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Ground state and magnetic susceptibility of intermediate-valence Tm impurities

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We consider the appropriate generalization of the Anderson model for a Tm impurity in a cubic crystal field. In the $4f^{12}$ configuration we include only the two multiplets of lowest energy: a singlet Γ_1 and a triplet Γ_4. Similarly we include only the doublet ground state of the $4f^{13}$ configuration, and (to make our numerical method feasible) we assume that the conduction-electron partial waves with symmetry Γ_8 can be neglected. We study the model using Wilson's renormalization group. The resulting ground state is a singlet or a doublet depending mainly on the relative strength of the hybridization of the $4f^{13}$ doublet with both $4f^{12}$ states. A doublet ground state is consistent with the experimental evidence.

I. INTRODUCTION

Due to their peculiar properties and the presence of strong correlations, the intermediate-valence and heavy-fermion systems are among the most interesting problems in solid-state physics. The main properties of these systems are well-known experimentally.[1] The Anderson model and its integer valence limit, the Kondo model, have played a decisive role in the understanding of the dilute magnetic alloys. The scaling behavior of these models has been established through numerical calculations with Wilson's renormalization group[2,3] (WRG). The low-temperature properties are described by the strong-coupling fixed point (infinitive value of the coupling constant), characterized by a nonmagnetic ground state and Fermi-liquid behavior. These models and their extension to an arbitrary degeneracy of the magnetic configuration have been solved exactly using the Bethe ansatz, and the predicted thermodynamic properties agree, in general, with the experiments in dilute systems fluctuating between one magnetic and one nonmagnetic configuration.[4]

The properties of systems in which both accessible configurations are magnetic are markedly peculiar. For example, TmSe is the only intermediate-valence compound that orders magnetically with a local moment $1.5\mu_B$, much smaller than those of the $4f^{12}$ and $4f^{13}$ configurations between which Tm fluctuates.[5] Instead of saturating at low temperatures, the magnetic susceptibility $\chi(T)$ of TmSe always increases with decreasing temperature until the Néel temperature $T_N = 3.2$ K is reached.[6] Specific-heat measurements under an applied magnetic field suggest that the ground state of TmSe is a doublet.[7] One might argue that the ground state of a Tm impurity would be nonmagnetic and that the magnetic order of TmSe is due to interatomic interactions.[8] However, careful experiments in the dilute system $Y_{1-x}Tm_xSe$ show a Curie-Weiss behavior of the magnetic susceptibility $\chi^{-1}(T) = T + \theta(x)$ with very small $\theta(x) \sim 0.1$ K, and $\theta(x) \to 0$ for $x \to 0$.[9] Also, magnetic neutron scattering experiments in compounds[10] and dilute systems[11] are very similar, showing an elastic peak and an inelastic peak centered at 10 meV, which were interpreted in terms of models with a doublet ground state in dilute[12] and periodic systems.[13]

The model of Mazzaferro, Balseiro, and Alascio (MBAM) mixes a doublet and a triplet,[12] and is equivalent to the model studied here if the Γ_1 singlet could be neglected. However, no attempt was made to justify the model in terms of realistic configurations. In spite of this, the model, an extremely anisotropic version,[14] and its extension to the lattice[15] were able to explain the above mentioned static[14–16] and dynamic[12,14,13] properties, including magnetoresistance.[14,15] Using WRG, Allub, Ceva, and Alascio confirmed that the ground state of the MBAM is a doublet.[17] The same result was obtained by Proetto, Balseiro, and Aligia using the Bethe ansatz.[18]

The appropriate generalization of the Anderson model to any two configurations $4f^n$ and $4f^{n+1}$, in the spherically symmetric case is implicit in the work of Lustfeld[19] and is derived in Ref. 20. The integrability of this model was studied, with the result that unfortunately when both realistic configurations are magnetic, the model is not solvable with the Bethe ansatz.[21] Several approximate treatments have been made for the case of Tm ($n = 12$) in the extreme case of j-j coupling, or (what is equivalent) neglecting the conduction-electron partial waves with $j = 5/2$.[8,19,22] All of them resulted in a nonmagnetic ground state, a fact difficult to reconcile with the experiments, as recognized in Ref. 22. A study of the localized (narrow-band) limit of the model (which in the case of the Anderson, Kondo, and MBAM models describes the strong-coupling fixed point of WRG and therefore the physics at low temperatures) shows that while in fact in the extreme (unrealistic) case of j-j coupling, the ground state is a singlet, for LS or intermediate coupling, the ground state has a huge degeneracy, and under a cubic crystal field, the most frequent degeneracy found is two (eight doublets are contained in the splitting of the magnetic states).[23] This result agrees better with the experiment. However, a detailed analysis shows that, in fact, unless one set of conduction-electron partial waves ($j = 7/2$ or $j = 5/2$) is artificially neglected (like for extreme j-j coupling), in the absence of crystal fields, the localized limit of this model does not correspond to a stable fixed point of WRG.[24] This is a necessary but not sufficient condition for the existence of non-Fermi-liquid properties in the model. Thus, the properties of the model for valence fluctuations between two realistic magnetic configurations (even in the simplest case of p electrons[20]) remains an interesting open problem, and the origin of the magnetic properties of Tm systems is still unexplained.

