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STATISTICAL MECHANICS OF MAGNETIC NON MAGNETIC TRANSITIONS OF RARE EARTH IONS IN METALS

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Using a simple model, and by means of a phenomenological extension of the Green's function method, it has been possible to give a more precise mathematical footing to the ideas put forward by Hirst, Maple, Wohleben and Coles regarding the demagnetization of rare earth ions in metals.

THE DEMAGNETIZATION of rare earth ions can take place in diverse circumstances: dilute alloys (La–Ce, (La, Th)–Ce), intermetallic compounds ($YbAl_3$, $CePd_3$), pure metals (α-Ce) as well as "ionic metals" such as the high pressure phase of SmS.[1–3] From the analysis of experimental results one is led to the following conclusions:

(1) Intermediate valence is found only when the rare earth ion is imbedded in a metallic host.

(2) It appears to be the mixture of two well defined ionic configurations which themselves correspond to integer occupation of the 4*f* shell.

(3) In concentrated compounds it is associated with anomalous lattice constants.

(4) The susceptibility of each ion saturates at a finite value at low temperatures.

(5) Associated with intermediate valence there appear large anomalies in both specific heat and conductivity.

These characteristics of the phenomena under study led the authors of references 1–3 to a description of the experimental results in terms of temporal fluctuations of the ions between the two ionic configurations involved.

A more formal approach becomes necessary in order to calcualte the properties in terms of some set of characteristic parameters . A suitable model problem may be easily described in the limit of zero linewidth using the partition function technique. It proves difficult however to extend this treatment to the case of finite lifetime of the 4*f* levels. A way to overcome this is to use a Green's function description, shifting its poles for the zero linewidth case away from the real axis. This still leaves the non trivial task of finding the Green's functions that yield the desired information and the ways to extract it from them for the given problem.

To solve this question we have studied a simple idealized model which, while simple to handle mathematically retains all the essential features involved in real systems.

We use an Anderson type model Hamiltonian for the localized levels:

$$H = \sum_M T_M C_M^+ C_M + U \sum_{M<M'} C_{M'}^+ C_{M'} C_M^+ C_M \qquad (1)$$

where $T_M = T_0 - \mu M H$ is the energy necessary to create a particle in the M-th localized level (M runs from $-3/2$ to $3/2$ in this example). H is the magnetic field. For $H = 0$ we have four degenrate states. C_M^+ (C_M) creates (annihilates) a particle in the M-th state. U represents the coulomb interaction between particles. In real system there will be several interactions; here we choose this form for the intra atomic Hamiltonian

Table 1. First three columns: eigenstates and eigenvalues of the model Hamiltonian. Last three columns: range of stability of the one, two, three and four particle states and statistical mean values of N *and the susceptibility*

State	Energy	N	Range of Stability	$\langle N\rangle$	χ
$\lvert 0\rangle$	0	0	$k_BT < \epsilon_0$	0	0
$\lvert M\rangle$	$T_0 - M\mu H$	1	$-U + k_BT < \epsilon_0 < -k_BT$	1	$\frac{15}{4}\,\beta\mu^{2/3}$
$\lvert M, M'\rangle$	$2T_0 + U - (M + M')\,\mu H$	2	$-2U + k_BT < \epsilon_0 < -U - k_BT$	2	$5\,\beta\mu^{2/3}$
$\lvert M, M'M''\rangle$	$3T_0 + 3U - (M + M' + M'')\mu H$	3	$-3U + k_BT < \epsilon_0 < -2U - k_BT$	3	$\frac{15}{4}\,\beta\mu^{2/3}$
$\lvert M, M', M'', M'''\rangle$	$4T_0 + 6U$	4	$\epsilon_0 < -3U - k_BT$	4	0

for mathematical simplicity.

If our localized levels are in thermodynamical equilibrium with an energy and particle reservoir (metallic matrix), the partition function can be calculated from $Z = Tr\, e^{-\beta(H - zN)}$ where

$$N = \sum_M C_M^+ C_M, \quad \beta = \frac{1}{k_BT}, \quad z = \text{chemical potential}.$$

Table 1 sketches the states and properties of the system. The exact eigenfunctions and eigenvalues are here simple to find. They are the model representation of the real $4f$ shell configurations for different numbers of particles in the shell.

