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To cite this version:

T. Saso. DYNAMICS OF VALENCE-FLUCTUATING Tm IMPURITIES. Journal de Physique Colloques, 1988, 49 (C8), pp.C8-703-C8-704. <10.1051/jphyscol:19888318>. <jpa-00228492>

HAL Id: jpa-00228492
https://hal.archives-ouvertes.fr/jpa-00228492
Submitted on 1 Jan 1988

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DYNAMICS OF VALENCE-FLUCTUATING Tm IMPURITIES

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Abstract. — A new formalism is presented for describing valence fluctuating Tm impurities. Starting from the self-consistent perturbation scheme valid at arbitrary temperatures, the present formalism incorporates not only the valence fluctuation between $4f^{12}$ and $4f^{13}$, but also the coupled $4f^{13}$ and a conduction electron scattering channel through $T$ matrix, the latter yielding a singlet ground state at low temperatures. Contribution of this channel to the $f$-electron spectral function is also discussed.

Tm ion has a unique feature among rare earth elements which show mixed valencies when dissolved in host metals and compounds [1]. It fluctuates between $4f^{12}$ (Tm$^{3+}$) and $4f^{13}$ (Tm$^{2+}$), but both states have nonvanishing total angular momentum ($j = 6$ for Tm$^{3+}$ and $j = 7/2$ for Tm$^{2+}$), which may be a source that most mixed valent systems containing Tm order magnetically at low temperatures [2]. On the other hand, an isolated magnetic ion embedded in a metal can hardly stay magnetic down to absolute zero temperature except some pathological cases [3, 4]. Thus the ground state of Tm ion in a metal may be a singlet, as was maintained in preceding theoretical studies. Yafet et al. [5] was the first to investigate the ground state of Tm impurity by the variational method, and the $1/N$ studies by Read et al. [7] followed. Since these studies were limited to the ground state properties, there remains much to be elaborated compared to simpler valence fluctuating systems like Ce ions, where the sophisticated theories have been developed for statics and even dynamics [8]. In the following we develop a theory for valence fluctuating Tm impurity along such scheme in pararell with that for Ce systems.

Neglecting the crystal field, the $f$-part, can be expressed as the sum of the partition function, $Z_f$, three different contributions

$$Z_f = \int_0^\infty \frac{dz}{2\pi i} e^{-\beta z} \{[j] R_j (z) + [J] R_J (z) + [J]^2 R_B (Z)\}. \tag{5}$$

Here, $[j] = (2j + 1)$ and $[J] = (2J + 1)$ denote the degeneracy of the states.

$$R_j (z) = (z - E_j - \Sigma_j (z))^{-1}$$

and

$$R_J (z) = (z - E_J - \Sigma_J (z))^{-1}$$

are called as resolvents, describing the $f^{12}$ and $f^{13}$ sectors, respectively, and $\Sigma_j (z)$ and $\Sigma_J (z)$ are the self-energy functions determined by the following coupled equations (see Figs. 1a and b):

$$\Sigma_j (z) = [J] \Gamma \int_{-\infty}^{\infty} d\varepsilon f (\varepsilon) R_J (z + \varepsilon), \tag{6a}$$

$$\Sigma_J (z) = [J] \Gamma \int_{-\infty}^{\infty} d\varepsilon (1 - f (\varepsilon)) R_J (z + \varepsilon). \tag{6b}$$

Here, $\Gamma$ denotes the mixing matrix element defined by

$$\Gamma = \sum_{\Lambda} B_{\Lambda} W_{\Lambda},$$

where $\Lambda = 5/2$ and $7/2$, $W_{\Lambda} = \rho V_{\Lambda}^2$.

$(V_{\Lambda} = < f^j \Lambda \lambda | V | c^j k \Lambda \lambda >$ is the single particle matrix element) and $B_{\Lambda} = | < j | f^{13} \lambda | j > |^2 / |j| |J|$ is the geometrical factor including reduced matrix element $(B_{5/2} = 1/56$, $B_{7/2} = 3/14)$. These equations are the same as in [9], where the singlet-forming channel is not taken into account. The last term in equation (5) describes the contribution from the singlet bound state, which consists of $f^{13}$ and one conduction electron. This state is orthogonal to $f^{12}$ and $f^{13}$ channels (the first and the second term in Eq. (5)) since the number of local electrons is different [10].

