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The dual nature of 5f electrons and the origin of heavy fermions in U compounds

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Abstract

We develop a theory for the electronic excitations in UPt_3 which is based on the localization of two of the 5f electrons. The remaining f electron is delocalized and acquires a large effective mass by inducing intra-atomic excitations of the localized ones. The measured de Haas–van Alphen frequencies of the heavy quasiparticles are explained as well as their anisotropic heavy mass. A model calculation for a small cluster reveals why only the largest of the different 5f hopping matrix elements is operative, causing the electrons in other orbitals to localize.

1. Introduction

There is growing evidence that actinide ions may have localized as well as delocalized 5f electrons. This picture, which was suggested by transport measurements [1], is supported by a great variety of experiments including, e.g., photoemission and neutron inelastic scattering experiments on UPd_2Al_3 [2–4] as well as muon spin relaxation measurements on UGe_2 [5]. The assumption is further supported by quantum chemical calculations on uranocene $U(C_8H_8)_2$ [6] which show a number of low-lying excitations which are due to rearrangements of the 5f electrons. There are speculations that the presence of localized 5f states might even be responsible for the attractive interactions leading to superconductivity [7]. We should like to mention that the dual model should allow for a rather natural description of heavy-fermion superconductivity coexisting with 5f-derived magnetism.

The above-mentioned observations form the basis of the dual model which provides a microscopic theory for the heavy quasiparticles in U compounds. The ansatz conjectures that the delocalized 5f states hybridize with the conduction states and form energy bands while the localized ones form multiplets to reduce the local Coulomb repulsion. The two subsystems interact, which leads to the mass enhancement of the delocalized quasiparticles. The situation resembles that in Pr metal where a mass enhancement of the conduction electrons by a factor of 5 results from virtual crystal field (CEF) excitations of localized $4f^2$ electrons [8].

The dual ansatz reproduces the dHvA data on UPt_3 [9] and UPd_2Al_3. Detailed Fermi surface studies of UGa_3 [10] and high-resolution photoemission measurements on URu_2Si_2 [11] show that the observed Fermi surfaces cannot be explained by assuming all 5f electrons to be itinerant or localized. Measurements of the optical conductivity in UPd_2Al_3 and UPt_3 [12] indicate that the enhanced effective masses m^* of the quasiparticles should result from the interaction of delocalized states with localized magnetic moments.

The coexistence of itinerant and localized 5f states is referred to as partial localization. It plays an important role in many intermetallic actinide compounds. Partial localization arises from interplay between the hybridization of the 5f states with the conduction electrons and the local Coulomb correlations. The underlying microscopic mechanism is an area of active current research [13, 14]. LDA calculations show that the hopping matrix elements for different 5f orbitals vary. But it is of interest to understand why only the largest one of them is important and why the other ones are suppressed.

In order to justify the above assumption we present model calculations which focus on the interplay between delocalization of 5f states and Hund's rule correlations. The results [15] clearly show how partial localization can arise in 5f systems. In addition, they suggest rather complex phase diagrams depending upon the strengths of the hopping matrix referring to different orbital elements. Variation of the intersite hopping by applying (hydrostatic) pressure should lead to (quantum) phase transitions of new types. We think the present model could be used to study the pressure dependence of the magnetization in UGe_2.

In addition to the full model Hamiltonian, we investigate a simplified version which treats the local Coulomb interaction in close analogy to the LDA + U approach. The results allow us to assess the general validity of this popular approximation scheme. Finally we compare the results from the full model Hamiltonian with those obtained from a Hartree–Fock approximation.