The coulomb energy U is of the order of several eV, so that quite generally $\beta U \gg 1$. This divides the behaviour of N and χ vs $\epsilon_0 = T_0 - z$ into wide regions in which they are nearly independent of ϵ_0. These regions are of width U and are separated from each other by zones if width k_BT in which N and χ vary continuously with ϵ_0. Table 1 shows in its last two columns values of N and χ in each of these regions.

Thus whenever $\epsilon_0 \simeq -n\,U + k_BT\,(n = 0, 1, 2, 3)$ we will have

$$0 < \langle N\rangle < 1, \quad 1 < \langle N\rangle < 2, \quad \text{etc.}$$

It is in these very narrow regions where the effect of linewidth of the localized levels will be drastic.

In order to incorporate linewidth effects we have to calculate first the Green's functions for our model. This is not very difficult to do in this case but might prove extremely complicated for a $4f$ shell where the number of the n-electron states is

$$\frac{14!}{(14 - n)!\, n!}$$

and in which exchange and L–S interaction have to be included. Postposing this question we will choose one of the "dangerous" regions and try to find the rules to obtain $\langle N\rangle$ and χ at a minimum cost of calculation. Let us take $\epsilon_0 \simeq -U$ (This corresponds in a more complicated case to $E(i) - E(i - 1) \simeq z$ where $E(i)$ is the energy of the i-particle configuration) so that $\langle N\rangle$ will fall between one and two. In order to obtain $\langle N\rangle$ and χ we need the occupation probability of the two particle states $\lvert MM'\rangle$. We will then consider the Green's function

$$G_{M'M} = \langle\langle C_M^+ \cdot C_M \cdot C_M ; C_M^+\rangle\rangle .$$

Itssequation of motion is[4]

$$\omega\, G_{M'M} = \frac{\langle C_{M'}^+ C_{M'}\rangle}{2\pi} + (T_M + U)\, G_{M'M}$$

$$+ \sum_{M'' \neq M', M} \langle\langle C_{M''}^+ C_{M''} C_{M'}^+ C_{M'} C_M ; C_M^+\rangle\rangle .$$

Thus we also need the three particle Green's function

$$F_{M''M'M} = \langle\langle C_{M''}^+ C_{M''} C_M^+ C_{M'} C_M ; C_M^+\rangle\rangle$$

The corresponding equation of motion will be

$$\omega\, F_{M''M'M} =$$

$$\frac{\langle C_{M''}^+ C_{M''} C_{M'}^+ C_{M'}\rangle}{2\pi} + (T_M + 2\,U)\, F_{M''M'M}$$

$$+ U \sum_{M''' \neq M'', M', M} \langle\langle C_{M'''}^+ C_{M'''} C_{M''}^+ C_{M''} C_{M'}^+ C_M ; C_M^+\rangle\rangle. \tag{2}$$

The next Green's function

$$\langle\langle C_{M'''}^+ C_{M'''} C_{M''}^+ C_{M''} C_{M'}^+ C_{M'} C_M ; C_M^+\rangle\rangle$$

will turn out to be proportional to the thermodynamical expectation value

$$\langle C_{M'''}^+ C_{M'''} C_{M''}^+ C_{M''} C_{M'}^+ C_{M'}\rangle .$$

Since this value will go to zero as $e^{-\beta U}$ for large U we can drop the last term in equation (2). Indeed in our example it would have been easy to continue since the equation of motion for the four particle Green's function would not have involved any higher ones. The fact that this last step is not needed is what makes the generalization of the procedure to more complicated cases possible. Solving then for $G_{M'M}$ we obtain:

$$G_{M'M} = \frac{1}{2\pi}\frac{n_{M'} - \sum\limits_{M''\neq M',M} n_{M''M'}}{\omega - T_M - U} + \frac{1}{2\pi}\frac{\sum\limits_{M''\neq M'',M} n_{M''M'}}{\omega - T_M - 2U} \tag{3}$$

