ELSEVIER

8 July 1996

Physics Letters A 217 (1996) 176–180

PHYSICS LETTERS A

Mixed valence and small moment magnetism

Eduardo Miranda

National High Magnetic Field Laboratory, Florida State University, Tallahassee, FA 32306, USA

Received 8 January 1996; revised manuscript received 11 April 1996; accepted for publication 16 April 1996
Communicated by J. Flouquet

Abstract

I propose that the phenomenon of "small moment magnetism" observed in some heavy fermion compounds is the consequence of a *weak admixture* of ordered excited *magnetic* f-shell states in an essentially Kondo quenched ground state. The magnitude of the dynamically generated admixture determines the size of the magnetization.

Heavy fermion materials continue to be an extraordinarily rich source of puzzling collective behavior in condensed matter physics [1]. Several of these compounds exhibit magnetic order with two different overall trends. In most materials, the transition into the ordered state leads to the formation of an antiferromagnetically ordered moment, whose magnitude is comparable with the free ion value. However, in a few other compounds the magnetic state is characterized by a minute value of the ordered moment: UPt_3 ($\mu = 0.02\mu_B$) [2], URu_2Si_2 ($\mu = 0.04\mu_B$) [3], $CeRu_2Si_2$ ($\mu < 0.001\mu_B$) [4], UPd_3 ($\mu \sim 0.01\mu_B$) [5], $CeAl_3$ ($\mu \sim 0.05\mu_B$) [6], for example.

This peculiar magnetic state shows some other anomalous properties. In URu_2Si_2, application of an external magnetic field strongly suppresses the low temperature value of the moment while leaving T_N largely unaffected [7]. Such behavior is rather anomalous since, in a conventional magnet, these two quantities are expected to scale with each other. In all of the above cases, except URu_2Si_2, the transition into the ordered state does not lead to noticeable effects on thermodynamic or transport properties. In the case of URu_2Si_2, however, large jumps in the specific heat [8], the nonlinear susceptibility [9] and resistivity [10] are observed. It is not at all clear how the appearance of such a small order parameter can lead to these large jumps. Attempts to explain this behavior have usually involved some multi-spin operator as the principal order parameter [9,11]. However, recent neutron scattering experiments in a magnetic field seem to be inconsistent with a multi-spin order parameter and instead point to a second order phase transition into a state with magnetic dipolar order [7].

Since this is a trend found in a variety of compounds, any microscopic theory should satisfy two criteria: (1) It should explain the origin of the small scale governing the size of the moments and (2) one should not have to fine tune the bare parameters of the model in order to generate this small scale. I suggest that mixed valence is essential to the understanding of the small moment enigma. Recently, Barzykin and Gor'kov [12] have analyzed this possibility within a macroscopic Landau functional description. I will develop a microscopic description where it is essential that the lowest f-multiplets of each valence state are both degenerate. Most past studies of heavy-fermion magnetism have focused on an Anderson lattice model

PII S0375-9601(96)00330-1

description of valence fluctuations between a magnetic configuration and one or two nondegenerate ones [13]. However, the physics of a Uranium ion is likely to be better described by a model that includes fluctuations between *two magnetic configurations* (most likely, $f^2(J=4) \rightleftharpoons f^3(J=9/2)$). The case of Ce is less clear. In the past, a model based on $f^1(J=5/2) \rightleftharpoons f^0(J=0)$ fluctuations has been widely employed [14]. However, there is spectroscopic evidence that contributions from $f^2(J=4)$ states are also very important [15].

A general model describing valence fluctuations between two Hund's rule coupled magnetic configurations can be written as [16,17]

$$H=\sum_{k\alpha}\epsilon(k)c^{\dagger}_{k\alpha}c_{k\alpha}+\sum_{j,M_1}E_1|jJ_1M_1\rangle\langle jJ_1M_1| \\ +V\sum_{j}(\langle\alpha,M_1|M_2\rangle c^{\dagger}_{j\alpha}|jJ_1M_1\rangle\langle jJ_2M_2|+\text{H.c.}). \tag{1}$$

The first term describes a band of uncorrelated electrons with angular momentum quantum numbers J_c and α. (J_1, M_1) and (J_2, M_2) are the corresponding quantum numbers of the f^n and f^{n+1} valence states, whose energies are E_1 and $E_2 = 0$, respectively. The last term describes the valence fluctuation processes at site j with amplitude V and $\langle\alpha, M_1|M_2\rangle \equiv \langle J_c, J_1; \alpha, M_1|J_2; M_2\rangle$ is a Clebsch-Gordan coefficient. The projection operators are actually Hubbard operators in the restricted Hilbert space of definite J_1 and J_2. Such models have been studied before in the context of Tm and other rare-earth and actinide ions [16]. The behavior of its one-impurity version has been clarified by an exact solution found for the case $J_c = 1/2$ [17]. In this case, the ground state of the system is always magnetic.