$R_B (z)$, the resolvent for this bound state channel, is expressed with the $T$-matrix $T_{\varepsilon'}(z)$ for $f^{13}$ and a conduction electron with incoming and outgoing energies $\varepsilon$ and $\varepsilon'$, respectively, as

$$R_B (z) = \rho^2 \int_{-\infty}^{\infty} d\varepsilon \int_{-\infty}^{\infty} d\varepsilon' (1 - f (\varepsilon)) (1 - f (\varepsilon')) \times$$

$$\times R_J (z - \varepsilon) \times T_{\varepsilon'} (z) R_J (z - \varepsilon'). \tag{7}$$

Fig. 1. — (a) (b) Diagrams for $\Sigma_j (z)$ and $\Sigma_J (z)$. Single and double dash lines denote $R_j (z)$ ($4f^{12}$) and $R_J (z)$ ($4f^{13}$), respectively, and the solid line denotes conduction electrons (holes). (c) Diagram for the $T$-matrix $T_{\varepsilon'}(z)$ (depicted by hatched box).
The argument $z$ denotes the total incoming energy of composite $f^{13} + c^1$ state. The $T$-matrix satisfies the following equation (see Fig. 1c)

\[ \rho T_{ce'} (z) = \Gamma_B \left[ R_j (z - \epsilon - \epsilon') + [J] \rho \times \right. \]
\[ \times \int d\epsilon'' \left( 1 - f (\epsilon'') \right) R_j (z - \epsilon - \epsilon'') \]
\[ \left. \times R_j (z - \epsilon') T_{e'' e''}(z) \right], \tag{8} \]

where $\Gamma_B = \rho V_f^2 \frac{|< J || f^j || j >|^2 / |J|^2} = \rho V_f^2 (39/112)$. It is not easy to solve equation (8) even numerically, but from the analysis in the limiting cases (see the following section) one infers that the $T$-matrix $T_{ce'} (z)$ may be singular when the total energy of the composite particle, $z$, coincides with the singlet binding energy, and the dependencies on $\epsilon$ and $\epsilon'$ may be weak. Therefore, we replace $T_{ce'} (z)$ in r.h.s. of equation (8) with its average $\bar{T} (z) = \langle T_{ce'} (z) \rangle_{ce'}$, where the average over $\epsilon$ and $\epsilon'$ is taken with the weight factor $g (\epsilon, \epsilon'; z) = (1 - f (\epsilon)) (1 - f (\epsilon')) R_j (z - \epsilon) R_j (z - \epsilon')$. Then, we can solve equation (8) as

\[ T_{ce'} (z) \simeq \bar{T} (z) = \frac{\bar{T}_0 (z)}{1 - [J] P_j (z) \bar{T}_0 (z)} \tag{9} \]

where $\rho \bar{T}_0 (z) = \Gamma_B < R_j (z - \epsilon - \epsilon') >_{ce'}$ and

\[ P_j (z) = \rho \int d\epsilon (1 - f (\epsilon)) R_j (z - \epsilon). \tag{10} \]

The single particle Green's function for $f$-electrons can be calculated with the same approximation as

\[ G_j (i\epsilon_n) = Z_j^{-1} \int_C \frac{dz}{2\pi i} e^{-\beta z} \left\{ R_j (z) R_j (z + i\epsilon_n) + \right. \]
\[ \left. + \bar{T} (z + i\epsilon_n) R_j (z) \right\} \left[ Q (z, i\epsilon_n) \right]^2, \tag{11} \]

where $\epsilon_n = (2n + 1) \pi T$ is the thermal frequency and

\[ Q (z, i\epsilon_n) = \rho \int d\epsilon' (1 - f (\epsilon')) \times \]
\[ \times R_j (z - \epsilon' - i\epsilon_n) R_j (z - \epsilon'). \]

Note that the first term in equation (11) is the same as in [9] and the second term denotes the contribution from the singlet channel.

In the Kondo regime where $f^{13}$ state is stable, we obtain from equation (9) as $\bar{T} (z) \simeq \tilde{T} (z)$, where $\tilde{T}_0 = E_J - [J] \Gamma \ln (D / (E_J - E_j))$ is renormalized $J$ level, $\rho \tilde{T}_0 (z) \equiv \rho \tilde{T}_0 (z \sim \tilde{E}_j) \sim \Gamma_B / (\tilde{E}_j - E_j)$ and $D$ is the effective cutoff $\sim E_j - E_j$. Hence $\tilde{T} (z)$ has a pole at $z = \tilde{E}_j - \Delta$ with $\Delta \simeq \tilde{D} \exp \left\{ -(E_j - \tilde{E}_j) / [J] \Gamma_B \right\} \simeq \left[ (E_j - E_j) / \tilde{D} \right] \exp \left\{ -(E_j - E_j) / [J] \Gamma_B \right\}$. The density of states of $f$-electrons, $\rho_f (\epsilon) = (-1/\pi)$, 

To discuss the intermediate valence regime, one has to solve equations (6a) and (6b) self-consistently, and then calculate $\bar{T} (z)$. Leaving full analysis for future publication, we comment that the present formalism reduces to those by Yafet et al. [5] and Newns et al. [6] if one omits $\Sigma_j (z)$ in $R_j (z)$ and calculate $\Sigma_j (z)$ up to the second order perturbation. In contrast to their formulation, however, the present theory offers not only self-consistent calculation scheme for ground state but also for the excitation spectrum.

The author thanks to Professor T. Kasuya, Professor O. Sakai, Professor Y. Kuramoto, Mr. Y. Shimizu and Mr. M. Ikeda for useful discussions.