Theory of Spin Fluctuations in Tm Compounds

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We calculate the spin and charge dynamical susceptibilities of an intermediate-valence system fluctuating between two magnetic configurations. Our results can explain the most important features of the neutron-scattering spectra of TmSe. We show that the energy of the inelastic peak found experimentally is connected with the energy of charge fluctuations.

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Inelastic-neutron-scattering experiments in intermediate-valence (IV) systems are very important since they can reveal the basic features of their spin dynamics. Until recently, most experiments were devoted to the study of Ce or Yb compounds.[1] In these systems, the rare-earth ions fluctuate between a magnetic and a nonmagnetic configuration. The neutron spectrum has been reported to be a quasielastic line with a weakly temperature-dependent width. Theoretical models consistent with this result exist in the literature.[2,3]

Recently, the inelastic-neutron-scattering spectrum of TmSe in the paramagnetic phase was reported by Loewenhaupt and Holland-Moritz.[1] TmSe is the only known mixed-valence rare-earth compound at normal pressure which fluctuates between two magnetic configurations: Tm^{3+} ($J=6$) and Tm^{2+} ($J=\frac{7}{2}$). Its neutron spectrum differs qualitatively from that observed for the other IV compounds. At low temperatures, it consists of two peaks, one quasielastic and one inelastic. The latter, of appreciable intensity, is rather broad and cannot be identified as arising from crystal-field splittings.[1] The width of the quasielastic peak goes to zero as the temperature approaches zero.

No theoretical interpretation of this peculiar behavior exists in the literature. In this Letter we report results from a model that describes the dynamics of an IV system in which the two configurations involved are magnetic. It allows one to understand the features of the low-temperature spectrum and makes it possible to identify the origin of the two peaks. Furthermore we calculate the charge-fluctuation power spectrum and show its similitude to the spin-fluctuation power spectrum.

From the start we make two basic assumptions: (a) Since the relevant features of the dynamic magnetic susceptibility of TmSe are determined by the accessibility of two magnetic configurations and not by their detailed structure, we may model them in the simplest way: The $4f^{12}$ is the highest spin configuration and we represent it by spin-1 states $|+\rangle$, $|0\rangle$, $|-\rangle$; the lowest spin configuration $4f^{13}$ is represented by spin-$\frac{1}{2}$ states $|\uparrow\rangle$, $|\downarrow\rangle$. A more realistic representation of the $J=\frac{7}{2}$ and $J=6$ states leads to similar results. (b) Since the double differential cross section is weakly dependent on the momentum transfer[4] we neglect interactions between different ions and reduce the system to a one-impurity problem. From the theoretical point of view, this assumption has been justified in Ref. 5.

The Hamiltonian we propose mixes the two configurations through the promotion of an electron from the $4f^{13}$ configuration to the conduction band. It is

$$H=H_{4f}+H_b+H_{\mathrm{hyb}}, \tag{1}$$

where

$$H_{4f}=E_{1/2}(|\uparrow\rangle\langle\uparrow|+|\downarrow\rangle\langle\downarrow|)+E_1(|+\rangle\langle+|+|0\rangle\langle 0|+|-\rangle\langle -|), \tag{2}$$

where $E_{1/2}$ and E_1 are the energies of the spin-$\frac{1}{2}$ and -1 states, respectively. H_b describes the dynamics of the conduction electrons and in the usual notation is given by

$$H_b=\sum_{k\sigma}\epsilon_k c_{k\sigma}{}^{\dagger}c_{k\sigma}. \tag{3}$$

We measure the one-particle energies ϵ_k from the Fermi level. H_{hyb} represents the mixing between the two configurations:

$$H_{\mathrm{hyb}}=\sum_k[V'(|\uparrow\rangle\langle +|c_{k\downarrow}+|\downarrow\rangle\langle -|c_{k\uparrow})+V(|\downarrow\rangle\langle 0|c_{k\downarrow}+|\uparrow\rangle\langle 0|c_{k\uparrow})+\mathrm{H.c.}]. \tag{4}$$

We take the mixing matrix elements independent of k, and in order to maintain rotational symmetry in the system we write $V' = \sqrt{2}\,V$. Experimental evidence of the smallness of crystal-field effects is reported by Batlogg *et al.*[6]