where

$$n_M = \langle C_M^+ C_M \rangle$$

and

$$n_{M'M} = \langle C_{M'}^+ C_{M'} C_M^+ C_M \rangle .$$

From equation (3) we can calculate $n_{MM'}$, in terms of n_M and $n_{M'M''}$ by use of (reference 4):

$$\begin{aligned} n_{M'M} &= \langle C_{M'}^+ C_{M'} C_M^+ C_M \rangle = \\ &i \int_{-\infty}^{+\infty} f(\omega)[G_{M'M}(\omega + is) - G_{M'M}(\omega - is)]\, d\,\omega \\ &= \int_{-\infty}^{+\infty} f(\omega)\, \delta\, (\omega - T_M - U)\, d\,\omega \\ &= (n_{M'} - \sum_{M''\neq M',M} n_{M''M'}) f(T_M + U) . \end{aligned} \tag{4}$$

In the above $f(x)$ is the Fermi function $= [1 + \exp(x - z)]^{-1}$ and we have neglected the second term in the R.H.S. of (3) since it goes to zero as $e^{-\beta U}$ when U goes to infinity. Notice that the limit must be taken in such a way that $T_M + U - z$ remains finite.

The Green's functions we have been considering enable us to calculate the occupation probabilities $n_{M'} n_{MM'}$ for each one particle or two particle states.

However it is often of interest to determine the probability of the system containing a given number of particle. In our particular case (where there may either be one or two particles present) we define $P_M^{(1)}$ as the probability of state M being occupied and $P_{MM'}^{(2)}$, as the probability of state MM' being occupied when the number of particles is one or two respectively.

Then the probability of having one (two) particles present in any of the possible states will be:

$$P^{(1)} = \sum_M P_M^{(1)} \, (P^{(2)} = \sum_{M<M'} P_{MM'}^{(2)})$$

clearly:

$$P^{(1)} + P^{(2)} = 1 . \tag{4'}$$

For the case in question $P_{MM'}^{(2)} = n_{MM'}$ *but* $P_M^{(1)} \neq n_M$ since n_M may be non-zero even when only two-particle states are occupied. The correct expression is:

$$P_M^{(1)} = n_M - \sum_{M'\neq M} n_{M'M} .$$

In the absence of an external magnetic field $T_M = T_0$ for all M. It then follows that all $n_{M'}$ as well as all $n_{MM'}$, are equal. Writing $n_M = n$ and $n_{MM'} = m$ equation (4) and (4') can be written:

$$m = (n - 2m) f(T_0 + U) \tag{5}$$

$$4n - 12m + 6m = 1 \tag{6}$$

giving n and m in terms of $T_M + U - z$ and θ.

The presence of a magnetic field H splits the one and two particle levels as shown in Table 1.

The susceptibility can be calculated to give:

$$\chi = P_1 \chi_1 + P_2 \chi_2 \tag{7}$$

where χ_1 and χ_2 are the susceptibilities obtained for the one and two particle regimes (cf Table 1).

One can check the validity of these equations by resorting back to the partition funcion z.

Existing experimental evidence indicates that hyridization of the localized and band states does not break the intra-atomic configurations, but rather that the eigenstates of the system will contain a mixture of the configurations corresponding to the non-hybridized states. In metals, this produces an uncertainty in the energy of each of the levels that can be incorporated into the Green's functions by simply shifting the poles slightly away from the real axis. Clearly a complete theory of the systems in question should calculate this shift as a function of energy, interaction Hamiltonian, etc. This procedure has proved extremely difficult even in the simple Anderson model which has no orbital degeneracy. Even using a simple Bloch waves model for the conduction states, one may expect hybridization to arise from several different causes and to depend strongly on the environment of the magnetic ion. We will show in what follows that most qualitative aspects of the experimental results can be explained on the basic of a phenomenologically introduced line-width. We assume then that the effect of hybridization is to introduce a term $i\,\Delta$ sign Im ω in the denominators of the R.H.S. of equation (3). This leads then to

