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Intermediate-valence Tm: An exactly solvable impurity model

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We propose an exactly solvable model for valence fluctuations between two magnetic configurations. Most of the peculiar features of the magnetic properties of paramagnetic intermediate-valence Tm compounds are well described by the model. We calculate valence, specific heat, static magnetic susceptibilities, magnetization, and magnetoresistivity. We also include the resulting dynamical magnetic susceptibility. The results are in good qualitative agreement with experiment.

I. INTRODUCTION

The discovery that Tm in TmTe could enter into a valence-fluctuation regime under pressure[1] did not raise great interest. This was, probably, not only because of the difficulties involved in high-pressure experiments, but also because it was thought that the properties of intermediate valence (IV) Tm ions would be similar to those of the other, more accesible, IV rare earths.[2]

Anomalies in the lattice parameter and in the magnetic susceptibility of single-crystal TmSe suggestive of IV[3] together with x-ray photon spectroscopy (XPS) spectra,[4] renewed interest in Tm chalcogenides and similar compounds.[5,6]

Experimental results showed that the magnetic properties of IV Tm compounds were completely different from the other known IV rare earths (Ce, Yb, Sm, Eu, for example).

In the following description of experimental results of the paramagnetic phases of IV Tm compounds, the first properties, (a) to (e), are common to all IV systems; (f) to (h) are found only in IV Tm compounds.

(a) XPS results[4]: The energy spectra of TmSe clearly show the simultaneous presence of $\mathrm{Tm}^{2+}(4f^{13}\,{}^2F_{7/2})$ and $\mathrm{Tm}^{3+}(4f^{12}\,{}^3H_6)$.

(b) X-ray absorption: From the analysis of extended x-ray absorption spectra[7] it is concluded that all Tm sites in TmSe are identical and that the valence of Tm ions is 2.5, in agreement with estimations from the static susceptibilities.

(c) Lattice parameter: Stoichiometric TmSe has a lattice constant[5,6] of 5.71 Å, indicative of a valence of 2.8. The same value is obtained for Tm in $\mathrm{Tm}_x\mathrm{Y}_{1-x}\mathrm{Se}$.[5]

(d) Specific heat: A large linear term $\gamma \sim 350$ mJ/mole K characterizes the paramagnetic regime.[8]

(e) Compressibility: The compressibility of TmSe is about twice that of SmS indicating also intermediate valence.[9]

(f) Magnetic susceptibility: The magnetic susceptibility of paramagnetic TmSe and of $\mathrm{Tm}_x\mathrm{Y}_{1-x}\mathrm{Se}$ increases with decreasing temperatures while in other IV systems it saturates at low temperatures. A large Van Vleck term is found in $\mathrm{Tm}_{1-x}\mathrm{Y}_x\mathrm{Se}$.[10] In TmSe, antiferromagnetic order sets in at $T \sim 3.5$ K. No other IV system orders magnetically.

(g) Dynamical magnetic susceptibility: The dynamical susceptibility of IV Tm is again completely different from that obtained for other IV systems.[11,12] At high temperatures it consists of a Lorentzian quasielastic peak (width, ~ 10 meV), which, for temperatures below 100 K, splits into an inelastic peak centered at about 10 meV and an elastic peak of width of the order of $k_B T$.

(h) Quite anomalous magnetic field dependences are also found in the specific heat[8] and in the electrical resistivity[10] of TmSe.

Among these properties, those connected to the occupation of the $4f$ shell in Tm, (a) to (e), are quite similar to those found in other IV compounds and are quite compatible with a resonant level picture of the $4f$ states[13] or an hybridized $4f$ band if intersite correlations must be taken into account. It is interesting to consider which of these effects is single ion in origin and which result from the concentrated system. In this paper we consider the single-ion effects and in a future paper the periodic system. The magnetic behavior of IV Tm described in (f) and (h) is hard to reconcile at first sight with a resonant level picture, for the effect of magnetic field within such a picture would be to displace different levels by μB and this is expected to be very small as compared with any of the other parameters in this picture; Δ, the energy difference between the two configurations or Γ, the width of the resonance. Thus, it would be hard to understand why small magnetic fields modify so radically the properties of the system.

To solve this paradox we will study a model that can be solved exactly. This allows us to get rid of complicated calculations or approximations. The model makes compatible a resonant level description of the $4f$ spectral densities with high correlations with the magnetic properties of Tm IV compounds.

The most important feature of the model is that it describes valence fluctuations between two configurations *both of which are magnetic.* We believe that this feature is a necessary condition to an appropriate descriptions of IV Tm ions.

Since the aim of the present work is to elucidate the physical processes that lead to the peculiar magnetic behavior of IV Tm systems, we do not try here to give a quantitative theory of their properties. Consequently, the model we propose is the simplest one that will satisfy our aim.

In Sec. II we set up the model Hamiltonian. In Sec. III we diagonalize it and calculate the partition function. Section IV is devoted to obtaining the different physical properties predicted by the model and Sec. V contain the discussion of results and conclusions.