In order to construct the lowest-energy states it is necessary to take maximum advantage of the mixing energy. Since H conserves total spin (as well as z component), this is accomplished by combining states of local spin-$\frac{1}{2}$ with conduction-electron states in such a way as to have total spin 1. This state can then mix with states corresponding to the local spin-1 configuration. This means that our Hamiltonian couples the local spin-$\frac{1}{2}$ configuration *ferromagnetically* to the conduction electrons. Conversely, local spin-1 states are coupled *antiferromagnetically* to the conduction electrons. The ground state is degenerate for $\Delta = E_1 - E_{1/2} > 0$ or $\Delta < 0$. If the valence state is such that one of the two configurations is dominant, the main result of hybridization is the ferromagnetic ($\Delta > 0$) or antiferromagnetic ($\Delta < 0$) coupling. The same reasoning leads, in the case of the Anderson Hamiltonian, to a completely different conclusion: The local and conduction electrons couple antiferromagnetically to form a singlet ground state.[7]

With these considerations in mind we first construct variational wave functions to describe the ground state of our Hamiltonian in a way similar to that used in Refs. 8 and 9. For shortness we discuss here only the wave functions for $\Delta > 0$, where the lowest unmixed states are those corresponding to the spin-$\frac{1}{2}$ configuration.

The proposed wave functions are

$$|\psi_{\uparrow}{}^0\rangle = a|\Phi, \uparrow\rangle + \sum_k a_k[(\tfrac{2}{3})^{1/2} c_{k\downarrow}{}^{\dagger}|\Phi, +\rangle + (\tfrac{1}{3})^{1/2} c_{k\uparrow}{}^{\dagger}|\Phi, 0\rangle] \tag{5a}$$

and

$$|\psi_{\downarrow}{}^0\rangle = a|\Phi, \downarrow\rangle + \sum_k a_k[(\tfrac{2}{3})^{1/2} c_{k\uparrow}{}^{\dagger}|\Phi, -\rangle + (\tfrac{1}{3})^{1/2} c_{k\downarrow}{}^{\dagger}|\Phi, 0\rangle]. \tag{5b}$$

Here $|\Phi, \uparrow\rangle$ symbolizes the state consisting of the filled Fermi sea and the impurity in the state $|\uparrow\rangle$. An equivalent notation is used for the states corresponding to the spin-1 configuration.

The variational equations for the coefficients are

$$E_0 a = \sqrt{3}\,V \sum_{k > k_F} a_k, \tag{6a}$$

$$E_0 a_k = (\Delta + \epsilon_k) a_k + \sqrt{3}\,Va, \tag{6b}$$

where k_F is the Fermi momentum and E_0 the energy of the ground state. We take the energy of the unperturbed state $|\Phi, \uparrow\rangle$ as zero.

Under the assumption of a constant density of states ρ extending from $-W$ to W for the conduction electrons, the secular equation is

$$E_0 = (3\Gamma/\pi) \ln|(E_0 - \Delta)/(E_0 - \Delta - W)|, \tag{7}$$

where $\Gamma = \pi\rho V^2$ is associated with the width of the localized states.

From all the wave functions that can be constructed by the promotion of an electron or hole, (5a) and (5b) are the lowest-energy ones. Including other electron-hole states does not affect the structure of the ground state. The equivalent procedure for the Anderson Hamiltonian has been used by Varma and Yafet[9] to construct the singlet ground state. We will use their ground-state wave function to calculate the dynamical properties corresponding to the Anderson Hamiltonian to demonstrate the difference between Tm and other rare-earth IV compounds.

We now calculate the spin power spectrum at zero temperature. It is given by the Fourier transform $\langle S^+, S^-\rangle_\omega$ of the correlation function $\langle S^+(t) S^-(0)\rangle$, where $S^+ = S_{1/2}{}^+ + S_1{}^+ = |\uparrow\rangle\langle\downarrow| + \sqrt{2}\,(|+\rangle\langle 0| + |0\rangle\langle -|)$. It can be expressed as

$$\langle S^+, S^-\rangle_\omega = \tfrac{1}{2} \sum_{\sigma\sigma'} |\langle \Psi_\sigma{}^0 | S^- | \Psi_{\sigma'}{}^0\rangle|^2 \delta(\omega) + \tfrac{1}{2} \sum_{\mu\sigma} |\langle \mu | S^- | \Psi_\sigma{}^0\rangle|^2 \delta(\omega - E_\mu + E_0). \tag{8}$$

