PHYSICAL REVIEW B **68**, 052508 (2003)

Fermi surface and heavy masses for UPd_2Al_3

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(Received 24 February 2003; published 22 August 2003)

We calculate the Fermi surface and the anisotropic heavy masses of UPd_2Al_3 by keeping two of the $5f$ electrons as localized. Good agreement with experiments is found. The theory contains essentially no adjustable parameter except for a small shift of the position of the Fermi energy of the order of a few meV. A discussion is given why localization of two f electrons is justified.

DOI: 10.1103/PhysRevB.68.052508 PACS number(s): 74.70.Tx, 71.18.+y, 71.10.Ay, 71.27.+a

There has been experimental evidence since a number of years that in UPd_2Al_3 the $5f$ electrons have a dual character. The large observed magnetic moment of $0.85\mu_B$ (Ref. 1) suggests localization of the f electrons. On the other hand, the large jump in the specific heat at the superconducting transition temperature $T_c = 2$ K implies a large Sommerfeld specific heat coefficient γ and moderately heavy fermion behavior.[2] This requires delocalized $5f$ electrons. The dual character is also found in a number of other physical properties such as photoemission, inelastic neutron scattering and muon spin rotation.[3–6] It is also observed in other metallic U compounds.[7,8] Moreover, the assumption is supported by quantum-chemical calculations on $U(C_8H_8)_2$ (Ref. 9) which exhibit a number of low-lying excitations caused by intra-atomic rearrangements of the $5f$ electrons. There are speculations that similar $5f$ excitations might even be responsible for the formation of Cooper pairs in superconductors.[10] In that case the dual model should allow for a natural description of heavy-fermion superconductivity coexisting with magnetism produced by $5f$ electrons.

We have previously applied the dual model in order to explain the mass enhancement of the quasiparticle excitations and the de Haas–van Alphen frequencies in UPt_3, the model system of heavy-fermion behavior in U compounds.[11] Our theory conjectured that the delocalized $5f$ states hybridize with the conduction electron states and form energy bands while the localized ones form multiplets in order to reduce the local mutual Coulomb repulsions. The interaction of the two subsystems, i.e., the delocalized with the localized one leads to a mass enhancement of the former. The situation resembles that of Pr metal where a mass enhancement of the conduction electrons by a factor of 5 results from virtual crystal-field excitations of the localized $4f$ electrons.[12] The same mechanism leads to the heavy quasiparticles in the recently discovered heavy-fermion superconductor $PrOs_4Sb_{12}$.[13] The role of the incompletely filled $4f$ shell is taken by an incompletely filled subshell of $5f$ electrons when U ions are considered instead.

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 an interplay between the hybridization of the $5f$ states with the environment and on-site Coulomb correlations. This is discussed below in more detail. The underlying microscopic origin is an area of active current research.[14–16] The associated physical picture is therefore quite different from the one suggested in Ref. 2, where two disjunct subsystems in **k** space were postulated.

The dual model should be contrasted with density functional based calculations which use the local density approximation. These have been successful in explaining the measured de Haas–van Alphen frequencies of systems such as UPd_2Al_3 or UPt_3,[17–19] but they fail to explain the observed heavy quasiparticle masses. For UPt_3 the observed masses are by a factor of 20 larger than the calculated ones and for UPd_2Al_3 the difference is roughly a factor of 4. When using the self-interaction corrected local spin-density approximation (SIC-LSDA) (Ref. 20) a ground state is found with coexisting localized (f^2) and delocalized $5f$ electrons of U. But the calculated density of states is too small by a factor of approximately 10 to account for the observed linear specific heat.

While the calculated energy bands are too broad for explaining the effective masses, they are too small in order to fit the observed photoemission data of UPt_3, UPd_2Al_3, or UBe_{13}.[21] The latter shows a broad peak just below the Fermi energy E_F and is quite different from the data of heavy quasiparticle systems which involve Ce^{3+} instead of U ions. Here a broad peak is found approximately 2 eV below E_F (Ref. 22) while at the Fermi energy a small Kondo resonance is detected. We add that even for UPd_3 which has localized $5f$ electrons and does not show heavy-fermion behavior, the photoemission data resemble that of the previously mentioned U compounds, except that there is no f weight at E_F. This indicates that despite the aforementioned successes the strong correlations in those materials are not properly treated by the presently used computational methods. Instead we find that a more microscopic understanding of heavy-fermion behavior is highly desirable.