In this paper we start from crystal-field split $4f^{12}$ and $4f^{13}$ configurations, for parameters adequate to the structure of TmSe. For simplicity, the Γ_8 conduction-electron partial waves are neglected. The Hamiltonian is derived in the next section. The fixed points of the model and, in particular, the strong-coupling one are discussed in Sec. III. The results of the WRG calculations are presented in Sec. IV. The effects of other states not included in the model are briefly discussed in Sec. V. Section VI contains a short summary.

II. MODEL

According to Hund's rules, the ground-state multiplet of Tm^{3+} ($4f^{12}$ configuration) in a spherically symmetric environment is $^3H_6$. Using group theory, one can see that under a crystal field of cubic symmetry, the states with total angular momentum $J = 6$, split into two singlets Γ_1 and Γ_2, a nonmagnetic doublet Γ_3, a triplet Γ_4, and two triplets Γ_5. Inelastic neutron measurements in TmSb, where Tm is trivalent, have determined that the ground state is the invariant singlet (Γ_1), while the first excited state, only 31 K above the ground state, corresponds to the triplet Γ_4 (the components of which transform like x, y, z under the symmetry operations of the group O_h).[25] Furthermore, the ordering of the different levels agrees with the theoretical one when the fourth-order crystal-field term is the dominant one.[26] In TmS, where Tm is also trivalent,[27] measurements of specific heat,[27] elastic constants and thermal expansion,[28] and electronic resonance of Gd^{3+} ions diluted in the matrix,[29] have led to the conclusion that, as in TmSb, the ground state is a Γ_1 with the first excited states Γ_4 lying very near (~ 20 K above). We retain only these two levels to represent Tm^{3+}.

For Tm^{2+} ($4f^{13}$ configuration), the Hund's rule multiplet $^2F_{7/2}$ splits into two doublets Γ_6, Γ_7, and a quadruplet Γ_8 under a cubic crystal field. The experimental ordering of these levels in TmTe, where Tm is divalent,[27] is controversial.[27,30] Theoretical results for point charges give a doublet ground state.[26] If one expects that the magnitude of the fourth- and sixth-degree terms of the crystal field are of similar magnitude in TmSb, TmS, and TmTe, then the experimental results for the two first compounds mentioned above imply that the ground state of Tm^{2+} in TmTe is the Γ_7 doublet.[26] Moreover, if the sixth-order term is small, the ground state is a doublet for any sign of the fourth-order term.[26] We assume that either the Γ_6 or the Γ_7 doublet is the ground state of Tm^{2+} and we retain only this doublet to describe the $4f^{13}$ configuration.

It remains for us to discuss which are the relevant conduction electrons. For a spherically symmetric system, they correspond to total angular momentum $j = 7/2$ and $j = 5/2$.[19,20,23] The former states under a cubic field split as the $4f^{13}$ configuration. The latter split into a Γ_7 doublet and a Γ_8 quadruplet. Because of their delocalization, one expects a larger splitting of the levels for the conduction electrons. The main hypothesis of this work is that (like for the $4f^{13}$ configuration), the Γ_8 conduction-electron quadruplets can be neglected. Their effect is discussed in Sec. V. Using group theory, one sees that only the conduction-electron doublets with the same symmetry as the doublet ground state of the $4f^{13}$ configuration (Γ_6 or Γ_7) hybridize this ground state with the Γ_1 or Γ_4 states of the $4f^{12}$ configuration. We further assume that only one of the relevant conduction-electron doublets needs to be retained (we believe that this is not essential).