In Eq. (8) $|\mu\rangle$ are the excited states of energy E_μ. The problem now is to approximate these states in some way. We take for them linear combinations of the same form as in (5a) and (5b). For example, the state

$$|\Psi_k{}^\mu\rangle = b_k{}^\mu c_{k\downarrow}{}^{\dagger}|\varphi, -\rangle + \sum_{k'} b_{kk'}{}^\mu c_{k'\uparrow}{}^{\dagger} c_{k\downarrow}|\varphi, \downarrow\rangle \tag{9}$$

is included in terms of the form $\langle \mu | S_1{}^- | \Psi_\uparrow{}^0\rangle$ in (8). Similarly $S_{1/2}{}^- |\Psi_\uparrow{}^0\rangle = a|\varphi, \downarrow\rangle$ and in the latter case we take as excited states those obtained from (5b) corresponding to energies $E_\mu > E_0$. We believe that these functions, although very rough approximations of the actual excited states, are sufficient for a qualitative understanding of the experiments.

The valence-fluctuation power spectrum can be calculated in a similar way. It can be defined as the Fourier transform of the occupation correlation function $\langle n(t)n(0)\rangle$[10]; here $n = |\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\downarrow|$.

Figure 1 summarizes our results for the zero-temperature dynamical susceptibilities. Figure 1(a) shows the magnetic susceptibility obtained from Hamiltonian (1). It displays a δ function at $\omega = 0$ corresponding to spin excitations within the degenerate ground state and a broader peak centered at about $|\Delta| + \Gamma$ arising from excited charge states connected to the ground state through H_{hyb}. Since the density of eigenstates $|\mu\rangle$ is uniform, the structure of the magnetic susceptibility results from the energy dependence of the matrix elements in Eq. (8), which depend strongly on the coefficients a and a_k of the ground state. For $\Delta/\Gamma = 1$ the fraction of the total intensity contained in the inelastic peak increases to about 15%. Quite similar features are found in the charge susceptibility [Fig. 1(b)]. The sharp edge at $\omega \sim \Delta$ is unrealistic and appears as a consequence of our approximation to the ground-state wave function. Inclusion of electron-hole states in our variational wave function [Eqs. (5a) and (5b)] softens it.

For comparison, the magnetic and charge susceptibilities corresponding to the Anderson Hamiltonian calculated in a similar way are shown in Figs. 1(c) and 1(d). In this latter case the charge susceptibility shows increased strength at low energies as a consequence of increased importance of electron-hole states. The peak at low energies of the magnetic susceptibility stems from transitions from the singlet ground state (total spin 0), to excited states slightly above in energy of total spin 1.

Recently, it has been suggested that the power spectrum of charge fluctuations can be probed directly by Raman scattering.[11] Thus, neutron and Raman scattering spectra in IV Tm compounds should show similar characteristics, contrary to what is expected in Ce or Yb compounds.

According to Ref. 6 the valence state of Tm can be varied from about 2.72^+ to 3^+ as x varies from 1.05 to 0.87. In light of our model, the intensity of the inelastic peak should decrease as x decreases from 1.05. The existence of a degenerate ground state implies divergent low-temperature static susceptibilities leading to magnetic order. The effective magnetic moment does not disappear at intermediate valence if the fluctuations take place between two magnetic configurations and its dynamics cannot be described even qualitatively by a spin-$\frac{1}{2}$ Kondo Hamiltonian in the usual way.