The situation in real materials is complicated by crystal field effects which lift the degeneracy of these configurations. In this case, one can choose to work within the lowest-lying multiplets of each configuration in order to describe the low-energy processes. I will assume that the configurations f^n and f^{n+1} and the conduction electron states have all been split into doublets and will confine the analysis to these low-energy manifolds. Appropriate point-group coupling coefficients should then be used. It is essential for the description given in this paper that *both* configurations be degenerate. One ground doublet is guaranteed by Kramers theorem and I will assume that the other crystal field ground multiplet is also a doublet. These assumptions are consistent with the point-group structure of the known small moment magnets. This model should be regarded as the minimal model capable of describing valence fluctuations between two degenerate configurations. This doublet–doublet model can be written explicitly as

$$H=\sum_{k\alpha}\epsilon(k)c^{\dagger}_{k\alpha}c_{k\alpha}+\sum_{j,\sigma}E_1|j\sigma\rangle\langle j\sigma| \\ +V\sum_{j}(c^{\dagger}_{j\uparrow}|j\uparrow\rangle\langle j+|+c^{\dagger}_{j\downarrow}|j\downarrow\rangle\langle j-|+\text{H.c.}), \tag{2}$$

where I used $M_1 \to \sigma = \uparrow\downarrow = \pm$ and $M_2 \to M = \pm$.

To make further progress, it is convenient to employ a modified version of the slave boson formalism previously used to study the infinite-U Anderson model [18]. In the present case, additional boson fields have to be introduced in order to describe the degenerate f^{n+1}-configuration. The valence changing Hubbard operators can be written as

$$|j\sigma\rangle\langle jM| \to f^{\dagger}_{j\sigma}b_{jM} \tag{3}$$

and an additional constraint has to be imposed on the auxiliary f- and b-fields, guaranteeing the occupation of each site by one and only one particle. This is most easily achieved in a Lagrangian language [18]

$$L=\sum_{k\alpha}c^{\dagger}_{k\alpha}\partial_{\tau}c_{k\alpha}+\sum_{j,\sigma}f^{\dagger}_{j\sigma}\partial_{\tau}f_{j\sigma}+\sum_{j,M}b^{\dagger}_{jM}\partial_{\tau}b_{jM}+H \\ +\sum_{j}\mathrm{i}\lambda_j(\tau)\Big(\sum_{\sigma}f^{\dagger}_{j\sigma}f_{j\sigma}+\sum_{M}b^{\dagger}_{jM}b_{jM}-1\Big), \tag{4}$$

where

$$H=\sum_{k\alpha}\epsilon(k)c^{\dagger}_{k\alpha}c_{k\alpha}+\sum_{j,\sigma}E_1f^{\dagger}_{j\sigma}f_{j\sigma} \\ +V\sum_{j}(\langle\alpha,\sigma|M\rangle c^{\dagger}_{j\alpha}f^{\dagger}_{j\sigma}b_{jM}+\text{H.c.}) \tag{5}$$

and $\lambda(\tau)$ is a Lagrange multiplier field.

The Lagrangian of Eq. (4) is invariant under the local gauge transformation

$$b_{jM} \to e^{i\theta_j(\tau)} b_{jM},$$
$$f_{j\sigma} \to e^{i\theta_j(\tau)} f_{j\sigma},$$
$$\lambda_j \to \lambda_j - \partial_\tau \theta_j(\tau). \tag{6}$$

Although an overall phase of the b-fields can be gauged away by Eq. (6), phase differences between its different components are physical and cannot be eliminated. Such phases do affect, for example, the total f-spin operator.

To investigate possible magnetic states of the system described by the Lagrangian of Eq. (4), I look for mean field solutions with a spontaneous staggered magnetization. These arise from a condensation of the bosonic fields b_{jM},

$$\langle b_{jM}\rangle = V \sum_{\alpha\sigma} \langle \alpha, \sigma | M\rangle \langle f_{j\sigma} c_{j\alpha}\rangle. \tag{7}$$

A finite value of the above quantity measures the amplitude for admixture of the states within the f^{n+1} multiplet into the coherent ground state. It also acts as a renormalization factor of the hybridization matrix element V in Eq. (5), leading to the formation of a lattice of *spin dependent* resonant scattering centers for the itinerant fermionic degrees of freedom. As usual, a bona fide condensation of the quantities in Eq. (7) is not possible, since it would violate a local gauge symmetry, which cannot be spontaneously broken [19]. However, symmetry does not preclude the expectation value of the absolute value of the b-fields ($\langle|b_{jM_2}|\rangle$) to be different from zero, since these operators do not carry the gauge charge. Treatments of magnetic states of this kind are very reminiscent of previous Schwinger boson descriptions of quantum magnetism [20].

