THE GROUND STATE OF DILUTE Tm SYSTEMS IS DEGENERATE

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PACS: 75.20.H - Local moment is dilute alloys, Kondo effect, valence fluctuations, heavy fermions.

Abstract. The ground state of the appropriate generalization of the impurity Anderson model for valence fluctuations between two realistic Tm^{+2} and Tm^{+3} configurations, is obtained in the atomic, narrow band limit, using the Lanczos' method. This limit describes the strong-coupling fixed point of renormalization-group treatments for intermediate valence and Kondo impurities. The resulting ground state is highly-degenerate and contains states of total angular momentum 0, 3/2, 2, 5/2, 4 and 9/2. The crystal electric field or an applied magnetic field should split the degeneracy favouring the magnetic states.

The intermediate valence and Kondo systems are among the most interesting and challeging problems for theoreticians, due to the presence of correlation energies of the order of 10 eV. The main properties of this systems are well known experimentally [1]. However most of the theoretical effort was deviated towards the somewhat related high Tc systems, leaving some important matters unsolved, like an adequate description of the Anderson and Kondo lattices (an accurate description based on Wilson's renormalization group exists only for two interacting Kondo impurities [2]) and of systems fluctuating between two magnetic configurations, like Tm ones. Most of the theoretical treatments are based on modifications of the impurity model proposed by Anderson in 1961 [3], or in the Kondo limit of it. The Kondo Hamiltonian is obtained from the Anderson one eliminating all states but those of a definite valence (corresponding to the magnetic configuration) through a canonical transformation [4]. The first accurate results in these models were obtained using Wilson's renormalization group [5,6]. Another very important progress in the understanding of the impurity systems, was brought by the exact solutions using the Bethe-ansatz, which allowed the calculation of static properties for realistic impurity configurations [7], including crystal field [1]. Dynamical properties were also calculated using the renormalization group [8].

A model for valence fluctuations between two magnetic configurations has been proposed by Mazzaferro et al. [9]. A simplification of it and its extension to the lattice [10] provides a qualitative explanation of the main properties, static [10] and dynamic [11] of Tm compounds. The experimental properties point towards a magnetic ground state of Tm impurities [12-14] and

TmSe and its alloys [14-17], probably a doublet [16]. Renormalization-group [18] and exact Bethe-ansatz [19] results confirmed that the ground state of the model of Ref.9 is a doublet. Extensions of the exact results to other magnetic impurity configurations [20,21], could not reach unfortunately the realistic cases for rare earths, since these cases are not Bethe-ansatz solvable [20]. Several approximate treatments for more realistic Tm configurations have been performed [22-24]. All of them resulted in a non-magnetic ground state. As recognized in Ref.24, this fact is difficult to reconcile with the experiments. It has been argued [23] that the magnetic behaviour of Tm compounds is due to magnetic interactions between Tm ions, but then, the divergent magnetic susceptibility [12] and neutron scattering experiments [13-14] of Tm impurities at low temperatures remain unexplained. On the other hand, all the above mentioned studies of valence fluctuations between two magnetic configurations, neglected one of both hybridization channels V_j ($j = l \pm 1/2$, see Eq.(8)) and only Lustfeld [22] considered magnetic states built from realistic Hund-rules ground-state multiplets of Tm^{+2} and Tm^{+3}. Our previous calculations [25] for p configurations ($l = 1$), show that it is crucial to take realistic configurations and both V_j into account, irrespective of their relative magnitude. Thus, it is apparent that to complete at least a qualitative understanding of the behaviour of intermediate valence and Kondo impurities, the ground state of Tm systems deserves further study.

In this letter, we present our results for the ground state of the Anderson model generalized for realistic Tm configurations, in the atomic limit. This limit not only provides a qualitative

description of the main features of the system [26], but also coincides with the strong-coupling or frozen-impurity fixed point (corresponding to zero temperature) of Wilson's renormalization group calculations [5,6]. The same fixed point in the integer valence (Kondo) limit was obtained at zero temperature by Lustfeld [22] using the multiplicative renormalization group. We shall show that the degeneracy of the ground state is the same in the intermediate valence regime and in both integer valence limits. In fact, we have reproduced the results that Lustfeld obtained for Tm systems, and interestingly enough, the conclusions are the opposite when the effects of $V_{5/2} \neq 0$ (see Eq.(8)) are included.