2. Heavy quasiparticles in UPt_3 and UPd_2Al_3: dual model

We make calculations for the heavy quasiparticles in UPt_3 and UPd_2Al_3 within the dual model considering two of the 5f electrons as localized, in agreement with the absence of any Kramers doublets in cases where a crystalline electric field (CEF) splitting of U states has been observed. The calculation of the heavy bands proceeds in three steps as described in [9]: first, the band structure is determined by solving the Dirac equation for the self-consistent LDA potentials but excluding the U 5f $j = \frac{5}{2}$, $j_z = \pm\frac{5}{2}$ and $j_z = \pm\frac{1}{2}$ states from band formation. The localized 5f orbitals are accounted for in the self-consistent density and, concomitantly, in the potential seen by the conduction electrons. The intrinsic bandwidth of the itinerant U 5f $j = \frac{5}{2}$, $j_z = \pm\frac{3}{2}$ electrons is taken from the LDA calculation while the position of the corresponding band centre C is chosen such that the density distribution of the conduction states as obtained within the LDA remains unchanged. The f occupancy per U atom for the delocalized 5f electrons amounts to $n_f = 0.65$ indicating that we are dealing with a mixed-valence situation. The calculated dHvA frequencies agree rather well with the observed ones [16] as shown in figure 1. We also include the corresponding results for UPd_2Al_3 which are compared to experimental data from [17].

In the second step, the localized U 5f states are calculated assuming the jj-coupling scheme. The Coulomb matrix elements are calculated from the radial functions of the *ab initio* band-structure potentials. We find a doubly degenerate ground state with $J_z = \pm 3$ which must be an eigenstate of $J = 4$ and has an overlap of 0.865 with the Hund's rule ground state $^3H_4$ derived from the LS-coupling scheme. In the hexagonal symmetry, the twofold degeneracy of the ground state is lifted by a CEF yielding the two states $|\Gamma_3\rangle$ and $|\Gamma_4\rangle$. Note that $|\Gamma_4\rangle$ has

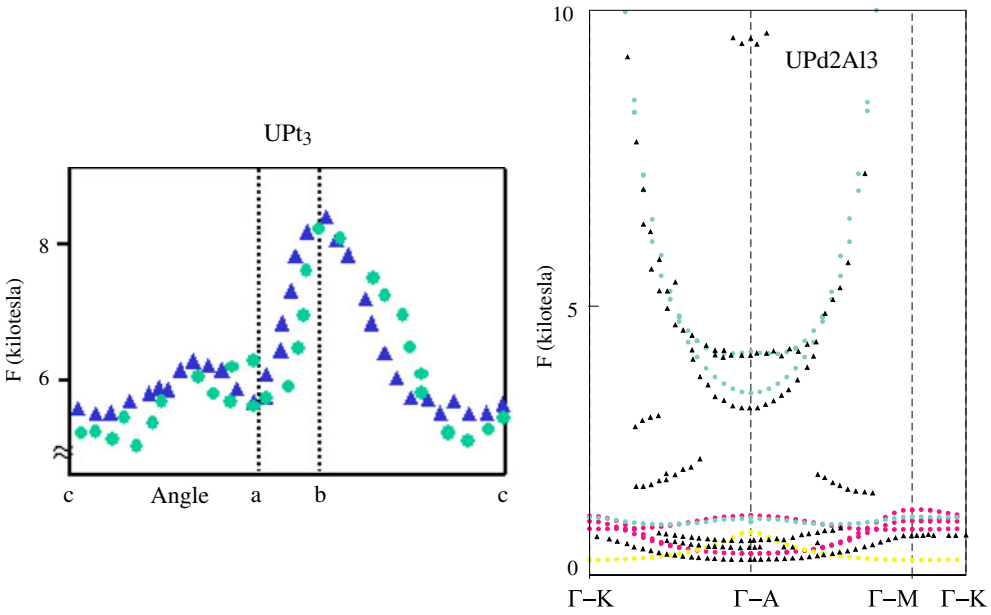

Figure 1. The de Haas–van Alphen cross-sections for the heavy quasiparticles as calculated within the dual model (circles) [9]. The experimental data for UPt_3 (triangles) are from [16] while those for UPd_2Al_3 (black triangles) are taken from [17].

(This figure is in colour only in the electronic version)

Table 1. Measured and calculated effective masses of UPt_3 for various directions of the magnetic field.

m^*	c	a	b
Experiment	110	82	94
Theory	128	79	104

been suggested as the ground state of UPd_2Al_3. We assume that the energy $\tilde{\delta}$ of the splitting between $|\Gamma_4\rangle$ and $|\Gamma_3\rangle$ is of order 20 meV for UPt_3. The coupling between the localized and delocalized f electrons is directly obtained from the expectation values of the Coulomb interaction U_{Coul} in the $5f^3$ states: $M = \langle f^1; \frac{5}{2}, \frac{3}{2}| \otimes \langle \Gamma_4 | U_{\mathrm{Coul}} | \Gamma_3 \rangle \otimes |f^1; \frac{5}{2}, \frac{3}{2}\rangle = 0.19$ eV.