II. MODEL

The model is based on two basic assumptions:

(a) The peculiar magnetic properties of Tm IV ions are determined by the availability of two magnetic configurations and not by their detailed structure. This allows us to model them in the simplest way: the two magnetic configurations are represented by spin-one states $|+\rangle$, $|0\rangle$, and $|-\rangle$ and by spin-one-half states $|\uparrow\rangle$ and $|\updownarrow\rangle$. We will simplify them further below in order to render the Hamiltonian exactly solvable.

(b) We will study, in this paper, the one impurity problem. All possible effects arising from Tm-Tm correlations are then ignored. Many of the magnetic properties of the paramagnetic phases of IV Tm compounds are also found in dilute IV Tm alloys.[14]

The dynamic of the system is given by a Hamiltonian that hybridizes the two configurations through the promotion of an electron from the spin-one configuration to the conduction band leaving the $4f$ shell in the spin-one-half configuration. The full Hamiltonian can be expressed as

$$H = H_{\text{band}} + H_{4f} + H_{\text{hyb}} \tag{1}$$

where, in the usual notation

$$H_{\text{band}} = \sum_{k\sigma} \epsilon_{k\sigma} C^{\dagger}_{k\sigma} C_{k\sigma} \ . \tag{2}$$

The second term in Eq. (1) represents the spin-one-half and spin-one configuration

$$H_{4f} = H_{1/2} + H_1 \tag{3}$$

with

$$H_{1/2} = E_{\uparrow} |\uparrow\rangle\langle\uparrow| + E_{\downarrow} |\downarrow\rangle\langle\downarrow| \ . \tag{4}$$

The energies of the states $|\uparrow\rangle$ and $|\downarrow\rangle$ are split by an external magnetic field B according to

$$E_{\uparrow} = E - \mu_0 B ; E_{\downarrow} = E + \mu_0 B \tag{5}$$

and

$$H_1 = E_{+} |+\rangle\langle +| + E_0 |0\rangle\langle 0| + E_{-} |-\rangle\langle -| \ . \tag{6}$$

The energies are split by B according to

$$E_{\pm} = (E + \Delta) \mp \mu_1 B \ . \tag{7}$$

The hybridization Hamiltonian reads

$$\begin{aligned} H_{\text{hyb}} = \sum_k V(& |+\rangle\langle\uparrow| C_{k\uparrow} + C^{\dagger}_{k\uparrow} |\uparrow\rangle\langle +| \\ & + |-\rangle\langle\downarrow| C_{k\downarrow} + C^{\dagger}_{k\downarrow} |\downarrow\rangle\langle -|) \\ & + V'(|0\rangle\langle\uparrow| C_{k\downarrow} + C^{\dagger}_{k\downarrow} |\uparrow\rangle\langle 0| \\ & + |0\rangle\langle\downarrow| C_{k\uparrow} + C^{\dagger}_{k\uparrow} |\downarrow\rangle\langle 0|) \ . \end{aligned} \tag{8}$$

Notice that operators of the type $|+\rangle\langle\uparrow|$ correspond to creation of an electron in the $4f$ shell and consequently they anticommute with $C_{k\sigma}$. We have assumed that the highest spin configuration contains one electron more than the other contrary to the situation in Tm. However, the results are the same if electrons are exchanged by holes for band as well as local states.[15,16]

The bra and ket notation describes highly correlated states corresponding to two consecutive occupation numbers of the $4f$ shell. Thus, the Coulomb interaction between localized electrons is implicitly assumed to be infinite.[17]

The parameters in the Hamiltonian can be chosen according to the point symmetry of the problem or to simulate different situations.

(i) $E_0 = E + \Delta$ and $V' = V/\sqrt{2}$ corresponds to the rotationally invariant situation. This choice of parameters has been used by the present authors[16] to study spin fluctuations in TmSe, and by Schlottmann and Falicov,[17] in a periodic version, to study the zero temperature phase diagram of TmSe. Anisotropy can be included in the model by a different choice of either $E + \Delta$, E_0 or V or V'.

(ii) Letting Δ go to infinity projects out states $|+\rangle$ and $|-\rangle$ rendering the $4f^{12}$ configuration nonmagnetic and leads to a Hamiltonian formally equal to the U infinite Anderson Hamiltonian.[18]

The alternative that we are going to use here, that retains the most important feature for IV Tm, i.e., fluctuations between two magnetic configurations, is to let E_0 go to infinity (or similarly $V' = 0$). The motivation for this alternative is not based on physical grounds, but because of the fact that it renders the Hamiltonian easily solvable.

Clearly, when E_0 goes to infinity, state $|0\rangle$ can be projected out of the subspace of interest and H_1 is left,

$$H_1 = E_+|+\rangle\langle+| + E_-|-\rangle\langle-| \ , \tag{9}$$

while H_{hyb} reduces to

$$H_{\text{hyb}} = \sum_k V(|+\rangle\langle\uparrow|C_{k\uparrow} + C_{k\uparrow}^\dagger|\uparrow\rangle\langle+| + |-\rangle\langle\downarrow|C_{k\downarrow} + C_{k\downarrow}^\dagger|\downarrow\rangle\langle-|) \ . \tag{10}$$

Had we chosen $V'=0$, H_{hyb} would look exactly as in (10) and H_1 would include the uncoupled state $|0\rangle$. Both possibilities lead to similar results. They cut off spin-flip scattering which is mediated by state $|0\rangle$. However, as in (i) the ground state is still degenerate[16] leading to the correct physics of valence fluctuations between magnetic configurations.

