Singlet Magnetism in Heavy Fermions

Victor Barzykin
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801-3080

Lev P. Gor'kov
National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Drive, Tallahassee, Florida 32306-4005 and L. D. Landau Institute for Theoretical Physics, Moscow, Russia

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We consider singlet magnetism for the uranium ions in UPt_3 and URu_2Si_2 assuming that time-reversal symmetry is broken for the *coherent state of intermediate valence*. The relative weight of the two involved configurations should be different for UPt_3 and URu_2Si_2. If in UPt_3 the configuration $5f^1$ on the U ion prevails in the coherent state below the magnetic transition, the magnetic moment will vanish for the particular choice of the *ionic* wave function. In the case of URu_2Si_2, the phase transition is nonmagnetic in the first approximation—the magnetic moment arises from a small admixture of a half-integer spin configuration.

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Heavy fermion (HF) compounds reveal enormously rich magnetic properties in which both localized states and conduction electrons are involved [1]. To be more specific, among the magnetic phases observed in U-based materials are the antiferromagnetic (AF) Néel state in U_2Zn_{17} [2], a "tiny-moment" AF state in URu_2Si_2 [3,4] and UPt_3 ($\langle\mu\rangle \sim 10^{-2}\mu_B$), and both quadrupolar and "tiny-moment" phases in UPd_3 [5,6]. This diversity may originate from the fine energy structure of 10–100 K for the uranium multiplets, somehow supplemented by strong electron correlations. In what follows we concentrate on the "tiny moment" antiferromagnetic transitions in the HF compounds UPt_3 and URu_2Si_2. In view of the smallness of the above energy scale we suggest that mixed valency (MV) phenomena may be involved.

While the small ordered antiferromagnetic moment is the common feature for both compounds, the phase transitions in them are very different. Thus a huge specific heat jump is observed at the Néel transition in URu_2Si_2 ($T_N \sim 17.5$ K), and no specific heat anomaly was seen in UPt_3. The well-defined excitations with large $\langle 0|J^z|1\rangle$ ($\sim 1.2\mu_B$) [3] matrix elements are detected in URu_2Si_2 by inelastic neutron scattering in the ordered state and again are absent in UPt_3 [7]. In URu_2Si_2 the excitations below T_N can be ascribed to the transitions between two well-defined singlet states of the Hund's rule ${}^3H_4$ multiplet for the U^{4+} ion. These excitations have a finite gap at zero temperature. However, as the temperature is raised, the gap in the spin-wave spectrum reduces and finally vanishes at the Néel point [8]. In our opinion, this signals the onset of large valency fluctuations above the Néel temperature. Although the standard singlet-singlet scheme describes fairly well the temperature behavior of the bulk magnetic susceptibility and the heat capacity [3], it fails to reconcile the small magnetic moment and huge specific heat anomaly at the Néel temperature. A multipolar magnetic order of different symmetry as the primary order parameter in URu_2Si_2 was also excluded from the symmetry analysis of the neutron scattering measurements [4]. In contrast, there is no specific heat jump associated with the transition in UPt_3, and no well-defined crystal field excitations were detected [7]. The tiny moment $M^2 \propto |T - T_N|$ displays a mean field behavior over a wide temperature range below $T_N \simeq 5$ K.

We argue that the effects of mixed valence of the U ions may be responsible for the properties of both compounds. The coherent wave function for the subsystem of uranium ions, which forms below the phase transition, then involves the low-energy levels of both configurations. We consider first UPt_3. For this compound we assume that $5f^2$ and $5f^1$ configurations are close in energy (on the scale of the f-level width). The degeneracy of either configuration is lifted by the strong spin-orbit interaction and the onset of the crystal field splitting, so that in the framework of the singlet magnetism scheme the low-energy states of the U ion are the ground state singlet of the $5f^2$ configuration and some excited state Kramers doublet Γ_{ex} of the $5f^1$ configuration. We choose the matrix element between the two low-energy levels as the order parameter:

$$\Psi = \langle 0|\Gamma_0\rangle\langle\Gamma_{ex}\alpha_{ex}|0\rangle . \quad (1)$$