Finally, we determine the renormalization of the effective masses which results from the coupling between the two 5f subsystems. The enhancement factor is calculated from the self-consistent solution of the self-energy equation [8] with the input taken from *ab initio* electronic structure calculations for the delocalized and the localized 5f electrons. The density of states with two localized 5f electrons is $N(0) \simeq 15.5$ states/(eV cell), the 5f weight per spin and U atom of the band states amounts to $4a^2 = 0.13$ while the transition matrix element connecting the low-lying singlet states in the localized $5f^2$ shell in the presence of a CEF equals $|M|^2 = 0.036$ eV^2. The only adjusted parameter is the energy $\tilde{\delta}$ characterizing the centres of gravity of the CEF excitations. By comparing with other U compounds such as UPd_2Al_3, we estimate $\tilde{\delta} \simeq 20$ meV. This general concept reproduces the quasiparticles rather well as can be seen from the results summarized in table 1. A similar analysis applies for UPd_2Al_3.

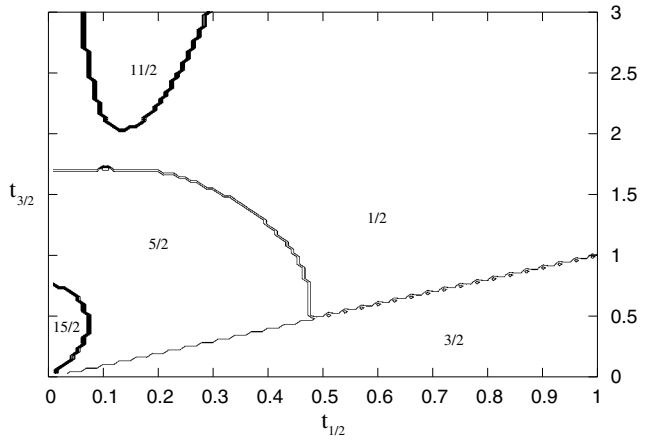

Figure 2. Magnetization of the ground state. The model predicts two 'high-spin' phases ($J_z = 15/2$ and $11/2$) with ferromagnetic intersite correlations $\langle \vec{J}^{(1)} \cdot \vec{J}^{(2)} \rangle$ for strong anisotropy $t_{3/2} \gg t_{1/2} = t_{5/2}$ and three 'low-spin' phases $J_z = 5/2, 1/2, 5/2$.

3. Partial localization from competition between angular correlations and hopping

The calculations start from small clusters which model the U sites in heavy-fermion compounds. We keep only the degrees of freedom of the 5f shells, the conduction states being accounted for by (effective) anisotropic intersite hopping. Here we consider the two-site model. The general results qualitatively agree with those found for a three-site cluster. The Hamiltonian reads

$$H = \sum_{j_z} t_{j_z} (c^{\dagger}_{j_z}(1) c_{j_z}(2) + \text{h.c.}) + H_{\text{Coul}}. \tag{1}$$

Here $c^{\dagger}_{j_z}(i)$ ($c_{j_z}(i)$), create (annihilate) an electron at site i (=1, 2) in the 5f $j = 5/2$ state with $j_z = -5/2, \ldots, 5/2$. The effective hopping between the sites is chosen to be diagonal in the orbital index j_z which seems to be compatible with LDA calculations for the U-based heavy-fermion systems UPt_3 and UPd_2Al_3. The local Coulomb repulsion

$$H_{\text{Coul}} = \sum_{i=1,2} \sum_{j_{z1} > j_{z2}} \sum_{j_{z3} > j_{z4}} \langle j_{z1} j_{z2} | U | j_{z3} j_{z4} \rangle c^{\dagger}_{j_{z1}}(i) c^{\dagger}_{j_{z2}}(i) c_{j_{z3}}(i) c_{j_{z4}}(i) \tag{2}$$