The aim of the present investigation is to show that the de Haas–van Alphen frequencies for the heavy-quasiparticle portion of the Fermi surface and the large effective masses (including their anisotropies), can be explained very well by treating two of the $5f$ electrons as being localized. We put the localized electrons into $5fj=\frac{5}{2}$ orbitals with $j_z=\pm\frac{5}{2}$ and $\pm\frac{1}{2}$. The $j_z=\pm\frac{3}{2}$ states are treated as itinerant electrons. The reason for this choice is explained below, but it is worth pointing out here that the $j_z=\pm\frac{3}{2}$ states hybridize strongest

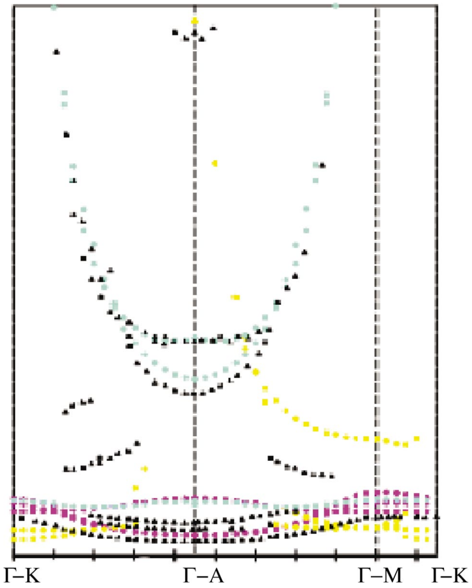

FIG. 1. (Color) Comparison of the measured (Ref. 19) (black symbols) and calculated de Haas–van Alphen frequencies for $\mathrm{UPd_2Al_3}$. The dominant part reflects a nearly cylindrical sheet of the Fermi surface.

among the different ones in a conventional LDA calculation.

The calculations of the heavy bands proceed in three steps. First, the band structure is determined by solving the Dirac equation for the self-consistent LDA potentials, thereby excluding the U $5f$ states with $j=\frac{5}{2}$, $j_z=\pm\frac{5}{2}$, and $j_z=\pm\frac{1}{2}$ from forming bands. Two $5f$ electrons in localized 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 $5fj=\frac{5}{2}$, $j_z=\pm\frac{3}{2}$ electrons is taken from the LDA calculation while the position of the corresponding band center C is chosen such that the density distribution of the conduction electrons remains the same as within the LDA. The f electron count per U atom for the delocalized $5f$ electrons amount to $n_f\simeq\frac{2}{3}$, i.e., the system is of a mixed valence type. The calculated de Haas–van Alphen frequencies are shown in Fig. 1 which also contains the experimental results from Refs. 18 and 19.

One notices that the agreement for the heavy quasiparticle branches is very good. The frequencies referring to the light parts of the Fermi surface are less well reproduced, but that is of no surprise. One cannot expect that die LDA reproduces well the relative shifts of the centers of the light bands which strongly effect the shape of the corresponding parts of the Fermi surface. The Fermi surface of the heavy quasiparticles in the antiferromagnetic phase consists of three sheets two of which are displayed in Fig. 2.

We assign the orbit α to the first sheet (K-centered ellipsoid) not shown in Fig. 2. The third sheet is the most important one and consists of a corrugated cylinder and a H-centered ellipsoid [see Fig. 2(a)] to which we assign the orbits γ and β and ϵ_2, ϵ_3, respectively. The branch ζ is assigned to the second sheet whose shape depends sensitively on the position of the Fermi energy [see Fig. 2(b)]. For example, a shift of the latter by 40 K changes that sheet from the one shown in Fig. 2(b) to that of Fig. 2(c). But the corresponding changes in the effective mass remain small.

In the second step we calculate the multiplet structure of the localized f^2 states. This is done within the jj-coupling scheme, because the spin-orbit splitting is rather large. Thus a 6×6 Coulomb matrix has to be diagonalized for the two-particle states built from $|j=\frac{5}{2},\, j_z=\pm\frac{5}{2}\rangle$ and $|j=\frac{5}{2},\, j_z=\pm\frac{1}{2}\rangle$ for the f^2 subshell. The Coulomb matrix elements are calculated following Condon and Shortley. Inputs are the Slater-Condon parameters F^K (Coulomb integrals) and G^K (exchange integrals). The latter are evaluated with the radial function $R^U_{f,5/2}(\mathbf{r})$ for U as obtained from a self-consistent band structure potential. Thereby the chosen energy is that of the center of gravity of the $5f$ bands. The required integrations are done within the atomic sphere surrounding the U ion. We note that we use the same Coulomb matrix as for $\mathrm{UPt_3}$ (Ref. 11), where also two $5f$ electrons with $j_z=\pm\frac{5}{2}$, $\pm\frac{1}{2}$ are considered. This is reasonable in view of the fact that in the nonrelativistic case the matrix elements agree up to two decimals with the ones computed in Ref. 9 for $\mathrm{U(C_8H_8)_2}$, indicating that they are insensitive to the chemical environment of U. The resulting eigenstates of the Coulomb matrix are no longer eigenstates of the total angular momentum J, but remain eigenstates of J_z.