We analyze the symmetry properties of this order parameter in a model-independent fashion by using the Landau theory of phase transitions. Since the excited state of the uranium ions has a half-integer spin, the symmetry analysis should involve the double group. The double point group has an additional element ($\tilde{E}$), a rotation by the angle 2π, which doubles the number of group elements. The wave function of an integer spin is invariant with respect to this transformation, while in the case of half-integer spin it changes sign. Thus, since Ψ transforms according to the representation $\tilde{\Gamma}_{ex} = \Gamma_0 \otimes \Gamma_{ex}$ under the action of the point group transformations, it is odd with respect to $\tilde{E}$.

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To enumerate various magnetic symmetry options, we start directly from the order parameter equation (1) and deduce magnetic classes which may develop below the Néel temperature. This analysis can be done in a fashion rather similar to the classification of superconducting classes [9,10] in the HF materials. The total point symmetry group in the "paramagnetic phase" is $G \otimes R \otimes \mathrm{U}(1)$, where G is the crystal double point group, R is the time-reversal symmetry, and U(1) is the group of the gauge transformation. The symmetry class is the subgroup of this group appearing below the phase transition. We refer the reader to Ref. [10] for the detailed description of this classification and the methods of construction of symmetry classes. In Ref. [9] the symmetry classes for the wave functions of integer spin (i.e., even with respect to the double group transformation $\tilde{E}$) were enumerated. The matrix element Eq. (1) requires consideration of the symmetry classes for the spinorial wave functions, which, as said above, are odd with respect to $\tilde{E}$. We have derived new symmetry classes for the wave function of half-integer spin. The classes relevant to the present case (i.e., for the double groups D_4' and D_6') are listed in Table I. The *magnetic class* (i.e., the point symmetry of spin correlators) can be obtained from the *symmetry class* by substituting unity for all the gauge factors. Thus, for example, for the representation $\tilde{E}_3$ of the group D_6' the magnetic moment is fully prohibited by the magnetic group for the phases II and III, as seen from Table I, otherwise the magnetic moment should always appear. Here we indicate an interesting possibility when the magnetic moment, although expected by the symmetry of the magnetic group in Table I, turns out to be equal to zero for the particular ionic wave function. A small magnetic moment can then be induced as a result of the interaction with the genuine order parameter [11]. This case is of the most interest to us in connection with the above mentioned puzzles in UPt_3. We found one example of this accidental cancellation, for the $5f^1$ configuration in the group D_6', which is considered below. No such cancellations were found in the case of D_4' (URu_2Si_2).

$J = 5/2$ multiplet of the $5f^1$ configuration in a D_6' group.—For $J = 5/2$ the sixfold degeneracy is lifted by the crystal field effects, leaving three Kramers doublets: $\tilde{E}_1$ ($|\pm 1/2\rangle$), $\tilde{E}_2$ ($|\pm 5/2\rangle$), and $\tilde{E}_3$ ($|\pm 3/2\rangle$). Nontrivial magnetic states cannot be constructed from the wave functions of $\tilde{E}_1$. For the $\tilde{E}_2$ representation the wave function can be written in the form

$$\Psi = \eta_1\psi_1 + \eta_2\psi_2, \tag{2}$$

with $\psi_1 = |5/2\rangle$ and $\psi_2 = |-5/2\rangle$. Making the substitution

$$\begin{aligned} \eta_1 &= u\sin\theta e^{i\phi_1}, \\ \eta_2 &= u\cos\theta e^{i\phi_2}, \end{aligned} \tag{3}$$