The Hamiltonian takes the form

$$H = E_2 \sum_{\sigma} |\sigma\rangle\langle\sigma| + E_1 |a\rangle\langle a| + E_3 \sum_{i=-1}^{1} |i\rangle\langle i| + \sum_{k\sigma} \varepsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + V_1 \sum_{k} \left[(c_{k\uparrow}^{\dagger} |\downarrow\rangle - c_{k\downarrow}^{\dagger} |\uparrow\rangle) \langle a| + \text{H.c.} \right]$$
$$+ V_3 \sum_{k} \left[c_{k\uparrow}^{\dagger} |\uparrow\rangle\langle 1| + c_{k\downarrow}^{\dagger} |\downarrow\rangle\langle -1| + \frac{1}{\sqrt{2}} (c_{k\uparrow}^{\dagger} |\downarrow\rangle + c_{k\downarrow}^{\dagger} |\uparrow\rangle) \langle 0| + \text{H.c.} \right] ; \quad (1)$$

here $|\sigma\rangle = |\uparrow\rangle$ or $|\downarrow\rangle$ represent the ground state of the $4f^{13}$ configuration, $|a\rangle$ represents the invariant ground state of the $4f^{12}$ configuration, and $|i\rangle = |1\rangle, |0\rangle$, or $|-1\rangle$ denote the Γ_4 states of this configuration, which transform under the operations of the symmetry group O_h, like the states of a spin $S = 1$ with projection i. The operator $c_{k\sigma}^{\dagger}$ creates a conduction-electron hole with absolute value of the momentum k, and transforming like $|\sigma\rangle$ under the operations of the point group. Equation (1) was written in a form that coincides in the limit $V_3 = 0$ or $V_1 = 0$ with two limits studied previously with WRG. The first limit coincides with the infinite U case of the Anderson model taking $V_d = V_1$ in Ref. 3 (the Γ_4 states are decoupled). While if $V_1 = 0$, Eq. (1) has the same form as Eq. (1) of Ref. 17 (with $V = V_3$ and other obvious substitutions), except for the presence of the term $E_1|a\rangle\langle a|$, which is irrelevant in this limit. Equation (1) is also the infinite U limit of the impurity version of an effective singlet-triplet model for cuprate superconductors.[31,32]

The model can be fully described in terms of four parameters Δ, Δ', Γ, and α defined as follows (see Fig. 1):

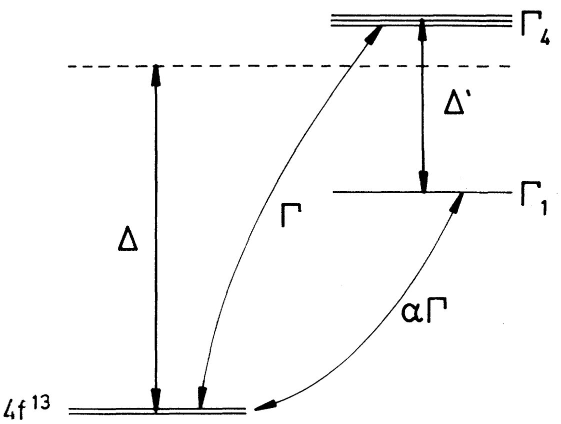

FIG. 1. Scheme of the energy levels and hybridization energies of the model [Eqs. (1) and (2)].

$$\Delta = \frac{3}{4}E_3 + \frac{1}{4}E_1 - E_2, \quad \Delta' = E_3 - E_1,$$

$$\Gamma = \pi\rho V_3^2, \quad \alpha = V_1^2/V_3^2. \tag{2}$$

Δ is the average over the four states of the $4f^{12}$ configuration of the energy necessary to take a hole from the Fermi energy (taken as the origin of one-particle energies) and put it in a $4f^{13}$ state, leaving a $4f^{12}$ state. Δ' is the crystal-field splitting of the $4f^{12}$ configuration. Γ is defined as in Ref. 17, where ρ is the conduction-electron density of states per spin at the Fermi level. α measures the relative strength of the hybridization of the Γ_1 singlet with respect to that of the Γ_4 triplet. As discussed above, we expect Δ' to be positive and of the order of 25 K. For intermediate-valence TmSe and $Y_{1-x}Tm_xSe$, one might expect $\Gamma > |\Delta|$ and Γ of the order of magnitude of 100 K. However, a good fit of different magnetic properties of TmSe has been obtained treating the compound as a concentrated system of impurities, described by model Eq. (1) but neglecting the states $|a\rangle$ and $|0\rangle$, with Γ=20 K and an effective Δ=100 K at zero temperature.[15] The dependence of the effective Δ with temperature is due to the inclusion of a repulsion between localized and conduction electrons in the model.[15] Instead for TmS (TmTe) $|\Delta|/\Gamma \gg 1$ and Δ should be negative (positive). We are not able to estimate the value of α.

The effective magnetic moment of both magnetic configurations can be calculated from the wave functions listed by Lea *et al.*[26] Here, as in Refs. 3 and 17, the coupling to the magnetic field **B** is taken of the form $-g\mu_B \mathbf{S}\cdot\mathbf{B}$, where **S** is the "spin." The spin operators are constructed in the usual way, taking $|\sigma\rangle$, $c_{k\sigma}^\dagger$ to correspond to spin-$\frac{1}{2}$ with projection σ, and similarly taking the states $|i\rangle$ as the respective states of a spin-1. This simplification affects the numerical value of the susceptibility but does not modify either its qualitative temperature dependence, or the different physical regimes and behaviors of the model.