I have investigated the stability of solutions which exhibit a commensurate antiferromagnetic moment and have found the following solution to be the only stable one (I assume a bi-partite lattice structure and $Q = (\pi, \pi, \pi)$): $i\langle\lambda\rangle = \epsilon_f - E_1$ and

$$\langle b_{jM}\rangle = \tfrac{1}{2} r (1 + M e^{i Q\cdot R_j}). \tag{8}$$

The energy of the fermionic modes is given by $\omega = \epsilon_f$ and by the roots of

$$(\omega - \epsilon_f)[(\omega - \epsilon_k^+)^2 - (\epsilon_k^-)^2] - 4\tilde{V}^2(\omega - \epsilon_k^+) = 0, \tag{9}$$

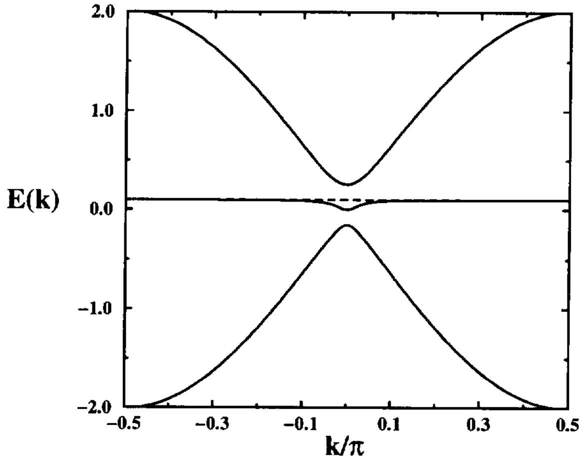

Fig. 1. Spectrum of the fermionic excitations of the doublet-doublet model at the mean field level. The solid lines are the three dispersive branches and the dashed one is the dispersionless branch at ϵ_f.

where $\epsilon^\tau(k) = \frac{1}{2}[\epsilon(k) + \tau\epsilon(k+Q)]$ and $\tilde{V} \equiv \frac{1}{2} V r$. There is a dispersionless mode with energy ϵ_f, corresponding to one f-fermion that is left unhybridized at each site. Fig. 1 shows the spectrum of fermions in the magnetic Brillouin zone. Note that gaps are opened up at the zone boundaries as in conventional spin density wave spectra.

Assuming nesting in the conduction band $\epsilon(k + Q) = -\epsilon(k)$ and a constant density of states, one can solve the mean field equations analytically. One finds that, as $T \to 0$ and for $D \gg |E_1| \gg \rho_0 V^2$

$$\epsilon_f(T \to 0) \sim 2r^2 T, \tag{10a}$$
$$\tilde{V}(T = 0) \sim D e^{-|E_1|/\rho_0 V^2}, \tag{10b}$$

where D is the half bandwidth and $\rho_0 = 1/2D$ is the density of states. Numerical solutions for $T > 0$ can be easily obtained. The variational quantities r and ϵ_f vanish at a temperature $T_c = (2e^\gamma/\pi)\tilde{V}(T = 0)$.

Due to the presence of the ϵ_f mode, the mean field solution exhibits a zero point entropy $S_0 \sim 2\ln 2$. This mode is expected to acquire dispersion and to broaden into a fermionic band as fluctuation effects are included, thus spreading the zero temperature entropy over a finite temperature interval. This is natural since fluctuations bring in inter-site correlations which are not included in the mean field picture. The entropy involved in the transition is small, of the order of r^2.

This is a consequence of the fact that most of the spin entropy is contained in the dispersionless mode which resides at $\epsilon_f = 0$ at $T = 0$. This small transition entropy is consistent with the behavior of all "small moment" magnets except URu_2Si_2. I will comment on the latter case below.