III. DIAGONALIZATION AND PARTITION FUNCTION

The Hamiltonian defined in Sec. II can be diagonalized by introducing the "creation" operators

$$\Gamma_{\lambda\uparrow}^\dagger = a_{\lambda\uparrow}|+\rangle\langle\uparrow| + \sum_k a_{\lambda k\uparrow} C_{k\uparrow}^\dagger (|\uparrow\rangle\langle\uparrow| + |+\rangle\langle+|) \tag{11}$$

and

$$\Gamma_{\lambda\downarrow}^\dagger = a_{\lambda\downarrow}|-\rangle\langle\downarrow| + \sum_k a_{\lambda k\downarrow} C_{k\downarrow}^\dagger (|\downarrow\rangle\langle\downarrow| + |-\rangle\langle-|) \tag{12}$$

and its hermitian conjugates (anihilation) operators.

The equation

$$[H, \Gamma_{\lambda\uparrow}^\dagger] = \epsilon_{\lambda\uparrow}\Gamma_{\lambda\uparrow}^\dagger \tag{13}$$

can be satisfied due to the particular structure of the Hamiltonian and yields two coupled equations for the coefficients $a_{\lambda\sigma}, a_{\lambda k\sigma}$

$$(E_+ - E_\uparrow)a_{\lambda\uparrow} + \sum_k V_k a_{\lambda k\uparrow} = \epsilon_{\lambda\uparrow} a_{\lambda\uparrow} \ , \tag{14}$$

$$V_k a_{\lambda\uparrow} + \epsilon_k a_{\lambda k\uparrow} = \epsilon_{\lambda\uparrow} a_{\lambda k\uparrow} \ . \tag{15}$$

From (14) and (15) we obtain the secular equation

$$\epsilon_{\lambda\uparrow} = E_+ - E_\uparrow + \sum_k \frac{V_k^2}{\epsilon_{\lambda\uparrow} - \epsilon_{k\uparrow}} \ . \tag{16}$$

Normalization requires

$$|a_{\lambda\uparrow}|^2 + \sum_k |a_{\lambda k\uparrow}|^2 = 1 \ . \tag{17}$$

This allows to determine $a_{\lambda\uparrow}$, $a_{\lambda k\uparrow}$ and $\epsilon_{\lambda\uparrow}$ in terms of the parameters of the Hamiltonian. The calculations are exactly the same as in Ref. 19 and yield, for a constant density-of-band-states ρ

$$|a_{\lambda\uparrow}|^2 = \frac{1}{\pi\rho}\frac{\Gamma}{(\epsilon_{\lambda\uparrow} - E_+ + E_\uparrow)^2 + \Gamma^2} \ , \tag{18}$$

where $\Gamma = \pi\rho V^2$.

Equivalent formulas hold for $a_{\lambda\downarrow}$ and $a_{k\lambda\downarrow}$.

The $\Gamma_{\lambda\sigma}$ operators satisfy the following anticommutation relations

$$[\Gamma_{\lambda\sigma}, \Gamma_{\lambda'\sigma'}^\dagger]_+ = \begin{cases} |+\rangle\langle+| + |\uparrow\rangle\langle\uparrow| & \text{for } \sigma=\sigma'=\uparrow \text{ and } \lambda=\lambda' \\ |-\rangle\langle-| + |\downarrow\rangle\langle\downarrow| & \text{for } \sigma=\sigma'=\downarrow \text{ and } \lambda=\lambda' \\ 0 \ \text{otherwise} \end{cases}$$

Clearly,

$$[\Gamma_{\lambda\sigma}^\dagger, \Gamma_{\lambda'\sigma'}^\dagger]_+ = 0 \ .$$

The fact that operators Γ do not satisfy fermion commutation relations is a consequence of the correlations between the local states.

In terms of these operators the Hamiltonian is diagonal and reads

$$H = \left(\sum_\lambda \epsilon_{\lambda\uparrow}\Gamma_{\lambda\uparrow}^\dagger\Gamma_{\lambda\uparrow} + \sum_k \epsilon_{k\downarrow}C_{k\downarrow}^\dagger C_{k\downarrow} + E_\uparrow\right)(|\uparrow\rangle\langle\uparrow| + |+\rangle\langle+|) + \left(\sum_\lambda \epsilon_{\lambda\downarrow}\Gamma_{\lambda\downarrow}^\dagger\Gamma_{\lambda\downarrow} + \sum_k \epsilon_{k\uparrow}C_{k\uparrow}^\dagger C_{k\uparrow} + E_\downarrow\right)(|\downarrow\rangle\langle\downarrow| + |-\rangle\langle-|) \ . \tag{20}$$

As can be seen from (20) the Hamiltonian separates into two spinless, Anderson Hamiltonians. However, they are *mutually excluding* as a consequence of the highly correlated local states involved.