We find a doubly degenerate ground state with $J_z=\pm3$. It must be an eigenstate to $J=4$ since the Pauli principle requires an even value of J and $J=0,2$ are excluded. The states $|j=\frac{5}{2},\, j=\frac{5}{2},\, J=4,\, J_z=\pm3\rangle$ have an overlap of 0.865 with the state ${}^3H_4$. The latter follows from Hund's rule when the LS coupling scheme is applied. The twofold degeneracy of the ground state is lifted by the crystalline electric field (CEF) which is acting on the $5f$ subshell with the localized

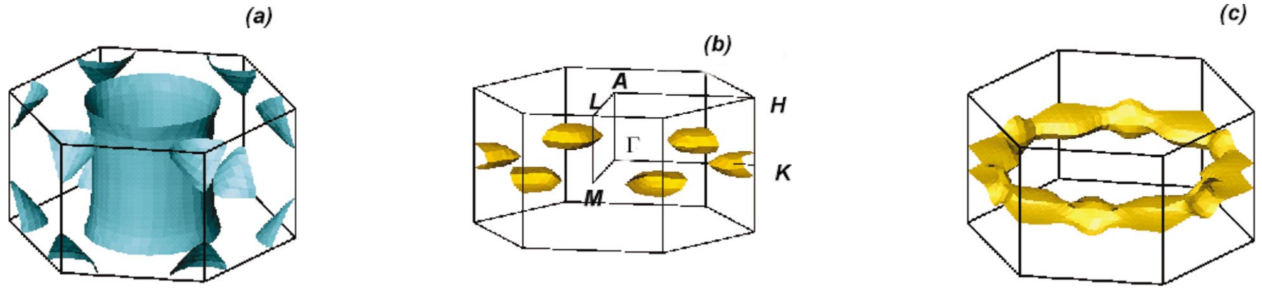

FIG. 2. (Color) Various calculated sheets of the Fermi surface of $\mathrm{UPd_2Al_3}$: (a) third sheet (cylinder and H-centered ellipsoid), (b) second sheet, (c) second sheet but with a Fermi energy shifted by 40 K.

electrons. From experiments a Γ_4 ground state has been suggested[23] so that the ground and first excited state are

$$|\Gamma_{3,4}\rangle = \frac{1}{\sqrt{2}}\left(|J=4;J_z=3\rangle \pm |J=4;J_z=-3\rangle\right). \tag{1}$$

For the splitting energy $\tilde{\delta}$ between the two states a value of 20 meV has been previously suggested[1] while a more recent value is 7 meV.[10] The latter value will be used in the following. We want to point out that the next higher doublet of the Coulomb matrix is one with $J_z = \pm 2$ with an excitation energy of approximately 0.4 eV. Therefore we may neglect all higher excited states and consider the two singlets $|\Gamma_4\rangle$ and $|\Gamma_3\rangle$ only.

In a third and final step we determine the effective masses which result from the interaction of the delocalized $5f$ electrons with the localized one. The renormalization of the band mass m_b is given by

$$\frac{m^*}{m_b} = 1 - \left.\frac{\partial \Sigma}{\partial \omega}\right|_{\omega=0}, \tag{2}$$

where $\Sigma(\omega)$ denotes the local self-energy of the delocalized $5f$ states. The latter is obtained by analytic continuation from the Matsubara frequencies $\epsilon_n = \pi T(2n+1)$ at the temperature T where it is given by

$$\Sigma(i\epsilon_n) = a^2 M^2 T \sum_{n'} \chi(i\epsilon_n - i\epsilon_{n'}) g(i\epsilon_{n'}) \tag{3}$$

in terms of the local susceptibility

$$\chi(i\epsilon_n - i\epsilon_{n'}) = -\tanh\frac{\tilde{\delta}}{2T}\,\frac{2\tilde{\delta}}{(i\epsilon_n - i\epsilon_{n'})^2 - \tilde{\delta}^2} \tag{4}$$

and the local propagator

$$g(i\epsilon_n) = \int dE\,\frac{N(E)}{i\epsilon_n - E - \Sigma(i\epsilon_n)}. \tag{5}$$