III. FIXED POINTS

In the two limiting cases in which the model was solved using WRG (the Anderson model if the Γ_4 states are disregarded,[3] or the model with two magnetic configurations of Mazzaferro, Balseiro, and Alascio if the Γ_1 states could be neglected[17]), the fixed points were identified taking the particular values zero or infinite for the different parameters of the model. In the present case, as we show below, there is also a fixed point characterized by an intermediate finite value of Γ. We discuss first the weak-coupling fixed points ($\Gamma = 0$). For them, the impurity is decoupled, the rest of the system is described by the free-electron Hamiltonian, and the impurity contribution to the magnetic susceptibility is given by[3]

$$\chi = \frac{(g\mu_B)^2}{k_B T}\langle S_{iz}^2\rangle, \tag{3}$$

where

$$S_{iz} = \frac{1}{2}(|\uparrow\rangle\langle\uparrow| - |\downarrow\rangle\langle\downarrow|) + |1\rangle\langle 1| - |-1\rangle\langle -1|. \tag{4}$$

The weak-coupling fixed points ($\Gamma = 0$) are listed below. Whenever possible, we retained the names given in the previous WRG studies of two limiting cases of our model.[3,17]

(1) Free orbital: $\Delta = \Delta' = 0$. In this case $\langle S_{iz}^2\rangle = 5/12$. Due to the larger number of states involved, $\langle S_{iz}^2\rangle$ differs from the corresponding value in the Anderson model[3] or the model with the state Γ_1 neglected.[17]

(2) Spin-$\frac{1}{2}$ local moment: $\Delta = +\infty, \Delta' = 0$. Thus, $\langle S_{iz}^2\rangle = 1/4$. This fixed point is present in both Refs. 3 and 17.

(3) Tm^{3+}: $\Delta = -\infty, \Delta' = 0; \langle S_{iz}^2\rangle = 1/2$. This fixed point has no analog in Refs. 3 and 17. It corresponds to a free Tm^{3+} ion at temperatures large compared to the splitting Δ'.

(4) Frozen impurity $\Delta = -\infty, \Delta' = +\infty; \langle S_{iz}^2\rangle = 0$.

(5) Spin-1 local moment: $\Delta = -\infty, \Delta' = -\infty; \langle S_{iz}^2\rangle = 2/3$. The last two fixed points have an analog in the studies of Refs. 3 or 17, respectively.

In Refs. 3 and 17, the only stable fixed point and the one that describes the system as low enough temperatures is the strong-coupling fixed point $\Gamma = +\infty$. In the present case, it turns out that this fixed point is not always stable. However, an analytical study of the system near this fixed point allows one to deduce the low-temperature behavior of the system. This is confirmed by the numerical calculations of the next section. Depending mainly on the value of α, we find two different strong-coupling fixed points and one intermediate-coupling fixed point. When Γ is much larger than all the other energies in the problem, we can solve trivially the problem taking all these energies zero. Calling $c_{0\sigma}^\dagger$ the creation operator of the Wannier function of the conduction electrons at the impurity site, putting $\epsilon_k/\Gamma = 0$ for all k, $\Delta'/\Gamma = 0$, but keeping eventually Δ/Γ finite, the ground state of Eq. (1) is the following. (a) For $\alpha \geq 3/2$, it is a singlet and has the same form as for the infinite U Anderson model:

$$|s\rangle = \frac{u(2\alpha)}{\sqrt{2}}(c_{0\uparrow}^\dagger|\downarrow\rangle - c_{0\downarrow}^\dagger|\uparrow\rangle) - v(2\alpha)|a\rangle, \quad u(x),v(x) > 0,$$

$$u^2(x) = \frac{1}{2} + \frac{\Delta}{2(\Delta^2 + 4xV_3^2)^{1/2}},$$
$$v^2(x) = 1 - u^2(x)\ , \tag{5}$$

with energy

$$E_s = \frac{E_1 + E_2}{2} - (\Delta^2/4 + 2\alpha V_3^2)^{1/2}\ . \tag{6}$$

(b) For $\alpha \le 3/2$, the ground state is a doublet, which we represent by $|d\uparrow\rangle$ and $|d\downarrow\rangle = S_t^-|d\uparrow\rangle$, where S_t^- is the lowering operator of the total spin:

$$|d\uparrow\rangle = u(\alpha + \tfrac{3}{2})c_{0\uparrow}^\dagger c_{0\downarrow}^\dagger|\uparrow\rangle + \frac{v(\alpha+\frac{3}{2})}{(2\alpha+3)^{1/2}} \times[(2\alpha)^{1/2}c_{0\uparrow}^\dagger|a\rangle + \sqrt{2}c_{0\downarrow}^\dagger|1\rangle - c_{0\uparrow}^\dagger|0\rangle]\ . \tag{7}$$