The eigenstates of the Hamiltonian are obtained by repeated application of the creation operators on the "vacuum" states $|\uparrow\rangle$ or $|\downarrow\rangle$. For example,

$$\psi_{N+M} = \Gamma_{\lambda_1\uparrow}^\dagger\Gamma_{\lambda_2\uparrow}^\dagger \cdots \Gamma_{\lambda_N\uparrow}^\dagger C_{k_1\downarrow}^\dagger C_{k_2\downarrow}^\dagger \cdots C_{k_M\downarrow}^\dagger|\uparrow\rangle \tag{21}$$

is an $N+M$ particles eigenfunction of (20) with eigenvalue

$$E_{N+M}=\epsilon_{\lambda_1\uparrow}+\epsilon_{\lambda_2\uparrow}+\dots+\epsilon_{\lambda_N\uparrow}+\epsilon_{k_1\downarrow}+\epsilon_{k_2\downarrow}+\dots+\epsilon_{k_M\downarrow}\ . \tag{22}$$

Similar states can be built operating with $\Gamma_{\lambda\downarrow}^{\dagger}$, $C_{k\uparrow}^{\dagger}$ on $|\downarrow\rangle$. In the absence of external magnetic fields, the two sets of states form a doubly degenerate set.

Defining the zero of energy at E and taking the Fermi energy equal to zero, the partition function can be written as

$$Z=Z_{\uparrow}+Z_{\downarrow}\ , \tag{23}$$

where

$$Z_{\sigma}=e^{\pm\beta\mu_0 H}\prod_{\lambda}(1+e^{-\beta\epsilon_{\lambda\sigma}})\prod_{k}(1+e^{-\beta\epsilon_k})\ , \tag{24}$$

$\sigma=\uparrow$ or $\downarrow$, $\beta=(k_B T)^{-1}$, and we take for simplicity $\epsilon_{k\sigma}=\epsilon_k$.

The fact that the partition function (23) cannot be expressed as a product of partition functions is again a consequence of the correlations implicit in the Hamiltonian.

To give an explicit and more transparent expression for Z, it is necessary to consider the spectrum of eigenvalues $\epsilon_{\lambda\sigma}$. Following Ref. 19 it is easy to show from Eq. (16) that the eigenvalues $\epsilon_{\lambda\uparrow}$ are shifted from ϵ_k, to order $1/N$, by

$$\delta_{\lambda\uparrow}=\epsilon_{\lambda\uparrow}-\epsilon_k=\frac{1}{\pi\rho}\tan^{-1}(\Gamma/\Delta-\bar{\mu}B-\epsilon_k)\ . \tag{25}$$

Here $\bar{\mu}=\mu_1-\mu_0$. To the same order in $1/N$ we can write

$$\ln Z_{\uparrow}=\beta\mu_0 H+2\sum_k\ln(1+e^{-\beta\epsilon_k})-\sum_k\frac{1}{e^{\beta\epsilon_k}+1}\frac{\beta}{\pi\rho_0}\tan^{-1}(\Gamma/\Delta-\bar{\mu}B-\epsilon_k) \tag{26}$$

or

$$Z_{\uparrow}=Z_{\text{band}}^{0}e^{\beta\varphi(B)}\ , \tag{27}$$

where

$$Z_{\text{band}}^{0}=\prod_k(1+e^{-\beta\epsilon_k})^2$$

is the partition function corresponding to a free-electron band, and

$$\varphi(B)=\frac{1}{\pi}\int_{-\infty}^{-\infty}d\epsilon\, f(\epsilon)\tan^{-1}(\Gamma/\Delta-\bar{\mu}B-\epsilon)+\mu_0 B\ . \tag{28}$$

Here $f(\epsilon)=(1+e^{-\beta\epsilon})$ is the Fermi function. $Z_{\downarrow}$ is obtained by changing B by $-B$ in (28).

The partition function factorizes then into a free band (Z_0) and an impurity partition function

$$Z=Z_{\text{band}}^{0}(e^{\beta\varphi(B)}+e^{\beta\varphi(-B)})\ . \tag{29}$$

In Sec. IV we will use this partition function to calculate the different thermodynamical quantities corresponding to the model Hamiltonian.

IV. PHYSICAL PROPERTIES

The different physical properties described by the model Hamiltonian depend essentially on four parameters: Δ and Γ, the energy and width of the resonant level, and μ_0 and μ_1 the magnetic moments associated to each configuration. For the following calculations it is convenient to introduce the average occupation probability of each of the local states $P_i(i=+,\ -,\ \uparrow,$ or $\downarrow)$. They are obtained from Z through

$$P_i=-\frac{1}{\beta}\frac{\partial\ln Z}{\partial E_i}\ .$$

A straightforward calculation using (16), (24), and (29) then gives

$$P_{+}=\frac{e^{\beta\varphi(B)}}{e^{\beta\varphi(B)}+e^{\beta\varphi(-B)}}\Phi(\Delta-\bar{\mu}B,\Gamma,T)\ , \tag{30}$$

where

$$\Phi(\Delta,\Gamma,T)=\int_{-\infty}^{\infty}d\epsilon\, f(\epsilon)\frac{1}{\pi}\frac{\Gamma}{(\epsilon-\Delta)^2+\Gamma^2}=\frac{1}{2}-\frac{1}{\pi}\operatorname{Im}\psi\left[\frac{1}{2}+\frac{\Gamma}{2\pi T}+i\frac{\Delta}{2\pi T}\right]\ . \tag{31}$$

$\operatorname{Im}\psi$ is the imaginary part of the digamma function.