TABLE I. Symmetry classes for the tetragonal and hexagonal groups. The prime indicates a double group. Only the classes for representations which are odd with respect to the 2π rotation, $\tilde{E}$, are listed. We use the usual notation $C_{\alpha n}^{+}$ ($C_{\alpha n}^{-}$) for the clockwise (counterclockwise) rotation by the angle $2\pi/n$ with respect to the axis α, as viewed from its positive direction. The elements of the group $\tilde{C}_3$ are $\tilde{C}_3 = \{E, \tilde{C}_3^{+}, \tilde{C}_3^{-}\}$, where $\tilde{C}_3^{\pm} = C_3^{\pm} \cdot \tilde{E}$. We use rectangular coordinates for both D_4' and D_6' groups. The z direction corresponds to the fourfold or the sixfold axis. The x direction is chosen to be perpendicular to the plane of the Brillouin zone boundary. The axes a and b for the group D_4' are along (1, 1, 0) and (1, −1, 0) directions, respectively. The last index in the symmetry class column enumerates different phases.

Group	Representation	Symmetry class	Generators of the class	Magnetic order
D_4'	$\tilde{E}_1$	I. $D_4'(E)_1$	$C_4^{-}e^{i\pi/4}, C_{2y}e^{i\pi}R$	M_z
		IIa. $D_2'(E)_1$	$C_{2z}R, C_{2b}e^{i\pi/2}R$	M_a
		IIb. $D_2'(E)_2$	$C_{2z}R, C_{2y}e^{i\pi/2}R$	M_x
	$\tilde{E}_2$	I. $D_4'(E)_2$	$C_4^{-}e^{i3\pi/4}, C_{2y}R$	M_z
		IIa. $D_2'(E)_1$	$C_{2z}e^{i\pi}R, C_{2b}e^{-i\pi/2}$	M_b
		IIb. $D_2'(E)_2$	$C_{2z}e^{i\pi}R, C_{2y}e^{-i\pi/2}R$	M_x
D_6'	$\tilde{E}_1$	I. $D_6'(E)_1$	$C_6^{-}e^{i\pi/6}, C_{2y}e^{i\pi/2}R$	M_z
		IIa. $D_2'(E)_1$	$C_{2z}e^{i\pi/2}R, C_{2y}e^{-i\pi/2}$	M_y
		IIb. $D_2'(E)_2$	$C_{2z}R, C_{2y}e^{i\pi/2}R$	M_x
	$\tilde{E}_2$	I. $D_6'(E)_2$	$C_6^{-}e^{i5\pi/6}, C_{2y}e^{i\pi/2}R$	M_z
		IIa. $D_2'(E)_1$	$C_{2z}e^{i\pi/2}R, C_{2y}e^{-i\pi/2}$	M_y
		IIb. $D_2'(E)_2$	$C_{2z}R, C_{2y}e^{i\pi/2}R$	M_x
	$\tilde{E}_3$	I. $D_6'(\tilde{C}_3)_1$	$C_6^{-}e^{i\pi/2}, C_{2y}e^{i\pi/2}R$	M_z
		II. $D_6'(\tilde{C}_3)_2$	$C_6^{-}R, C_{2y}e^{i\pi/2}R$	$T_{xyy} = -T_{xxx}$
		III. $D_6'(\tilde{C}_3)_3$	$C_6^{-}e^{i\pi/2}R, C_{2y}e^{-i\pi/2}$	$T_{yxx} = -T_{yyy}$

we arrive at the following form of the Landau functional:

$$F = -\alpha\tau u^2 + \beta_1 u^4 + \beta_2 u^4 \sin^2(2\theta) + \gamma u^{12} \sin^6(2\theta)\cos(6[\phi_1 - \phi_2]). \quad (4)$$

The phases obtained using Eq. (4) then are the following.

(I) $\beta_1 > 0$, $\beta_2 > 0$. $\theta = \pi k/2$, corresponding to the symmetry class $D_6'(E)$. This phase has a magnetic moment along the direction of the C_6 axis (the wave function $|5/2\rangle$ or $|-5/2\rangle$).