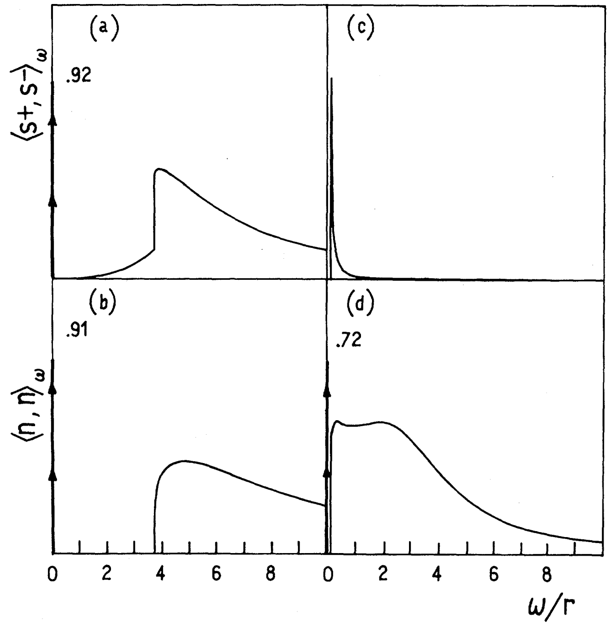

FIG. 1. Charge and spin dynamical susceptibilities at $T = 0$, $\Delta/\Gamma = 4$ (arbitrary scale). (a) $\langle S^+, S^-\rangle_\omega$ as obtained from Eq. (8). (b) $\langle n, n\rangle_\omega$ from Hamiltonian (1). Both show a δ-like peak at $\omega = 0$ and an inelastic broader peak at energies near Δ. (c) and (d) Same quantities obtained from the Anderson Hamiltonian. In this case Δ is the energy difference between the spin-0 configuration and the spin-$\frac{1}{2}$ configuration. The fraction of the total intensity contained in the δ functions are indicated in the figures.

From the ideas presented above, we can draw the following conclusions:

(a) A model that includes mixing between the two simplest magnetic configurations allows one to understand most features of the paramagnetic phase of TmSe, indicating that they will be common to IV systems fluctuating between two magnetic valence states.

(b) The coupling of the local spin to the conduction electrons will be *ferromagnetic* if the lowest spin configuration is energetically favored. The coupling is *antiferromagnetic* in the opposite case. The differences should appear when comparing the properties of TmTe under pressure[12] and of Tm_xSe.[6]

(c) The ground state is degenerate, leading to Curie-like susceptibilities and an elastic neutron scattering component.

(d) When fluctuations occur between two magnetic configurations, the charge and spin susceptibilities have similar power spectra. This is *not* the case when fluctuations take place between magnetic and nonmagnetic configurations. Pressure or alloying often changes the average occupation of the $4f$ shell without destroying completely the homogeneity of the system. This implies changes in the parameters Δ and Γ of the model and can provide direct tests of the theory presented here. Implicit in the one-impurity treatment of the problem is the prediction that the inelastic peak is a feature that does not depend on concentration of Tm sites and should also appear in dilute systems.

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Electron Transfer and the Valence States of Cerium and Platinum in Cubic Friauf-Laves Compounds with the Platinum Metals

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An analysis of the observed values of the lattice constants of the crystalline solutions $CeIr_2$-$CePt_2$ and other Friauf-Laves intermetallic compounds leads to the conclusion that at 14 at.% $CePt_2$ in $CeIr_2$ the platinum atom has transferred one electron to cerium and forms nine covalent bonds in pivoting resonance, without having a metallic orbital, whereas in $LaPt_2$ and $CePt_2$ it has 0.72 metallic orbital, an unshared electron pair, and covalence 7.28. The choice of valence states 3^+ and 4^+ of cerium in different compounds is also discussed.

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Barberis *et al.*[1] have determined the values of the lattice constant (cube edge) for the crystalline solutions $CeOs_2$-$CeIr_2$ and $CeIr_2$-$CePt_2$, which have the Friauf-Laves cubic structures $C15$, and have interpreted the values, in comparison with those for the compounds $LaOs_2$, $LaIr_2$, $LaPt_2$, $PrOs_2$, $PrIr_2$, and $PrPt_2$, as showing that the cerium atom is present as the tetrapositive ion in the compounds with osmium and iridium and the tripositive ion in the compound with platinum. Values of the lattice constants are shown in Fig. 1. There is a striking feature shown in this figure: the sharp bend in the $CeOs_2$-$CeIr_2$-$CePt_2$ curve at $Ce(Ir_{0.87}Pt_{0.13})_2$. I point out that this feature can be explained by application of known structural principles.

In the elemental metals Re, Os, Ir, Pt, and Au, with the atoms arranged in cubic or hexagonal closest packing, the observed interatomic distances (average of two for hcp) have a minimum about 30% of the way between Os and Ir; that is, for 8.3 valence electrons (electrons outside the xenon closed shell), as is shown in Fig. 2. This observation, which applies also to the sequence Tc, Ru, Rh, Pd, and Ag, has been interpreted[3] in terms of the 0.72 orbital, called the metallic orbital, that serves a special function in conferring metallic properties on metals.[4,5]