The energy of the doublet is

$$E_d = \frac{E_1 + E_2}{2} - [\Delta^2/4 + (\alpha + 3/2)V_3^2]^{1/2}. \tag{8}$$

In case (a), the strong-coupling limit is stable, corrections to it are described in terms of irrelevant operators, and the physics at low enough temperatures is the same as that of the ordinary Anderson model.[3]

In case (b), the most important correction to the strong-coupling limit is a marginal operator, which corresponds to a Kondo interaction of $|d\sigma\rangle$ with the spin of the second Wannier function around the impurity

$$H' = J\left(c_{1\mu}^\dagger \frac{\sigma_{\mu\nu}}{2} c_{1\nu}\right)\left(\frac{\sigma_{\kappa\rho}}{2}|d\kappa\rangle\langle d\rho|\right). \tag{9}$$

Writing the hopping term between the first and second Wannier function around the impurity as ($t\sum_\sigma c_{0\sigma}^\dagger c_{1\sigma}+$ H.c.) (proportional to $\xi_0(f_{0\mu}^\dagger f_{1\mu}+$ H.c.) in the notation of Ref. 3) and performing second-order perturbation theory in this term, one obtains after some algebra

$$\frac{J}{t^2} = \frac{\left[u(2\alpha)u(\alpha+3/2) + \frac{2\alpha}{(\alpha+3/2)^{1/2}}v(2\alpha)v(\alpha+3/2)\right]^2}{[\Delta^2 + (\alpha+3/2)V_3^2]^{1/2} - [\Delta^2 + 2\alpha V_3^2]^{1/2}} - \frac{\left[u(1)u(\alpha+\frac{3}{2}) + \frac{1}{(\alpha+3/2)^{1/2}}v(1)v(\alpha+3/2)\right]^2}{[\Delta^2 + (\alpha+3/2)V_3^2]^{1/2} - [\Delta^2 + V_3^2]^{1/2}}$$
$$+\frac{\left[u(2\alpha)v(\alpha+3/2) - \frac{2\alpha}{(\alpha+3/2)^{1/2}}u(\alpha+3/2)v(2\alpha)\right]^2}{[\Delta^2 + (\alpha+3/2)V_3^2]^{1/2} + [\Delta^2 + 2\alpha V_3^2]^{1/2}} - \frac{\left[u(1)v(\alpha+3/2) - \frac{1}{(\alpha+3/2)^{1/2}}u(\alpha+3/2)v(1)\right]^2}{[\Delta^2 + (\alpha+3/2)V_3^2]^{1/2} + [\Delta^2 + V_3^2]^{1/2}}$$
$$+\frac{4\alpha-2}{2\alpha+3}v(\alpha+3/2)\frac{1}{\Delta/2 + [\Delta^2 + (\alpha+3/2)V_3^2]}\ . \tag{10}$$

It is easy to verify that J has the same sign as $\alpha - 1/2$. This allows us to distinguish three cases:

(b1) $0 \le \alpha \le 1/2$. The Kondo interaction is ferromagnetic, physically irrelevant at the end.[2] The strong-coupling limit is stable and the ground state is a doublet.

(b2) $1/2 < \alpha < 3/2$. The Kondo interaction is antiferromagnetic, it grows in the iterative procedure,[2] and the strong-coupling limit is unstable. This situation is analogous to what happens in the overscreened multichannel Kondo model[34,35] (OMCKM). However, in the latter case, after the correction to the strong-coupling limit grows, the problem takes again the form of the strong-coupling limit. This self-similarly property ensures that all conduction electrons are affected by the interaction at low enough energies and the OMCKM behaves as a marginal Fermi liquid.[36] In contrast, in our model the ordinary Kondo interaction Eq. (9) with positive (antiferromagnetic) J, leads to a singlet ground state and Fermi-liquid behavior. This is confirmed in the numerical calculations. In particular, examination of the eigenvalues leads us to conclude that the corrections to the low-temperature fixed point grow as Λ^{-1}, where Λ is the parameter of the logarithmic discretization.[3] In contrast, the marginal-Fermi-liquid behavior is characterized by fractional exponents.[37,38]