(IIa) $\beta_1 > 0$, $-\beta_1 < \beta_2 < 0$, $\gamma < 0$. $\theta = \pi/4 + \pi k/2$, $\phi_1 - \phi_2 = \pi n/3$.

(IIb) $\beta_1 > 0$, $-\beta_1 < \beta_2 < 0$, $\gamma > 0$. $\theta = \pi/4 + \pi k/2$, $\phi_1 - \phi_2 = \pi/6 + \pi n/3$.

The symmetry class of the wave function is $D_2'(E)$ in both cases, and the class for magnetic averages is $D_2(C_2)$. A nonzero average moment in the plane perpendicular to the sixfold axis is expected for the magnetic class $D_2(C_2)$. However, with the wave function $|-5/2\rangle + |5/2\rangle$ a symmetric five-point correlator is instead the lowest-order spin average:

$$T^{xxxxx} = -T^{xxxyy} = T^{xyyyy}, \quad (5)$$

with $T^{ijklm} = \langle J^i J^j J^k J^l J^m \rangle$.

In the case of the representation $\tilde{E}_3$ all the phases are determined by the fourth order terms of the Landau functional,

$$F = -\alpha\tau u^2 + \beta_1 u^4 + \beta_2 u^4 \sin^2(2\theta) + \gamma u^4 \sin^2(2\theta)\cos(2[\phi_1 - \phi_2]). \quad (6)$$

(I) $\beta_1 > 0$, $\beta_2 > |\gamma|$: $\theta = \pi k/2$ [the class $D_6'(\tilde{C}_3)_1$]. This phase corresponds to the magnetic class $D_6(C_6)$ with the magnetic moment parallel to the direction of the C_6 axis (the wave functions $|3/2\rangle$ or $|-3/2\rangle$).

(II) $\beta_1 > 0$, $|\gamma| - \beta_1 < \beta_2 < |\gamma|$, $\gamma > 0$. $\theta = \pi/4 + \pi k/2$, $\phi_1 - \phi_2 = \pi/2 + \pi n$ [the class $D_6'(\tilde{C}_3)_2$]. The corresponding magnetic class is $D_6(D_3)$. The average magnetic moment is prohibited by the symmetry of the magnetic class, and the wave function $|3/2\rangle + |-3/2\rangle$ gives the triple spin correlator of the form

$$T^{xyy} = \langle J^x J^y J^y \rangle = -T^{xxx} = -\langle J^x J^x J^x \rangle \quad (7)$$

as the magnetic order parameter.

(III) $\beta_1 > 0$, $|\gamma| - \beta_1 < \beta_2 < |\gamma|$, $\gamma < 0$. $\theta = \pi/4 + \pi k/2$, $\phi_1 - \phi_2 = \pi n$ [the symmetry class is $D_6'(\tilde{C}_3)_3$]. The nonzero average for this wave function is the triple spin correlator rotated by an angle $\pi/2$ compared to the one in case (II).

We now apply the above analysis to the experimental situation in UPt_3. Since no crystal field excitations have been seen in UPt_3 [7], mixing of different configurations may be quite strong. As a result, the small magnetic moment lying in the plane perpendicular to the sixfold axis in UPt_3 can be explained if the excited Kramers doublet is $\tilde{E}_2$, with $J^z = \pm 5/2$, of the $5f^1$ configuration [the symmetry class $D_2'(E)_2$ in Table I]. Recall that the magnetic moment lying in the plane is not prohibited by symmetry, but merely does not appear on this particular ionic Kramers doublet. This moment cancellation is accidental, and a small magnetic moment may appear also as a result of admixture of the higher-energy-level multiplets. The entropy loss is small due to the weakness of multipolar interactions.