Notice that Φ goes monotonically from 1 to 0 as Δ goes from $-\infty$ to ∞,[20] and that the P_i's satisfy the following equalities: $P_{+}+P_{-}+P_{\uparrow}+P_{\downarrow}=1$ and

$$P_{+}+P_{\uparrow}=\frac{e^{\beta\varphi(B)}}{e^{\beta\varphi(B)}+e^{\beta\varphi(-B)}}\ . \tag{32}$$

The resonant character of the model is reflected again in Eq. (30): the average occupation of the local states is given by an integral over occupied states of their spectral densities which are proportional to a Lorentzian function. The prefactor to the Lorentzian in (30) ($P_{+}+P_{\uparrow}$) results from the highly correlated character of the localized states and leads to the peculiar magnetic properties resulting from the model.

In what follows we will calculate the different physical properties using $\mu_0=(4.58/\sqrt{3})\mu_B$ and $\mu_1=(7.3/\sqrt{3})\mu_B$. These values are chosen such as to reproduce the susceptibilities of Tm^{2+} and Tm^{3+} ions, respectively.

A. Valency

Intermediate valence of the R-E ions can be detected through XPS intensities, lattice parameters, x-ray absorption spectroscopy, Mössbauer isomer shifts, etc. Often, the results do not show qualitative agreement. For example, the valencies of Tm in TmSe inferred from lattice constant and magnetic susceptibility are 2.77 and 2.46, respectively.

If we identify $|+\rangle$ and $|-\rangle$ states with the $4f^{12}$ configuration of Tm, the valence predicted by the model is given by

$$v = 2 + P_+ + P_- \ , \tag{33}$$

which, according to (30) is for $B=0$:

$$v = 2 + \phi(\Delta, \Gamma, T) \ . \tag{34}$$

The application of an external magnetic field favors the highest μ configuration giving rise to a magnetodilation effect. The change in occupation can be calculated from (32). For $\bar{\mu}B/\Gamma \ll 1$, we find that the change in v can be written as

$$\delta v = \frac{\partial \phi}{\partial \Delta} \bar{\mu} B [1 - 2f(-2\mu_{\text{eff}} B)] \tag{35}$$

where

$$\mu_{\text{eff}} = \mu_1 \phi(\Delta, \Gamma, T) + \mu_0 [1 - \phi(\Delta, \Gamma, T)] \ . \tag{36}$$

As will be seen below, this magnetodilatation effect is connected with a Van Vleck term in the magnetic susceptibility. Using our choice of parameters $\bar{\mu} > 0$, (35) would lead to a volume decrease with external field. The $T=0$ valence change is given by

$$\delta v = \frac{1}{\pi} \frac{\Gamma}{\Delta^2 + r^2} \bar{\mu} B \ ,$$

which, for Δ and $\Gamma \sim 10^{-2}$ eV leads to a very small valence change at reasonable magnetic fields.

B. Specific heat

The low-temperature specific heat of TmSe shows again dual features; On one side a large linear term $\gamma \sim 350$ mJ/K^2 indicates a high density-of-states characteristic of resonant levels and on the other side, a Schottky anomaly corresponding to level splitting in the presence of external fields (which degenerates into a discontinuity at the ordering temperatures).

The impurity internal energy derived from Z, can be written in the form

$$\mathcal{E}_{\text{imp}} = (P_+ + P_\uparrow)\mathcal{E}_+ + (P_- + P_\downarrow)\mathcal{E}_- \ , \tag{37}$$

where

$$\mathcal{E}_\pm = \mp \mu_0 B + \frac{1}{\pi} \int_{-\infty}^{\infty} d\epsilon\, f(\epsilon)\, \epsilon \frac{\Gamma}{(\epsilon - \Delta \pm \bar{\mu} B)^2 + \Gamma^2} \ . \tag{38}$$

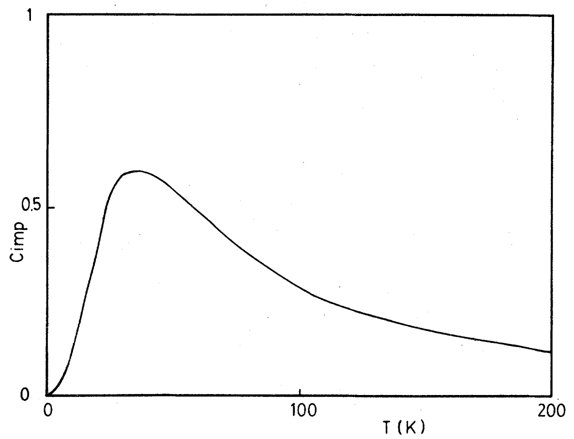

FIG. 1. Specific heat per Tm ion as a function of temperature for $B=0$, $\Gamma=27$ K, and $\Delta=80$ K $(k_B=1)$.