Assuming spherical symmetry, the Hamiltonian for a Tm impurity in a metal has the following form:

$$H = H_{ion} + H_{band} + H_{mix} \tag{1}$$

Due to the strong intra-atomic correlations, only the ground state multiplet of the $4f^{12}$ and $4f^{13}$ configurations need to be considered in the description of the ionic part:

$$H_{ion} = E \sum_{M_o} |J_o M_o><J_o M_o| + (E+\Delta) \sum_{M_1} |J_1 M_1><J_1 M_1| \tag{2}$$

where $|J_1 M_1>$ denotes the state of total angular momentum J_1 and projection M_1 of the configuration $4f^{12+1}$. These states are given by the Hund rules (L- S coupling). In Refs.23 and 24, the comparison between the energy of magnetic and non-magnetic states was done using j-j coupling, which simplifies the description of the ionic states, but modifies the degeneracy of the ground state, as we shall show.

In spherical coordinates, the second term of Eq.(1) can be written as:

$$H_{band} = \sum_{k l \mu \sigma} \epsilon_{kl} \, c^{+}_{k l \mu \sigma} c_{k l \mu \sigma} \qquad (3)$$

where k is the absolute value of the momentum, l and μ are the angular momentum and its projection and σ describes the spin. Since only conduction states with l=3 can mix with the 4f states, the subscript l can be dropped. Thus, neglecting the unimportant energy dependence of the hybridization energy V_k, H_{mix} can be written as:

$$H_{mix} = V \sum_{k \mu \sigma} (f^{+}_{\mu \sigma} c_{k \mu \sigma} + \text{h.c.}) \qquad (4)$$

In the total angular momentum representation ($j = l \pm 1/2$, $m = \mu + \sigma$), Eqs.(3) and (4) take the form:

$$H_{band} = \sum_{k j m} \epsilon_{k} \, c^{+}_{k j m} c_{k j m} \qquad (5)$$

$$H_{mix} = V \sum_{k j m} (f^{+}_{j m} c_{k j m} + \text{h.c.}) \qquad (6)$$

Expressing the f operators in terms of the many body states entering Eq.(2), one obtains [25,22,27]:

$$H_{mix} = \sum_{k j m M_0 M_1} V_j \langle J_o j M_o m | J_1 M_1 \rangle (c^{+}_{k j m} | J_0 M_0 \rangle \langle J_1 M_1 | + \text{h.c.}) \qquad (7)$$

where the $\langle J_o j M_o m | J_1 M_1 \rangle$ are Clebsh-Gordan coefficients. The V_j can be evaluated using fractional parentage coeficients [27]. We

followed a simpler approach valid for Hund rules multiplets [25]. The result is:

$$V_{7/2} = 1.6690 \text{ V}, \quad V_{5/2} = 0.4818 \text{ V} \tag{8}$$

Thus, the appropriate Hamiltonian for an impurity in jellium can be written in the form of Eqs. (1), (2), (5), (7) and (8). This Hamiltonian is implicit in the work of Lustfeld [22]. He assumed $|\Delta| >> V$ and eliminated one of the ionic configurations by means of a Scrieffer-Wolff transformation. In order to simplify the model he also neglected $V_{5/2}$. The Hamiltonian with $V_{5/2} = 0$ is equivalent [25] to that of Refs. 23 and 24 with ionic states given by j-j coupling, for which $j = l + 1/2$.

We solved the complete Hamiltonian in the atomic limit:

$$\epsilon_{kjm} = \epsilon_F \quad \text{for all } k \tag{9}$$

We took the origin of energies at the Fermi energy ϵ_F ($\epsilon_F = 0$). In this limit, the relevant Hilbert space has finite dimension, since only the Wannier states of conduction electrons at the impurity site can hybridize with the ionic states. Since there are $2(2l+1) = 14$ of these Wannier states and $J_0 = 6$, $J_1 = 7/2$, the total number of states of the relevant Hilbert space is $2(J_0 + J_1 + 1) \times 2^{14} = 344064$.