There are contributions to the staggered magnetization of the system from both f-valence states and the antiferromagnetically polarized conduction sea. At $T = 0$

$$\langle S_{fz}\rangle \sim [(3\pi/2)\rho_0\widetilde{V}S_1 + S_2]r^2, \qquad (11)$$

$$\langle S_{cz}\rangle \sim (\pi/2)\rho_0\widetilde{V}S_c r^2. \qquad (12)$$

Here S_1, S_2 and S_c are, respectively, the spin projections of the f^n, f^{n+1}-configurations and of the conduction electrons along the z-axis of staggered magnetization, in the crystal field doublets. Because of the factor $\rho_0\widetilde{V}$ in the S_1 and S_c terms, the largest contribution to the total staggered moment comes from the f^{n+1}-configuration. The latter is proportional to r^2, a measure of the degree of admixture of the excited f^{n+1}-configuration in the ground state. This is the central result of this paper. The exponentially small, dynamically generated scale given by r^2 (Eq. (10b)) sets the size of the moment. This is the charge fluctuation scale also present in the conventional Anderson model. The fermionic excitations, on the other hand, form an almost quenched Fermi sea and their contribution is governed by the much smaller spin fluctuation scale $\widetilde{V}$. Note that the distinction between these two different scales is rigorous and can be proved by scaling[1].

It is unclear whether one should identify T_c with the Néel temperature T_N. A similar phase transition occurs in the slave boson description of the infinite-U Anderson model, where it is known to be spurious [18]. The inclusion of fluctuation effects may cause the phase transition to occur at a point where r still has a finite albeit small value. In this case, the transition would be induced by the usual thermal disordering of the local spins.

To consider the effect of an applied magnetic field, I assumed $S_1 = S_c = 1/2$ and $S_2 = 1$ and all the g-factors to be equal to 1. It is now necessary to allow for different values of the variational parameter r on the different sub-lattices A and B ($r_1 = r_A$ and $r_{-1} = r_B$)

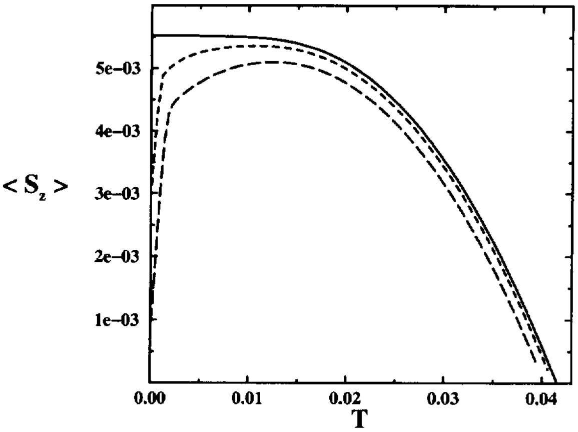

Fig. 2. Staggered magnetization of the doublet–doublet model versus temperature for different applied magnetic fields: $h = \mu_B H = 0$ (solid line), $h = 5 \times 10^{-3}$ (short-dashed line) and $h = 9 \times 10^{-3}$ (long-dashed line). Model parameters are $D = 2$, $\rho_0 V^2 = 0.25$ and $E_1 = -1$.

$$\langle b_{jM}\rangle = \tfrac{1}{2}r_M(1 + M e^{iQ\cdot R_j}). \qquad (13)$$

Physically, this means that the coherent occupation of the f^{n+1}-configuration at each site varies according to whether it belongs to sub-lattice A or B. In contrast, in a conventional antiferromagnet, the occupation of the sites remains unaltered. Fig. 2 shows the behavior of the staggered magnetization versus T, for different applied magnetic fields $h = \mu_B H$. The applied field suppresses the staggered moment, especially at lower temperatures, while the transition temperature is not significantly affected. This is not the typical mean-field behavior and is a consequence of the appearance of the small scale ϵ_f. This anomalous behavior is in good qualitative agreement with the results of Mason et al. [7]. However, this has only been measured in URu_2Si_2, which is precisely the compound with the anomalous jump at the transition.

I would now like to comment on the effect of fluctuations around the mean field theory. First, there are fluctuations of the Lagrange multiplier field $\lambda(\tau)$. These are responsible for enforcing the constraint of one pseudo-particle per site at every point in time. They are soft modes which are a consequence of the gauge invariance introduced in the model by the slave boson substitution of Eq. (3). They have a major role

---

[1] For a thorough discussion of the distinction between these two scales, see the second paper of Ref. [16].

in lifting the degeneracy of the ϵ_f mode. Once reinstated, these fluctuations tend to cancel out most of the zero point entropy of the ϵ_f mode. This has the effect of turning the linear in T term in the free energy, which originates from the zero point entropy, into a quadratic one, further stabilizing the magnetic solution. Secondly, there are fluctuations in the b_M-fields. The fluctuations in the absolute value of the b-fields are gapped, since the mean field theory is stable, and are not expected to be essential at the lowest temperatures. The remaining fluctuations are the internal phase differences between the two components of b_M, which are related to the spin orientation of the f^{n+1}-configuration. They therefore contribute to the disordering of the staggered magnetization. In the present doublet–doublet model they are gapped, because rotational symmetry is explicitly broken by the spin–orbit interaction and crystal field effects. In a more realistic treatment, the gap is given by the crystal-field excitation energies which serve as a cutoff for these phase fluctuations. As was discussed before, it is possible that these quantum and thermal disordering effects will drive the transition before the variational parameter r vanishes.