Using these expressions for the internal energy, we derive the impurity contribution to the specific heat

$$C_{\text{imp}} = \left((P_+ + P_\downarrow)\frac{\partial E_+}{\partial T} + (P_- + P_\downarrow)\frac{\partial E_-}{\partial T} \right) + \frac{1}{T^2}(P_+ + P_\uparrow)(P_- + P_\downarrow)(E_+ - E_-)^2 \ . \tag{39}$$

The first term depends weakly on B, and is essentially the contribution to the specific heat of a resonant level. It gives rise to a linear temperature dependence for $T \ll \Delta$, Γ, and a Schottky-type peak at $T \sim (\Delta^2 + \Gamma^2)^{1/2}$. The second term gives rise to a Schottky anomaly at $T \sim \mu_{\text{eff}} B$ and vanishes for $B=0$.

Figures 1 and 2 show the temperature dependence of the specific heat for Tm ions for $\Delta = 80$ K and

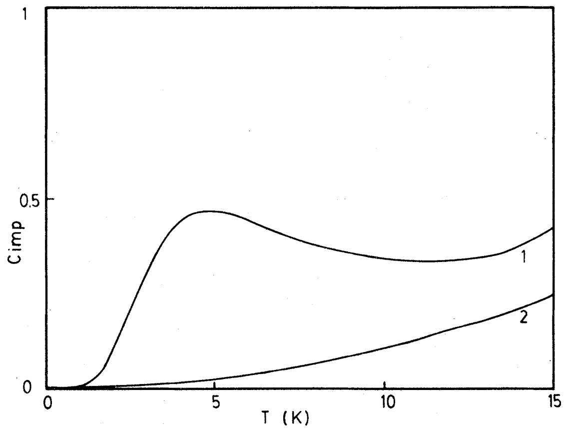

FIG. 2. Low-temperature specific heat per Tm ion, Δ and Γ as in Fig. 1, $\mu_B B = 2$ K and $\mu_0 = (4.58/\sqrt{3})\mu_B$ and $\mu_1 = (7.3/\sqrt{3})\mu_B$. Curve 1 is the total specific heat. Curve 2 corresponds to the field-independent term. The difference fits a spin-one-half $\mu = \mu_{\text{eff}}$ Schottky anomaly $(k_B = 1)$.

$\Gamma = 27$ K. Figure 1 corresponds to the first term in Eq. (39). We use $k_B = 1$. Figure 2 is the total low-temperature specific heat for an external magnetic field $B = 2K/\mu_B$.

C. Static magnetic susceptibility

As in the specifc heat, we find dual features in Tm intermediate valence compounds, a large Van Vleck-like term characteristic of resonant levels on one side and a Curie-like term on the other.

The susceptibility derived from (24) is

$$\chi = \frac{\mu_{\text{eff}}^2}{T} \bar{\mu}^2 \frac{\partial}{\partial \Delta} \phi(\Delta, \Gamma, T) \quad . \tag{40}$$

Clearly, the first term represents the Curie susceptibility. The second term depends more weakly on temperature and at low temperatures it is proportional to the local density of states $\Gamma/\pi(\Delta^2+\Gamma^2)$. The change in valence δv induced by a magnetic field is proportional to this last term.

A plot of the inverse susceptibility as a function of temperature is given in Fig. 3(a) for different values of Δ and $\Gamma = 27$ K. Figure 3(b) shows the variation of μ_{eff} with temperature. It can be seen that curvature in χ^{-1} appearing at low temperatures is due in this model to the variation of μ_{eff} with temperature which in turn is due to temperature-induced valence changes in the Tm ion.

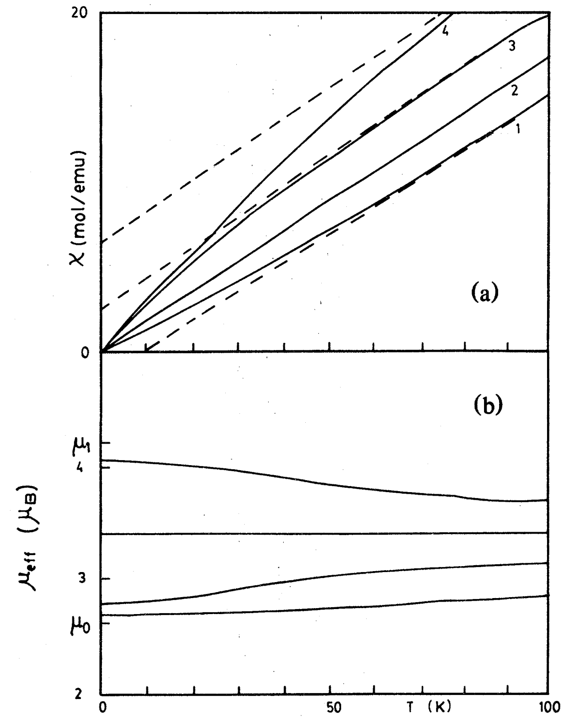

FIG. 3. (a) inverse susceptibility and (b) μ_{eff} as a function of temperature for different values of Δ. Other parameters as in Figs. 1 and 2. Curves 1, $\Delta = -80$ K; curves 2, $\Delta = 0$; curves 3, $\Delta = 80$ K and curves 4, $\Delta = 200$ K.