Here $2N(E)$ is the total density of states at the energy E as obtained from the band structure, when two $5f$ electrons are kept localized. The prefactor a denotes the $5f$ weight per spin and U atom of the conduction electron states near E_F. The matrix element M describes the transition between the localized states $|\Gamma_4\rangle$ and $|\Gamma_3\rangle$ due to the Coulomb interaction U_{Coul} with the delocalized $5f$ electrons. It is given by

$$M = \left\langle f^1;\frac{5}{2},\frac{3}{2}\right| \otimes \langle \Gamma_4 | U_{\mathrm{Coul}} | \Gamma_3 \rangle \otimes \left| f^1;\frac{5}{2},\frac{3}{2}\right\rangle \tag{6}$$

and is directly obtained from the expection values of the Coulomb interaction in the $5f^3$ states. The difference

$$\langle f^1;\tfrac{5}{2},\tfrac{3}{2}| \otimes \langle f^2;4,3|U_{\mathrm{Coul}}|f^2;4,3\rangle \otimes |f^1;\tfrac{5}{2},\tfrac{3}{2}\rangle - \langle f^1;\tfrac{5}{2},\tfrac{3}{2}|$$
$$\otimes \langle f^2;4,-3|U_{\mathrm{Coul}}|f^2;4,-3\rangle \otimes |f^1;\tfrac{5}{2},\tfrac{3}{2}\rangle$$

is -0.38 eV. From this we obtain $M = -0.19$ eV. When we want to write M in the form of an exchange coupling between the delocalized and localized $5f$ states we need to know the Landé factor g. We find $g_{\mathrm{eff}} = 0.63$ and with this value an exchange integral of size $I \simeq 1$ eV. This is of the correct size for $5f$ electrons.

TABLE I. Effective masses for H 11 c. The experimental data are taken from Inada *et al.* (Ref. 19).

	m^* (exp)	m^* (theory)
ζ	65	59.6
γ	33	31.9
β	19	25.1
ϵ_2	18	17.4
ϵ_3	12	13.4
α	5.7	9.6

In order to evaluate Eq. (2) we need to know $N(E)$ and a. We extract the quantities from LDA calculations with two $5f$ electrons being localized. For simplicity, we model $N(E)$ by a Lorentzian. The actual value at the Fermi level $N(0) = 2.76$ states/(eV cell spin) corresponds to the one found in Ref. 20 A value of $a^2 = 0.44$ is obtained and the value $\tilde{\delta} = 7$ meV is used.

The self-consistent calculation yields a mass enhancement of 9.6. The resulting calculated quasiparticle masses are in excellent agreement with experiment (see Table I).

What remains to be discussed is the justification for treating two of the $5f$ electrons in orbitals $j_z = \frac{5}{2}$ and $\frac{1}{2}$ as localized. As pointed our before the hybridization of the $j_z = \pm\frac{3}{2}$ orbital with the neighboring atomic orbitals is larger than the one for the orbitals with $j_z = \pm\frac{5}{2}$ and $\pm\frac{1}{2}$. So why are we allowed to neglect the hybridization of the latter orbitals altogether? The answer is found when the effects of intra-atomic correlations are taken into account, i.e., those resulting from the on-site Coulomb and exchange effects. For a demonstration a two-site model was treated in Ref. 14 with anisotropic hopping between the two U sites. An intermediate valency of 2.5 was used for the two atoms. Let $|\psi_0\rangle$ denote the ground state of that system and t_α the hopping parameters for the different orbitals. It was found in Ref. 14 that whenever one hopping parameter t_α dominates the others, i.e., $t_\alpha \gg t_{\alpha'}, t_{\alpha''}$, the corresponding ground state expectation values is

$$T_{\alpha'} = \frac{\langle \psi_0 | t_{\alpha'} c^\dagger_{\alpha'}(1) c_{\alpha'}(2) | \psi_0 \rangle}{\langle \psi_0 | \sum_\alpha t_\alpha c^\dagger_\alpha(1) c_\alpha(2) | \psi_0 \rangle} \ll \frac{t_{\alpha'}}{\sum_\alpha t_\alpha}, \tag{7}$$

i.e., the effective hybridization anisotropies are strongly enhanced by intra-atomic interaction. The operators $c^\dagger_\alpha(i)$

($c_\alpha(i)$) create (destroy) an f electron on site i in orbital $j_z = \alpha$. The smaller hopping matrix elements are therefore suppressed.

In conclusion we have shown that the heavy quasiparticles of the U compound UPd_2Al_3 can be explained without any adjustable parameter by means of the dual character of $5f$ electrons. This includes the large anisotropies of the heavy-quasiparticle masses. This strengthens the trust in the theory which was previously applied to UPt_3 but contained one fit parameter in that case.

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