(b3) $\alpha = 1/2$. In this case (when in addition $\Delta' = 0$), the model Eq. (1) can be solved exactly. Its eigenstates are the direct product of those of the ordinary Anderson model in the infinite U limit and a free spin-$\frac{1}{2}$. The additional SU(2) symmetry of the model in this limit is characterized by the operators $O^+, O^- = (O^+)^\dagger$, and $O_z = [O^+, O^-]/2$ (which commute with H), with

$$O^+ = |\uparrow\rangle\langle\downarrow| + \frac{|1\rangle(\langle 0| + \langle a|) + (|0\rangle - |a\rangle)\langle -1|}{\sqrt{2}}\ . \tag{11}$$

The reduction of the model to an Anderson one plus a free spin-$\frac{1}{2}$ is realized through the following representation of the states of the $4f^{12}$ configuration:

$$|a\rangle = \frac{1}{\sqrt{2}}(d_\uparrow^\dagger|\downarrow\rangle - d_\downarrow^\dagger|\uparrow\rangle),\quad |1\rangle = d_\uparrow^\dagger|\uparrow\rangle,$$
$$|0\rangle = \frac{1}{\sqrt{2}}(d_\uparrow^\dagger|\downarrow\rangle + d_\downarrow^\dagger|\uparrow\rangle),\quad |-1\rangle = d_\downarrow^\dagger|\downarrow\rangle\ , \tag{12}$$

where $d_\sigma^\dagger$ is a fermion operator, which creates the localized electron in the infinite U Anderson model. Since the ground state of this model is a singlet,[3,4,21] the ground state of our model Eq. (1) for $\Delta' = 0$ and $\alpha = 1/2$ is a doublet.

To summarize, at high enough temperatures the model should be characterized by the free-orbital regime, with an impurity magnetic susceptibility $\chi = 5(g\mu_B)^2/(12k_BT)$. At low enough temperatures either χ saturates (singlet ground state) or $\chi = (g\mu_B)^2/(4k_BT)$ (doublet ground state). For $\Delta' = 0$, the singlet ground state occurs when $\alpha > 1/2$. At intermediate temperatures, depending on the parameters, the system can go through different regimes characterized at the beginning of this section. This is illustrated in the next section.

IV. NUMERICAL RESULTS

The technique of WRG was described in detail in Ref. 3. We have followed the same numerical procedure. With the same notation as in Ref. 3, we took $\Lambda = 3$, $\bar{\beta} = 0.775$, and kept 850 states after each iteration.

The numerical results confirm that for $\Delta' = 0$, the ground state is a magnetic doublet if $\alpha < 1/2$ and a singlet if $\alpha > 1/2$. If $\alpha < 1/2$, the ground state remains magnetic for positive values of Δ'. This situation is the one that agrees with the experimental data for Tm impurities and compounds in the fcc structure of TmSe, as discussed in the Introduction. For $\alpha = 1/4$, the critical value of $\Delta'(\Delta'_c)$ above which the ground state is nonmagnetic is of the order of Γ (see Table I).

In the following we take small values of Γ and negative values of Δ to stress the effect of Δ' and display features of the spin-1 local moment regime, although these values do not necessarily correspond to an experimental situation. In Fig. 2, we show typical numerical results for $\Delta' = 0$, a negative value of Δ, and different values of α. For $\alpha = 1/4$ and very large temperatures, the system is in the free-orbital regime (characterized by the corresponding fixed point, as explained in the previous section). Lowering the temperature in an exponential scale, the system passes near the "Tm^{3+}" fixed point (see Sec. III), but actually the effective magnetic moment is intermediate between those of the Tm^{3+} and Tm^{2+} configuration, reflecting the intermediate-valence character of the system. The value $k_BT\chi/(\mu_B g)^2 = 1/2$ is obtained at intermediate temperatures for larger values of $-\Delta/\Gamma$. Lowering further the temperature, the system crosses over to the spin-$\frac{1}{2}$ local moment regime and the ground state is a doublet. For α slightly lower than 1/2, the behavior of $T\chi$ as a function of T is very similar. Instead, for α slightly larger than 1/2, the ground state is a doublet and $T\chi \to 0$ for $T \to 0$, although the system remains in the spin-$\frac{1}{2}$ local moment regime up to very low temperatures.