The origin of the small magnetic moment in URu_2Si_2 must be quite different. As shown in Table I, for the group D_4' the magnetic moment along the fourfold axis is always present for the MV order parameter equation (1). In addition, in contrast to UPt_3, we found no accidental cancellation of the moment due to a particular choice of the wave function for both $5f^1$ and $5f^3$ configurations. Therefore we assume that the transition takes place from the mixed valency paramagnetic phase into a state where the coherent function with $5f^2$ component overwhelms in Eq. (1). The crystal-field excitations become well defined below the Néel transition [8]. We propose that the real matrix element between two singlet levels in the $5f^2$ configuration prevails in the order parameter, so that the phase transition is mostly structural in character. This matrix element, according to the symmetry analysis of the Bragg reflexes for neutron scattering in the ordered state [4], must have the symmetry A_z and double the unit cell. Thus, the ground and excited integer spin states with the symmetries xy and $x^2 - y^2$ or A_1 and A_z both could be involved in the phase transition. Such an assumption would account for the large specific heat jump observed at the Néel point, and the intensive crystal field excitations below T_N. In order to explain the small magnetic moment, we recall that the valence of the uranium ion has a finite (although, in this case, small) probability to fluctuate, so that the coherent wave function of the ionic subsystem below the phase transition has a small admixture of a different half-integer spin configuration ($5f^1$ or $5f^3$). Therefore the number of particles on the uranium sites is not conserved, and the time-reversal symmetry below T_N is broken. Then the nonmagnetic order component may be coupled to the magnetic moment on the half-integer spin component, $Q_z(|\eta_1|^2 - |\eta_2|^2)$. Here $\eta_1\psi_\uparrow + \eta_2\psi_\downarrow$ is the spinor admixture to the coherent wave function from the $5f^1$ (or $5f^3$) configuration and $Q_z = \langle\Psi|xy\rangle\langle x^2 - y^2|\Psi\rangle$ (or $A_1 \otimes A_z$) is the real matrix element for the nonmagnetic component. In other words, the smallness of the moment is then ascribed to the valence fluctuations, reduced at the transition.

In Ref. [12] the phase transition in URu_2Si_2 was assigned to the quadrupolar order parameter (xy or $x^2 - y^2$). Such a model, as noted above, contradicts the neutron scattering Bragg peak pattern [3,8], as shown in [4].

To complete the above discussion, we make a few comments concerning the above concept of phase transitions in the MV intermetallides. As was first suggested in Ref. [13], valency fluctuations may be considered as excitations of an electron above the Fermi energy changing

the ionic configuration locally (e.g., $5f^36d \leftrightarrow 5f^26d^2$ for the U ion). For a single impurity the generalized isotropic Anderson model has been solved analytically [14]. It was shown that for such a model the resulting ground state could have a small magnetic moment depending on the value of the parameters chosen. On the other hand, the two ionic configurations are expected to differ in energy, at least on the scale of the spin-orbit coupling (i.e., at least a few tenths of eV). It has been indicated by many authors (see Ref. [15] and references therein) that a further reduction of that scale can be supplemented by the coupling to the lattice due to the essential difference in ionic sizes of the two electronic configurations.

This coupling gives rise to large polaronic effects which, in particular, strongly renormalize the matrix elements mixing both configurations [16]. We adopted above this concept of the strong involvement of the lattice variables in the phenomena related to the mixed valence compounds. For the $5f$ orbitals, having large spatial extent, it could be useless to describe the ionic state in terms of single electron shells. The polaronic effects may be responsible for electronic localization, if the core Coulomb attraction at a given site is strong, but cannot lead to a localized ground state by themselves. From this point of view the conduction electrons scatter on resonant complexes having both the energy levels and their widths tuned by the interactions with the quantized lattice displacements and the electroneutrality condition. Such a regime may survive down to lowest temperatures leading to Fermi liquid heavy fermion properties, in accordance with the scaling behavior of the single impurity Anderson model. On the other hand, the lattice interactions might fix the ultimate symmetry for these polaronic complexes without destroying completely their coupling to the conduction sea. We assume that this is what happens in URu_2Si_2 at T_N. If the above interpretation of the experimental data is correct, and the structural component prevails, the smallness of the average magnetic moments in URu_2Si_2 reflects the fact that the width of the level (given by the mixing matrix element squared) is small compared to the bare spin-orbital energy.