We now prove that the quantum numbers of the ground state are the same for all non-zero values of the parameters, including in particular the strong-coupling limit of the Kondo Hamiltonian [22]. We define the proyection operators:

$$P_1 = \sum_{M_1} |J_1 M_1\rangle\langle J_1 M_1| \tag{10}$$

One can easily verify that:

$$P_1 H_{mix} P_1 = 0 \quad ; \quad P_1 H_{mix}^2 (1 - P_1) = 0 \quad , \; P_1 + P_0 = 1 \tag{11}$$

Let us assume that we have diagonalized $P_0 H_{mix}^2 P_0$:

$$P_0 H_{mix} P_0 |0,n\rangle = \lambda_n^2 V^2 |0,n\rangle \tag{12}$$

λ_n is real, and can be taken positive, since it is the norm of the state $V^{-1} H_{mix} P_0 |0,n\rangle$, and from (12) $P_0 |0,n\rangle = |0,n\rangle$. Let us consider the states $|0,n\rangle$ for which $\lambda_n > 0$ (at least one should exist if $H_{mix} \neq 0$). For each of them we define a partner with $P_1 |1,n\rangle = |1,n\rangle$:

$$|1,n\rangle = \frac{P_1 H_{mix} P_0}{\lambda_n V} |0,n\rangle = \frac{H_{mix}}{\lambda_n V} |0,n\rangle \tag{13}$$

where the second equality was obtained using (11). The symmetry of H_{mix} imposes that $|1,n\rangle$ has the same J_t, projection J_t^z and number of particles N as $|0,n\rangle$. Applying H_{mix} to the first two members of Eq.(13) and using (11) and (12) one obtains

$$H_{mix} |1,n\rangle = \lambda_n V |0,n\rangle \tag{14}$$

In the strong-coupling (atomic) limit one has:

$$(H_{ion} + H_{band}) |i,n\rangle = (E + i\Delta) |i,n\rangle \tag{15}$$

Therefore, in this limit, all the eigenvalues are E, E+Δ and those that result from the 2x2 matrices defined by Eqs.(13) to (15). The lowest eigenvalue of each of these matrices is:

$$E_n = E + \Delta/2 - [(\Delta/2)^2 + \lambda_n^2 V^2]^{1/2} \qquad (16)$$

Thus, the largest λ_n determines the ground state energy independently of Δ, V, E. The ground state has them the form:

$$|n\rangle = a_0|0,n\rangle - a_1|1,n\rangle \qquad (17)$$

where $a_1 > 0$ and:

$$a_1^2 = \frac{1}{2} - \frac{(i - 1/2)\,\Delta}{2[(\Delta/2)^2 + V^2\lambda_n^2]^{1/2}} \qquad (18)$$

We have obtained the lowest eigenvalue (largest λ_n) in each subspace of given total number of particles $N_T = N + 12$ and total angular momentum projection J_n^z. We used the ordinary Lanczos method and a modified version of it [28], which is more suitable to obtain an accurate wave function. For $N \leq 3$ and $N \geq 12$ we used also exact diagonalization. The lowest eigenvalues obtained with different methods coincide up to the precision used (relative error $<10^{-15}$). For each J_t^z, the degeneracy of the lowest eigenvalue was obtained using repeatedly the modified version. Comparing the results for different projections J_t^z, the absolute value of the total momentum J_t was obtained.

For comparison purposes, we have also obtained the ground state in the hypothetical cases 1)$V_{5/2} = 0$ and 2) $V_{7/2} = 0$. In the first one, the band states with $j = 5/2$ can be disregarded, since they do not hybridize with the f states. This fact allows us to diagonalize exactly the resulting simplified atomic Hamiltonian. For $|\Delta| >> V_{7/2}$, this Hamiltonian has been already considered by Lustfeld [22]. In agreement with his results, the largest λ_n which determines the ground state energy E_{g0} through Eq.(16), is obtained for $N = 2$ and is $\lambda_{max} = \sqrt{2}\, V_{7/2}/V = 2.3603$. The

corresponding ground sate $|g_0>$ is a mixture of two singlets: one obtained combining the $|J_1M_1>$ with the $c^+_{7/2m}$ operators (the $|1,n>$ of Eq.(17)) and the other one is a combination of the $|J_0M_0>$ with the states of total angular momentum 6 of two band particles with j = 7/2. A singlet is also obtained in Refs.23 and 24.

Proceeding in a similar way for $V_{7/2} = 0$, we obtain a magnetic ground state with $J_t = 7/2$ with $\lambda_{max} = V_{5/2}/V$ in the subspace with N = 1.

The results for the realistic case with both V_j satisfying Eq.(8) are summarized in Table I. The last two columns correspond to the mean values $J^z_i = <i,n|J^z_{imp}|i,n>$ for the state of minimum energy (see Eq.(17)) and maximum J^z_t for each N. The impurity angular momentum J^z_{imp} is given by:

$$J^z_{imp} = \sum_i \sum_{M_i} M_i |J_iM_i><J_iM_i| \qquad (19)$$

The mean value of the magnetic moment of the Tm ion for the above mentioned states is:

$$\mu = \sum_i a_i^2 g_i J^z_i \qquad (20)$$

g_i is the Landé factor of the $4f^{12+i}$ configuration.