depends upon the Coulomb matrix elements

$$\langle j_{z1} j_{z2} | U | j_{z3} j_{z4} \rangle = \delta_{j_{z1}+j_{z2}, j_{z3}+j_{z4}} \sum_{J} \langle \tfrac{5}{2} j_{z1} \tfrac{5}{2} j_{z2} | J J_z \rangle U_J \langle J J_z | \tfrac{5}{2} j_{z3} \tfrac{5}{2} j_{z4} \rangle \tag{3}$$

where J denotes the total angular momentum and $J_z = j_{z1} + j_{z2} = j_{z3} + j_{z4}$. The sum is restricted to even values of J, i.e., $J = 0, 2, 4$, to satisfy the antisymmetry requirement. In the actual calculations, we use the parameters U_J determined from the LDA 5f wavefunctions in UPt_3, i.e., $U_{J=4} = 17.21$ eV, $U_{J=2} = 18.28$ eV and $U_{J=0} = 21.00$ eV. Finally, the $\langle \frac{5}{2} j_{z1} \frac{5}{2} j_{z2} | J J_z \rangle$ denote the Clebsch–Gordan coefficients.

To simulate the situation in the U-based heavy-fermion compounds we consider the model in the intermediate-valence regime with an average f valence close to 2.5.

The eigenstates of the Hamiltonian equation (1) are characterized by $J_z = J_z^{(1)} + J_z^{(2)}$, where J_z is the z-component of the total angular momentum of the two-site system, while $J_z^{(1)}$ and $J_z^{(2)}$ refer to the angular momentum projections of the individual sites. We study the evolution of

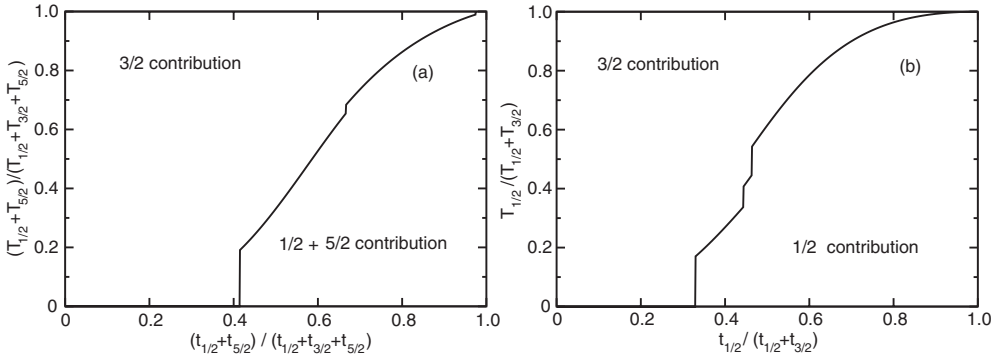

Figure 3. Partial localization is reflected in the relative contributions T_α (see the text) of the various orbitals to the kinetic energy in the correlated ground state for (a) $t_{5/2} = 0$ and (b) $t_{1/2} = t_{5/2}$. Dominant hopping strongly suppresses the remaining contributions.

the ground state with the hopping parameters $t_{3/2}$, $t_{5/2}$ and $t_{1/2}$. The energy variation is smooth except for a kink along the isotropic line $t_{1/2} = t_{3/2} = t_{5/2}$. The character of the ground state, however, changes, as can be seen by considering the total magnetization J_z of the ground state displayed in figure 2. The phase diagram is strongly affected by magnetic fields. Standard electronic structure calculations for extended systems such as the Hartree–Fock method or an LDA + U-type ansatz generally overestimate the stability of the ferromagnetic phases and fail to describe the subtle breaking-up of the Hund's rule correlations. Partial localization becomes clearly evident in the contributions of the different j_z-channels to the gain in kinetic energy as shown in figure 3. Whenever one hopping parameter t_α dominates, i.e., $t_\alpha \gg t_{\alpha'}, t_{\alpha''}$, we find for the corresponding ground-state expectation values $T_{\alpha'} = \frac{\langle\Psi_0|t_{\alpha'}c^\dagger_{\alpha'}(1)c_{\alpha'}(2)|\Psi_0\rangle}{\langle\Psi_0|\sum_\alpha t_\alpha c^\dagger_\alpha(1)c_\alpha(2)|\Psi_0\rangle} \ll \frac{t_{\alpha'}}{\sum_\alpha t_\alpha}$, indicating that contributions of the smaller hopping matrix elements are suppressed.

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