DYNAMICS OF VALENCE-FLUCTUATING Tm IMPURITIES

T. Saso

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

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
DYNAMICS OF VALENCE-FLUCTUATING Tm IMPURITIES

T. Saso

Department of Physics, Tohoku University, Sendai, 980 Japan

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 $4f^{12}$ ($\text{Tm}^{3+}$) and $4f^{13}$ ($\text{Tm}^{2+}$), but both states have nonvanishing total angular momentum ($J = 6$ for $\text{Tm}^{3+}$ and $J = 7/2$ for $\text{Tm}^{2+}$), which may be a source that most mixed valence 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 parallel 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

$$Z_f = \int_{C} \frac{dz}{2\pi i} e^{-\beta z} \left\{ [J] R_j(z) + [J] R_f(z) + [J^2] R_B(Z) \right\}$$

(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

$$R_f(z) = (z - E_f - \Sigma_f(z))^{-1}$$

are called as resolvents, describing the $4f^{12}$ and $4f^{13}$ sectors, respectively, and $\Sigma_j(z)$ and $\Sigma_f(z)$ are the self-energy functions determined by the following coupled equations (see Figs. 1a and b):

$$\Sigma_j(z) = [J] \int_{-\infty}^{\infty} dz J f(z) R_f(z + \epsilon),$$

(6a)

$$\Sigma_f(z) = [J] \int_{-\infty}^{\infty} dz (1 - f(z)) R_f(z + \epsilon).$$

(6b)

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

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

where $\Lambda = 5/2$ and $7/2$, $W_{\Lambda} = \rho V\Lambda$ and $R_{\Lambda}$ is the mixing matrix element defined by

$$\rho V\Lambda = < f^J \lambda \lambda | V | f^J \lambda \lambda >$$

is the single particle matrix element and $B_{\Lambda} = < J | f^J \lambda | J >$ 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 $T_{\text{ee}}$ (for $f^{13}$) and a conduction electron with incoming and outgoing energies $\epsilon$ and $\epsilon'$, respectively, as

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

$$R_J(z - \epsilon) \times T_{\text{ee}}(\epsilon) R_J(z - \epsilon').$$

(7)

Here, $\Sigma_B(z)$ is the self-energy function determined by the following coupled equations (see Figs. 1a and b):

$$\Sigma_B(z) = [J] \int_{-\infty}^{\infty} dz J f(z) R_f(z + \epsilon),$$

(6a)

$$\Sigma_f(z) = [J] \int_{-\infty}^{\infty} dz (1 - f(z)) R_f(z + \epsilon).$$

(6b)

Fig. 1. — (a) (b) Diagrams for $\Sigma_j(z)$ and $\Sigma_f(z)$.

Single and double dash lines denote $R_j(z)$ ($4f^{12}$) and $R_f(z)$ ($4f^{13}$), respectively, and the solid line denotes conduction electrons (holes). (c) Diagram for the $T$-matrix $T_{\text{ee}}(\epsilon)$ (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)

\[
\rho T_{ee'} (z) = \Gamma_B [R_J (z - \varepsilon - \varepsilon') + [J] \rho \times \int \frac{d\varepsilon''}{1 - f (\varepsilon'')} R_J (z - \varepsilon - \varepsilon'') \times R_J (z - \varepsilon) T_{ee''} v_e (z)],
\]

where \( \Gamma_B = \rho V_f^2 \left| \langle J \| f^J \| J \rangle \right|^2 / [J]^2 = \rho V_f^2 (39/112) \). 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 \( T_{ee'} (z) \) may be singular when the total energy of the composite particle, \( z \), coincides with the singlet binding energy, and the dependencies on \( \varepsilon \) and \( \varepsilon' \) may be weak. Therefore, we replace \( T_{ee'} (z) \) in r.h.s. of equation (8) with its average \( \bar{T} (z) = < T_{ee'} (z) >_{ee'} \) where the average over \( \varepsilon \) and \( \varepsilon' \) is taken with the weight factor \( g (\varepsilon, \varepsilon'; z) = (1 - f (\varepsilon)) (1 - f (\varepsilon')) R_J (z - \varepsilon - \varepsilon') R_J (z - \varepsilon) \). Then, we can solve equation (8) as

\[
T_{ee'} (z) \simeq \bar{T} (z) = \frac{T_0 (z)}{1 - [J] P_J (z) \bar{T}_0 (z)}
\]

where \( \rho \bar{T}_0 (z) = \Gamma_B < R_J (z - \varepsilon - \varepsilon') >_{ee'} \) and

\[
P_J (z) = \rho \int \frac{d\varepsilon}{1 - f (\varepsilon)} R_J (z - \varepsilon).
\]

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

\[
G_f (i \varepsilon_n) \simeq Z_f^{-1} \int_0^\infty \frac{dz}{2\pi} e^{-\beta z} \{ R_J (z) R_J (z + i \varepsilon_n) + + \bar{T} (z + i \varepsilon_n) R_J (z) \} [Q (z, i \varepsilon_n)]^2
\]

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

\[
Q (z, i \varepsilon_n) = \rho \int \frac{d\varepsilon'}{(1 - f (\varepsilon'))} \times R_J (z - \varepsilon' - i \varepsilon_n) R_J (z - \varepsilon')
\]

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 \( \bar{T} (z) \simeq \bar{T}_0 / \{ 1 - [J] \rho \bar{T}_0 \bar{T}_0 (D / z - \bar{E}_J) \} \), where \( \bar{E}_J = E_J - [J] \Gamma \ln (D / (E_J - E_J)) \) is renormalized \( J \) level, \( \rho \bar{T}_0 \equiv \rho \bar{T}_0 (z - \bar{E}_J) \sim \Gamma_B / (\bar{E}_J - E_J) \) and \( \bar{D} \) is the effective cutoff \( \sim E_J - E_J \).

Hence \( \bar{T} (z) \) has a pole at \( z = \bar{E}_J - \Delta \) with \( \Delta \simeq \bar{D} \ln [-(E_J - \bar{E}_J)] / [J] \Gamma_B \simeq [(E_J - E_J) / D] \ln [-(E_J - E_J)] / [J] \Gamma_B \). The density of states of \( f \) electrons, \( \rho_f (\varepsilon) = (-1/\pi) \Im G_f (\varepsilon + i 0) \) can be calculated from equation (12), and will have peaks at around \( \varepsilon \sim -(E_J - E_J) \) and \( -\Delta \).

In the \( f^{12} \)-limit, one obtains \( \rho \bar{T} (z) \simeq \rho \bar{T}_0 (z) \simeq \bar{T}_B / (2\bar{E}_J - E_J - z) \) with \( \bar{E}_J \simeq E_J - \Delta' \) and \( \Delta' = D \exp \{ -(E_J - E_J) / [J] \Gamma \} \). Thus, \( \bar{T} (z) \) has a pole at \( z \sim E_J - 2\Delta' \). The density of \( f \)-states yields peaks at \( \bar{E}_J - E_J \) and \( -2\Delta' \).

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 \( \Sigma_f (z) \) in \( R_J (z) \) and calculate \( \Sigma_f (z) \) 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. Kuramato, Mr. Y. Shimizu and Mr. M. Ikeda for useful discussions.