Two facts are remarkable in these results: the high degeneracy of the ground state and the low value of μ. The first fact was already found in valence fluctuations between two magnetic p configurations [25] and shows the existence of a hidden symmetry in the model. This degeneracy should be partially lifted by the crystalline electric field. Since the $J_t = 0$ states are

unaffected by this field, it favours the magnetic states. Decomposing all the degenerate irreducible representations under a cubic field, only one singlet is contained in the result, while the most frequent degeneracy is two (eight doublets are obtained). The ground state of TmSe seems to be a doublet [16], in agreement with our results. The low value of μ, which is also in qualitative agreement with experiment [17] can be understood from the fact that if only the dominant hybridization channel $V_{7/2}$ is taken into account, the ground state $|g_0>$ is a singlet. E_{g0} is very near to the ground state energy E_g of the true problem, satisfying Eqs.(8). The difference in λ_{max} is only 0.0487 (about 2%). However, the real ground state has a non-vanishing impurity magnetization μ, under an infinitesimally small applied magnetic field, as shown in Table I. This situation reminds that occuring in some heavy-fermion systems, where the Gutzwiller wave function has an energy near to the ground-state energy but belongs to an irreducible representation different from that of the true ground state [29]. For $V_{5/2}= 0$, eigenstates of different J_t but all with $\mu = 0$ and the same energy E_{g0} can be obtained applying up to 6 operators $c^{+}_{5/2m}$ to $|g_0>$. However, when $V_{5/2}$ is turned on, these states hybridize with other ones for which $J^z_i \neq 0$. The fact that for Tm $V_{5/2}$ is small compared to $V_{7/2}$ explains the small values of J^z_i and $E_{g0} - E_g$, but the same different values of J_t are present in the ground state for all values of $V_{5/2} \neq 0$.

In summary, solving a generalized Anderson model in an approximation which retains all correlations of the problem and is supported by renormalization-group arguments at T = 0, a highly degenerate ground state is found for Tm impurities if crystal field is neglected. However the Tm moment in these states, μ, is

fairly small in qualitative agreement with neutron experiments in TmSe [17]. A quantitative comparison cannot be made, since corrections to the strong-coupling limit introduced by irrelevent operators [6] and interactions between Tm ions should modify the value of μ. Under a cubic crystal field, the ground state splits into 8 doublets, 6 triplets, 4 quadruplets and 1 singlet. Experiments in TmSe agree with a doublet ground state. Since the same degeneracy of the ground state is obtained for any value of $0 \neq V_{5/2} / V_{7/2} \neq \infty$, this result is valid also for Tb ions fluctuating between oxydation states +3 and +4, because in this case $J_0 = 7/2$, $J_1 = 6$, and the corresponding Hamiltonian can be mapped into that for $Tm^{+2} \leftrightarrow Tm^{+3}$ by means of a special electron-hole transformation [20,25]. Our results complement the exact ones obtained previously [7] for valence fluctuations between one magnetic and one non-magnetic configurations and allow us to conclude that the generalized Anderson model provides an explanation, at least qualitative of the main properties of all rare earth impurities near or at a valence instability.

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Table I

N	λ_n	J_t	J_0^z	J_1^z
0	0	6	6	0
1	1.7371	7/2		
2	2.4090	0	0	0
3	2.4090	5/2	-0.0824	-0.0530
4	2.4090	0,2,4	-0.1315	-0.0845
5	2.4090	3/2,5/2,9/2	-0.1474	-0.0947
6	2.4090	0,2,4	-0.1305	-0.0839
7	2.4090	5/2	-0.0814	-0.0523
8	2.4090	0	0	0
9	2.2966	7/2		
10	2.2141	6		
11	2.1135	15/2		
12	1.9720	8		
13	1.7492	15/2		
14	1.3627	6		
15	0	7/2	0	7/2

Table caption

Physical magnitudes corresponding to the states of minimum energy for a total of N + 12 electrons at the Tm site. λ_n gives the energy according to Eq.(16) J_t is the total angular momentum and the J_i^z define the magnetic moment of the Tm ion according to Eqs.(20) and (18) for the state of maximum J_t^z.