.

Thus, with decreasing temperature, there is first a ferromagnetic state between $T_C$ and $T_K$ and then a mixed Kondo-ferromagnetic state below $T_K$ with a clear decrease of the ferromagnetic magnetization. In the ferromagnetic phase, the magnetic moment is almost saturated, reaching a value close to 1. In the Kondo-ferromagnetic phase, the $f$-moment is partially screened, and the $f$-moment is reduced to a value close to 1/2. This is in agreement with the description given by Nozières and Blandin [14] of the underscreened Kondo effect: the conduction electrons cannot completely screen a $S = 1$ localized spin, and the system is described below $T_K$ by an effective $S = 1/2$ spin, which can order due to the intersite exchange.

This model applies well to the compound NpNiSi$_2$: the right panel of figure 1 shows the magnetization curves of this compound [7]. The magnetization obtained at a small magnetic field $B=0.05$ T as a function of temperature shows the onset of ferromagnetism at $T_C=51.5$ K. A sharp collapse of the magnetization is observed at $T^*$ of order 12 K. There are at least three arguments in favor of the fact that this collapse is due to the Kondo effect: (i) the magnetic resistivity exhibits a Log$T$ dependence above $T_C$; (ii) the deduced electronic specific heat coefficient at low temperatures (below $T^*$) is large: $\gamma=133$ mJ/mol K$^2$; (iii) the saturated moment $\mu_{sat} = 1.07 \mu_B$ at 5 K is rather small, as shown in figure 1. This small value may be explained by a partial polarization of conduction electrons with spins opposite to those of localized electrons, exactly like in the underscreened Kondo Lattice case [7].
Thus, our model can give a good explanation of the magnetization curves of the NpNiSi₂ compound, if we take the Kondo temperature $T_K$ equal to $T^*$ of order 12 K, which is clearly much smaller than the Curie temperature $T_C=51.5$ K.

There is another ferromagnetic and Kondo neptunium compound, namely Np₂PdGa₃, which has been recently studied experimentally [3]. The magnetic resistivity, which follows a $\log T$ decrease above the Curie temperature $T_C = 62.5$ K and the electronic specific heat constant, which is equal to $\gamma=120$ mJ/mol K$^2$ at very low temperatures, clearly indicate a Kondo behavior in addition to the ferromagnetic one [3]. The magnetization curves show a broad maximum below $T_C$, which has been interpreted as the possible development of a ferromagnetic order influenced by a narrow domain wall or strong magnetocrystalline anisotropy and the two ZFC- and FC-magnetization curves have a different behavior at low temperatures [3]. However, a more probable explanation comes again from the Kondo effect which reduces the magnetization and the estimated Kondo temperature is here 35 K, which is also smaller than $T_C$ [3].

In conclusion, we have shown that the UAL model for $T_K < T_C$ gives a good description of the magnetization of NpNiSi₂ at low temperatures. However, we remark that we have applied the UAL model to neptunium compounds, although the configuration of Np atoms is different from our starting configuration $5f^2$ appropriate to uranium compounds and moreover the crystalline field effect plays probably an important role [3]. Finally, the present underscreened Kondo lattice model accounts well for the results obtained for $T_K < T_C$ and further experimental studies are necessary for a more detailed understanding of the behavior of the Kondo-ferromagnetism coexistence below the Kondo temperature.

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4. References
[1] Doniach S 1976, Proceedings of the Valence Instabilities and Related Narrow-Band Phenomena, ed R D Parks (New York: Plenum Press), p 168
[2] Schoenes J, Vogt O, Lohle J, Hulliger F and Mattenberger K 1996 Phys. Rev. B 53 14987
[3] Tran V H, Griveau J C, Eloiirdi R, Müüler W and Colineau E 2010 Phys. Rev. B 82 094407
[4] Perkins N B, Nunez-Regueiro M D, Iglesias J R and Coqblin B 2007 Phys. Rev. B 76 125101
[5] Thomas C, Simões A S R, Iglesias J R, Lacroix C, Perkins N B and Coqblin B 2011 Phys. Rev. B 83 014415
[6] Bukowski Z, Troc R, Stepian-Damm J, Sulkowski C and Tran V H 2005 J. Alloys Compd. 403 65
[7] Colineau E, Wastin F, Sanchez J P and Rebizant J 2008 J. Phys.: Condens. Matter 20 075207
[8] Lacroix C and Cyrot M 1979 Phys. Rev. B 20 1969
[9] Coleman P and Andrei N 1989 J. Phys.: Condens. Matter 1 4057
[10] Iglesias J R, Lacroix C and Coqblin B 1997 Phys. Rev. B 56 11820
[11] Link P, Benedict U, Wittig J and Wuhl H 1992 J. Phys.: Condens. Matter 4 5585
[12] Cornelius A L, Schilling J S, Vogt O, Mattenberger K and Benedict U 1996 J. Mag. Mag. Mater. 161 169
[13] Thomas C, Ph. D. Thesis, U.F.R.G.S., Porto Alegre, Brazil (May 2011)
[14] Nozières P and Blandin A 1980 J. de Physique 41 193