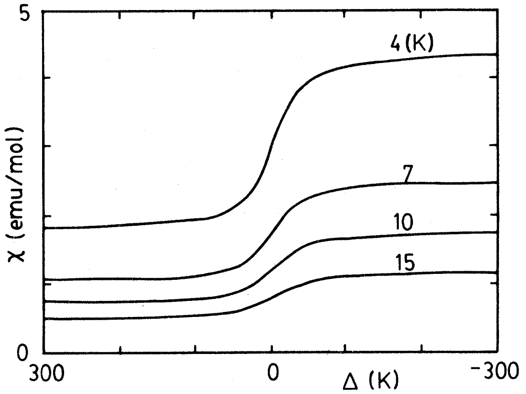

FIG. 4. Magnetic susceptibility as a function of Δ for different temperatures. Other parameters as in Fig. 3. Curve 1, $T = 4$ K; curve 2, $T = 7$ K; curve 3, $T = 10$ K; curve 4, $T = 15$ K.

In Fig. 4 we show the variation of the susceptibility as a function of Δ for $\Gamma = 27$ K and different temperatures.

At moderate magnetic fields, the magnetization as a function of magnetic field at different temperatures follow a spin-$\frac{1}{2}$ Brillouin law with $\mu = \mu_{\text{eff}}$.

D. Magnetoresistivity

A large magnetoresistance has been detected in TmSe and in $\text{Tm}_x\text{Y}_{x-1}\text{Se}$.[6,10] This effect is contained in the model presented here.

To calculate the magnetoresistance, we proceed as follows: The scattering cross section for spin-up conduction electrons of energy ϵ_λ is proportional to the square of the sine of the phase $\delta_{\lambda\uparrow}$, which can be identified with the quantity defined in Eq. (25). Since the spin-up conduction electrons can only be scattered by going into the $|\uparrow\rangle$ states to produce $|+\rangle$ (or vice versa), we can write for the relaxation time of the spin-up conduction electron at the Fermi level

$$[\tau_\uparrow(0)]^{-1} = \text{const} \frac{1}{\pi} \frac{\Gamma}{\Delta^2+\Gamma^2} (P_+ + P_\uparrow) \quad . \tag{41}$$

Similarly,

$$[\tau_\downarrow(0)]^{-1} = \text{const} \frac{1}{\pi} \frac{\Gamma}{\Delta^2+\Gamma^2} (P_\downarrow + P_-) \quad . \tag{42}$$

The conductivity, then, is proportional to the inverse of the occupation probabilities

$$\sigma = \text{const} \left[\frac{1}{P_+ + P_\uparrow} + \frac{1}{P_- + P_\downarrow} \right] , \tag{43}$$

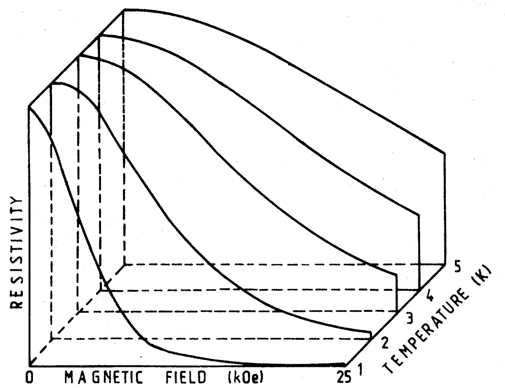

FIG. 5. Normalized magnetoresistance $R(N)/R(0)$ as a function of external magnetic field B for different temperatures. μ_0, μ_1, Γ, and Δ as in the other figures.

where the main field dependence is contained in the P_i's. By defining $M_1=(P_+ + P_\uparrow)-(P_- + P_\downarrow)$, we can write

$$R=\sigma^{-1}=\text{const}(1-M_1^2) \ . \tag{44}$$

Using (30) we obtain, for $\bar{\mu}B/\Gamma \ll 1$,

$$M_1=1-2f(2\mu_{\text{eff}}B) \ . \tag{45}$$

Figure 5 shows the ratio $R(B)/R(0)$ as a function of B for different temperatures.

E. Dynamical magnetic susceptibility

The inelastic neutron scattering spectrum of TmSe described in Sec. I, paragraph (g) is connected to the Fourier transform of the local spin-correlation function $G(t)=[M_Z(t)M_Z(0)]$. The spin operator M_Z can be expressed in our notation as

$$M_Z=\mu_0(|\uparrow\rangle\langle\uparrow|-|\downarrow\rangle\langle\downarrow|) + \mu_1(|+\rangle\langle+|-|-\rangle\langle-|) \ .$$