As in the Néel state, where the average spin helps to describe (below T_N) the symmetry changes in otherwise strongly perturbed spin correlations, the matrix element equation (1) has served to implement this more general idea. The parameter equation (1) describes the classification of the electronic degrees of freedom in the new coherent state of the lattice resulting from the trapping of electrons at T_N by distortions around the uranium ions. At the transition hybridization leaves the number of electrons not fixed at the local site, i.e., the coherent electronic component may become a quantum mixture of the two options. Inside the trapped state it is the uranium potential which electrons experience at very short distances, but a truly local state would not be possible without a local lattice adjustment. If this view is correct, the lattice distortions are not separable from the localization of electrons, though the electrons do not preserve their number on each site. In this sense there is no room for questions about the statistics of the mechanism which drives the transition, utilizing the lattice degrees of freedom and forming an electron state coherently for each trap.

In summary, we relate the phenomenon of small magnetic moment in some uranium compounds to mixed valency features. We suggest that the small magnetic moments in UPt_3 and URu_2Si_2 are different in origin. In UPt_3 the coherent wave function corresponds to the $5f^1$ configuration, while the magnetic moment vanishes for a particular choice of the wave function. In the case of URu_2Si_2 the phase transition is primarily structural, with the small magnetic moment resulting from a small admixture of a state of another valency.

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[1] J. A. Mydosh, Phys. Scr. **19**, 260 (1987).
[2] H. R. Ott and Z. Fisk, in *Handbook on the Physics and Chemistry of the Actinides,* edited by A. J. Freeman and G. H. Lander (Elsevier, New York, 1987), Vol. 5, p. 86.
[3] C. Broholm *et al.,* Phys. Rev. Lett. **58**, 1467 (1987); E. D. Isaaks *et al.,* Phys Rev. Lett. **65**, 3185 (1990); T. E. Mason *et al.,* Phys Rev. Lett. **65**, 3189 (1990); C. Broholm *et al.,* Phys. Rev B **43**, 12 809 (1991).
[4] M. B. Walker *et al.,* Phys. Rev. Lett. **71**, 2630 (1993).
[5] W. J. L. Buyers and T. M. Holden, in *Handbook on the Physics and Chemistry of the Actinides* (Ref. [2]), Vol. 2, p. 239.
[6] K. A. McEwen, U. Steigenberger, and J. L. Martinez, Physica (Amsterdam) **186-188B**, 670 (1993).
[7] G. Aeppli *et al.,* Phys. Rev. Lett. **60**, 615 (1988).
[8] W. J. L. Buyers *et al.,* Physica (Amsterdam) **199B**, 95 (1994).
[9] G. E. Volovik and L. P. Gor'kov, Sov. Phys. JETP **61**, 843 (1985) [Zh. Eksp. Teor. Fiz. **88**, 1412 (1985)].
[10] L. P. Gor'kov, Sov. Sci. Rev. A., Phys. **9**, 1 (1987).
[11] L. P. Gor'kov, Europhys. Lett. **16**, 301 (1991); V. Barzykin and L. P. Gor'kov, Phys. Rev. Lett. **70**, 2479 (1993).
[12] P. Santini and G. Amoretti, Phys. Rev. Lett. **73**, 1027 (1994).
[13] L. L. Hirst, Phys. Kondens. Mater. **11**, 255 (1970).
[14] P. Schlottmann, Z. Phys. B **59**, 391 (1985); A. A. Aligia *et al., ibid.* **62**, 311 (1986).
[15] C. M. Varma and V. Heine, Phys. Rev. B **11**, 4763 (1975).
[16] D. Sherrington and S. Von Molnar, Solid State Commun. **16**, 1347 (1975).