In Fig. 3 we show a situation similar to that of Fig. 2 for $\alpha = 1/2$, but with nonzero $\Delta' = 10^{-4}$ and smaller values of Γ. As a consequence of the presence of a positive Δ', the ground state is a singlet for the smaller values of $\Gamma(\Gamma \lesssim \Delta')$. The fact that Γ is an order of magnitude smaller than in Fig. 2 allows the system to be nearer to the Tm^{3+} regime [for which $k_BT\chi/(\mu_B g)^2 = 1/2$] at intermediate temperatures. However, the most striking difference between Figs. 2 and 3 is that the system in the latter passes near the spin-1 local moment regime at intermediate temperatures, higher than those corresponding to the Tm^{3+} regime, if Γ is large enough to overcome the effect of a positive Δ' (which favors the Γ_1 state). To obtain the spin-1 local moment regime it is necessary also that $\Delta < 0$ and $\alpha < 1/2$.

In the different cases illustrated in Figs. 2 and 3, all the weak-coupling regimes mentioned under the points (1) – (5) in the previous section were reached as unstable fixed points (this was verified studying the variation of the eigenvalues) except the "frozen impurity" one. We could not obtain a set of parameters for which the ground state is a doublet but $T\chi$ is very small at some finite temperatures.

In Fig. 4 we show the effect of increasing Δ' on the temperature dependence of the magnetic susceptibility. For $\Delta' \sim \Gamma$ one has one of the situations previously discussed, with a doublet ground state. For larger Δ', after passing near the Tm^{3+} regime, $T\chi$ decreases rapidly reflecting the singlet character of the ground state.

TABLE I. Critical value of Δ', which separates the region of the singlet ground state $\Delta' > \Delta'_c$ from that of the doublet ground state $\Delta' < \Delta'_c$ for different parameters. The energies Γ, Δ, and Δ'_c are measured in units of the half band width of the conduction electrons D (Ref. 3).

α	Γ	Δ	Δ'_c
0.5	any	0	0
0.45	0.01	0	0.0045
0.25	0.01	0	0.014
0.25	0.01	-0.02	0.0069
0.25	0.1	0	0.073

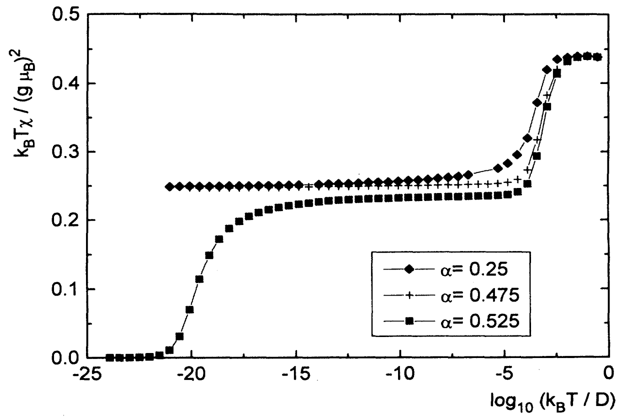

FIG. 2. Product of the magnetic susceptibility χ and temperature T as a function of $\log_{10}T$ for $\Gamma = -\Delta = 10^{-3}$, $\Delta' = 0$ [in units of the half band width D (Ref. 3)] and different values of α (0.25, 0.475, and 0.525).

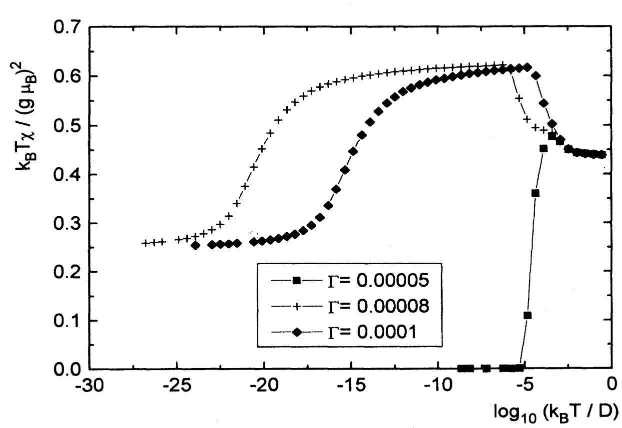

FIG. 3. Same as Fig. 2 for $\Delta = -10^{-3}$, $\Delta' = 10^{-4}$, $\alpha = 1/4$, and several values of Γ (5×10^{-5}, 8×10^{-5}, and 10^{-4}).

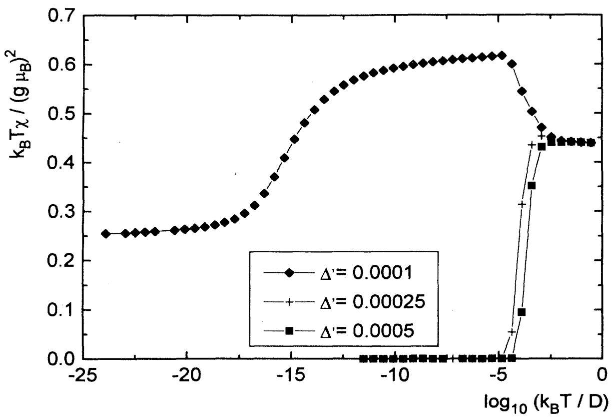

FIG. 4. Same as Fig. 2 for $\Delta = -10^{-3}$, $\Gamma = 10^{-4}$, $\alpha = 1/4$, and several values of Δ' (10^{-4}, 2.5×10^{-4}, and 5×10^{-4}).