The present results are consistent with the small thermodynamic signature observed in all "small moment" transitions except that of URu_2Si_2. It is tempting to speculate that, unlike in the other compounds, the transition in URu_2Si_2 is accompanied by a *significant change in the occupation of the f-level.* Such a transition would be beyond the scope of a conventional Landau treatment of magnetism, as the formation of the order parameter would occur together with the concomitant localization of some of the carriers. This localization process would certainly make a large amount of spin entropy available for the state below the transition. The latter would be unavailable above T_N since its itinerant character and the Pauli principle would make its entropy very small. This is reminiscent of a Mott–Hubbard localization transition, and would correspond to the transfer of degrees of freedom from the itinerant subsystem to the localized one. Additional Coulomb interactions are needed to describe this transition and it remains to be determined whether it can be a second order one.

In conclusion, I have proposed that the phenomenon of small moment magnetism is due to the small admixture of magnetically ordered orbitals in the ground state. In this description, the *major* factor determining the size of the ordered moment is the dynamically generated charge fluctuation scale that sets the magnitude of the admixture of these orbitals. The behavior of the staggered magnetization in a magnetic field is consistent with the anomalous behavior observed in URu_2Si_2.

I acknowledge useful discussions with W.J.L. Buyers, P. Coleman, L.P. Gor'kov and J.R. Schrieffer. This work was supported by the National High Magnetic Field Laboratory at Florida State University.

References

[1] P.A. Lee et al., Comm. Cond. Matt. Phys. 12 (1986) 99.
[2] G. Aeppli et al., Phys. Rev. Lett. 60 (1988) 615.
[3] C. Broholm et al., Phys. Rev. B 43 (1991) 12809.
[4] A. Amato et al., Phys. Rev. B 50 (1994) 619.
[5] K.A. McEwen, U. Steigenberger and J.L. Martinez, Physica B 186-188 (1993) 670.
[6] S. Barth et al., Phys. Rev. Lett. 59 (1987) 2991.
[7] T.E. Mason et al., J. Phys. Condens. Matter 7 (1995) 5089.
[8] T.T.M. Palstra et al., Phys. Rev. Lett. 55 (1985) 2727.
[9] A.P. Ramirez et al., Phys. Rev. Lett. 68 (1992) 2680.
[10] W. Schlabitz et al., Z. Phys. B 62 (1986) 171.
[11] V. Barzykin, L.P. Gor'kov and A.V. Sokol, Europhys. Lett. 15 (1991) 869;
P. Chandra and P. Coleman, Phys. Rev. Lett. 66 (1991) 100;
V. Barzykin and L.P. Gor'kov, Phys. Rev. Lett. 70 (1993) 2479;
P. Santini and G. Amoretti, Phys. Rev. Lett. 73 (1994) 1027.
[12] V. Barzykin and L.P. Gor'kov, Phys. Rev. Lett. 74 (1995) 4301.
[13] S. Doniach, Physica B 91 (1977) 231;
P. Fazekas and E. Müller-Hartmann, Z. Phys. B 85 (1991) 285;
Y. Kuramoto and K. Miyake, J. Phys. Soc. Japan 59 (1990) 2831.
[14] B. Coqblin and J.R. Schrieffer, Phys. Rev. 185 (1969) 847.
[15] J.W. Allen, Physica B 171 (1991) 175.
[16] Y. Yafet, C.M. Varma and B. Jones, Phys. Rev. B 32 (1985) 360;
N. Read et al., J. Phys. C 19 (1986) 1597;
M. Baliña and A.A. Aligia, Physica B 171 (1991) 109.
[17] P. Schlottmann, Z. Phys. B 59 (1985) 391;
A.A. Aligia, C.A. Balseiro and C.R. Proetto, Phys. Rev. B 33 (1986) 6476.
[18] P. Coleman, Phys. Rev. B 29 (1984) 3035;
N. Read and D.M. Newns, J. Phys. C 16 (1983) 3273, L1055.
[19] N. Read, J. Phys. C 18 (1985) 2651;
P. Coleman, Phys. Rev. B 35 (1987) 5072.
[20] D.P. Arovas and A. Auerbach, Phys. Rev. B 38 (1988) 316.