Here again it is possible to calculate exactly the desired quantity $G(\omega)$. The detailed derivation of $M(\omega)$ will be presented in a future paper. We will give here only the resulting expression

$$G(\omega)=\mu_{\text{eff}}\delta(\omega)+\frac{\bar{\mu}^2}{4}\frac{1}{\pi}\frac{2\Gamma}{\omega^2+4\Gamma^2}\coth\frac{\omega}{2T}\left[\text{Im}\psi\left(\frac{1}{2}-i\frac{\Delta-\omega+i\Gamma}{2\pi T}\right)+\frac{2\Gamma}{\omega}\text{Re}\left|\psi\left(\frac{1}{2}-i\frac{\Delta-\omega+i\Gamma}{2\pi T}\right)\right.\right.$$
$$\left.\left.-\psi\left(\frac{1}{2}-i\frac{\Delta+i\Gamma}{2\pi T}\right)\right|-(\omega\rightarrow-\omega)\right] \ , \tag{47}$$

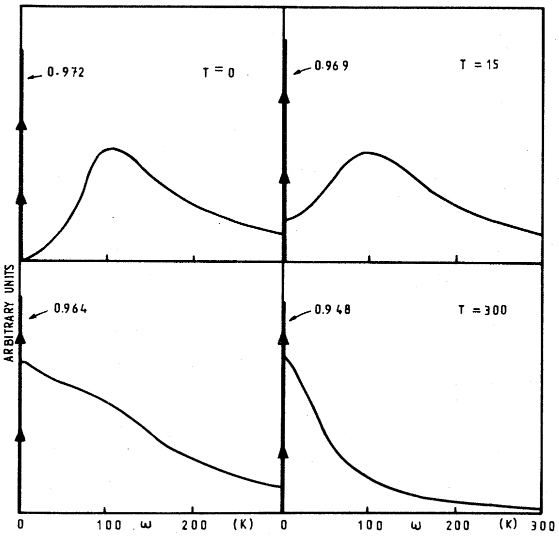

FIG. 6. Fourier transform of the spin-spin correlation function $G(\omega)$ as function of ω. Parameters as in Fig. 1.

which is plotted as a function of ω for $\Delta=80$ K and $\Gamma=27$ K at different temperatures in Fig. 6.

As can be seen, $G(\omega)$ contains a broad Lorentzian function at high temperatures that becomes a broad inelastic peak at low temperatures. This feature is the most peculiar behavior found in the neutron spectra of TmSe.[11,12] The width of the elastic peak at finite temperature cannot be obtained from this model, where spin-flip scattering arising from V' in our Hamiltonian (8) is taken to be zero. Even considering this shortcoming, the model presented here offers a simple explanation of the origin of the inelastic peak and its evolution with temperature, without having to invoke strange crystal fields that disappear when the temperature is raised. A calculation of the charge dynamical susceptibility leads, in this case, to exactly the same analytical dependence as the spin dynamical susceptibility, in agreement with the conclusion of Ref. 16.

V. DISCUSSION

We have shown that the peculiarities found in the magnetic properties of Tm IV compounds can be explained naturally by a simple model that describes valence fluctuations between two magnetic configurations.

In order to describe in a transparent way the physical origin of the dual (resonant and free-spin) characteristics of systems that fluctuate between two magnetic configurations, we have made drastic simplifications in the description of the $4f$ shell electronic structure. However, since our aim is to understand the origin of the qualitative differences between the properties of IV systems like TmSe and SmS for example, this is not a serious shortcoming. The essential feature, i.e., that both configurations are magnetic, is mantained.

The point is that for valence fluctuations between two magnetic configurations, the ground state has to be degenerate to give rise to a Curie-like susceptibility at low temperatures, and yet, the resonant character of the local levels has to be retained to lead to a large linear term in the specific heat, for example. This is achieved in this model by considering highly correlated ionic states which can hybridize through promotion of an electron to a continuum of states. By choosing $V'=0$ [Eq. (8)], we can write a Hamiltonian that separates into two exactly equal parts, both resonant, correlated between themselves to mutually exclude each other. The degeneracy occurs because the ground states of both of them have the same energy.

Several aspects relevant to a quantitative theory of IV Tm ions have been left out for the sake of clarity. In our point of view the two most important are:

(a) The full degeneracy of the $J=\frac{1}{2}$ and $J=6$ ground-state configurations of Tm^{2+} and Tm^{3}, and its lifting by crystal fields.[21]

(b) For TmSe or other concentrated compounds, the periodicity effects leading to intersite correlations. These effects are indeed important below the ordering temperature. Magnetic interactions arising from the IV character of the Tm ions play a dominant role in the ordered phases of TmSe.[22] Gaps can open up in the density of states and lead to insulating ground states for stoichiometric TmSe.[23]

Concerning point (a) we would like to remark that even for our simple initial Hamiltonian with V and V' different from zero, it is possible to make a different choice of parameters which can lead to a *singlet ground state.* This is easy to see because by now taking V instead of V' equal to zero the Hamiltonian reduces to a form equivalent to the U infinite Anderson Hamiltonian.

However, we have shown that even in the rotationally invariant case $V=\sqrt{2}\,V'$ the ground state is degenerate.[16] In any case, this shows that unlike the magnetic-nonmagnetic case, anisotropy can play an important role here.

Concerning point (b), the model studied here can be extended to consider a periodic lattice. Assuming any ordered magnetic structure, the Hamiltonian can again be solved exactly and it is possible to determine the energetic stability of the given structure. This will be the subject of a forthcoming paper.

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