V. EFFECT OF STATES NOT INCLUDED IN THE MODEL

As explained in Sec. II, we have neglected excited multiplets in both localized magnetic configurations. The results presented in the last section suggest that the effect of these multiplets is not significant if the resonant level width Γ_i of them [defined in a similar way as in Eq. (2)] is smaller than the crystal-field splitting. In the opposite case in which the crystal field of both $4f$ configurations is neglected, but no new conduction electrons are added in the model, we expect that the physics is similar to the isotropic model but neglecting the $j = 7/2$ conduction partial waves[23,24] and the Bethe ansatz solvable models in which two magnetic configurations are hybridized through $j = 1/2$ conduction electrons.[21] In both cases, the ground state is magnetic.

The nature of the conduction electrons in Eq. (1), and particularly the neglect of the Γ_8 states (which are present in the splitting of both $j = 7/2$ and $j = 5/2$ partial waves under a cubic crystal field), is the most serious approximation. These states hybridize the Γ_6 and Γ_7 doublets of the $4f^{13}$ configuration, with the Γ_4 triplet but *not* with the Γ_1 singlet of the $4f^{12}$ configuration. Thus, we expect that addition of the Γ_8 conduction-electron partial waves favors a magnetic ground state. On the other hand, the addition of these states allows the possibility of overcompensation of the localized magnetic moments, as it is clear in the localized (narrow-band) limit of the isotropic model, where the magnetic moment of the magnetic states in the degenerate ground state points in opposite direction as the impurity magnetic moment, which in addition is strongly reduced in magnitude.[23] This situation has some similarities with the multichannel Kondo model,[33,34,36] which presents marginal-Fermi-liquid behavior. In the physical realizations of the two-channel Kondo model so far proposed, the Γ_8 states play an essential role.[33] However, non-Fermi-liquid behavior was not observed in Tm systems. The possibility of this behavior in the isotropic model remains open.[24]

If the crystal field is strong enough, other conduction states that do not come from the splitting of the $j = 7/2$ and $j = 5/2$ may be important. Gonçalves da Silva constructed different conduction states starting from the d orbitals of the nearest neighbor of one Tm atom in TmSe.[39] A more realistic model might be constructed starting from the states nearer to the Fermi level obtained in a band-structure calculation for YSe. Another physical ingredient that might be important for a quantitative comparison with experiment is the Coulomb repulsion between localized and conduction electrons.[15] The effect of this repulsion has been studied with WRG in Ref. 40, and it is roughly equivalent to a temperature-dependent renormalization of Δ. However, our model Eq. (1) is enough to explain the main features of the magnetic behavior of Tm impurities mentioned in the Introduction.

VI. SUMMARY

We have proposed a model for Tm impurities in which only the lowest doublet state of the $4f^{13}$ configuration (Tm^{2+}) and the two lowest (nearly degenerate) crystal-field split multiplets of the $4f^{12}$ configuration (Tm^{3+}) in the TmSe structure are retained. Also only the lowest doublet conduction-electron partial waves of the same symmetry of the doublet retained for Tm^{2+} is taken into account in the hybridization term. Our calculations using Wilson's renormalization group,[2,3] show that for sufficiently strong hybridization of the excited Γ_4 triplet of Tm^{3+}, the ground state is a doublet. This result agrees with the experimental evidence mentioned in the Introduction,[5–7,9–11] particularly the magnetic susceptibility for very dilute systems.[9] It also gives some justification to simplified models, with a doublet ground state, used to explain qualitatively different properties of Tm systems (static and dynamic magnetic susceptibility, magnetoresistance, and other).[12–18] The temperature dependence of the magnetic susceptibility shows different regimes, which are characterized by the corresponding fixed points of WRG. The doublet ground state of the model contains an admixture of nonmagnetic states [the weight of $|a\rangle$ in Eq. (7)]. This agrees qualitatively with the reduced effective moment of magnetically ordered TmSe observed by magnetic neutron scattering.[5]

Inclusion of other conduction states neglected in the model favor the magnetic ground state, but probably with a further reduction of the effective impurity magnetic moment.[23] This might lead eventually to non-Fermi-liquid behavior,[24] but this behavior was not experimentally observed in Tm systems.

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