$$n_{MM'} = n_{M'} - \sum_{M''\neq M',M} n_{M''M'} \quad \psi(\epsilon_M, \Delta, \theta) \quad (8)$$

where

$$\psi(\epsilon_M, \Delta, \theta) = \frac{d\,\omega}{e^{\omega/\theta+1}} D(\omega, \epsilon_M, \Delta) \qquad (9)$$

here

$$D_M\,(\omega, \epsilon_M, \nabla) = \frac{1}{\pi} \frac{\Delta}{(\omega-\epsilon_M)^2 + \Delta^2} \qquad (10)$$

and

$$\epsilon_M = T_M + U - z\,.$$

This equation together with equation (4′) allows us to calculate the thermodynamical quantities of interest.

In general Δ could be different for each M, and would depend on ω and also on n_M and $n_{MM''}$.

In real systems, assuming that the main source of hybridization is an Anderson type mixing between localized and band states, one should resort to the rules of fractional parentage in order to determine the relative magnitudes of the different M's and possible selection rules.

We expect from experimental evidence that Δ will be such that it will go to zero whenever either $P^{(1)}$ or $P^{(2)}$ go to zero.

Furthermore equation (14) reduces to the exact result in the limit $\Delta \to 0$.

The effect of Δ is to replace the Dirac δ function appearing in equation (4) by a "Lorentz like" function. Since we are interested in qualitative aspects rather than in exact results we will take all Δ's equal and we will approximate ψ by

$$\psi(\epsilon, \Delta, \theta) = \left(1 + \exp\frac{\epsilon}{\Delta+\theta}\right)^{-1} \qquad (11)$$

This function reduces to the correct limit for $\Delta = 0$. For $\theta = 0$, it corresponds to choosing a hyperbolic density of states (5) for the localized levels.

Since the form of ψ is the same as in the case of zero linewidth, but with $\Delta + \theta$ replacing θ, it is easy to obtain now form (14) and (10)

$$n = \frac{2\psi+1}{4+2\psi} = \frac{1+3\,e^{-\epsilon_0/\Delta+\theta}}{4+6\,e^{-\epsilon_0/\Delta+\theta}}$$

$$m = \frac{\psi}{4+2\psi} = \frac{e^{-\epsilon_0/\Delta+\theta}}{4+6\,e^{-\epsilon_0/\Delta+\theta}}$$

$$P^{(1)} = (1 + \tfrac{6}{4}\,e^{-\epsilon_0/\Delta+\theta})^{-1}$$

$$P^{(2)} = (1 + \tfrac{4}{6}\,e^{\epsilon_0/\Delta+\theta})^{-1}$$

and

$$\chi(\epsilon_0, \Delta, \theta) = P^{(1)}\,\frac{15}{4}\,\frac{\mu^2}{3(\Delta+\theta)} + P^{(2)}\,5\,\frac{\mu^2}{3(\Delta+\theta)} \qquad (12)$$

These formulae describe the main experimental results in intermediate valence compounds and alloys as outlined in points 1, 2 and 4 at the beginning of this paper. They also give a precise meaning to the parameter ϵ defined in reference (2) and (3).

The intermediate valence regime will thus take place when the Fermi level falls within $\Delta + \theta$ of $E(2) - E(1)$. This coincidence could in turn give rise to the anomalies found in the specific heat and in the conductivity.

In concentrated systems, the weight factors associated with strong correlation effects which appear in the Green's functions lead to temperature induced phase transitions (6). An additional complication in the case of concentrated systems is that both ϵ_0 and z will strongly depend on n and m (see reference 6). Before going on to the conclusions we would like to point out that even though it could prove a difficult task to use the procedure when dealing with the $4f$ shell (since then it might seem necessary to consider the 14 one-particle states) inspection of the model shows that it is sufficient to consider only those states which fall in a range of energies $\Delta + \theta$ above the ground state of each configuration.

From the analysis of the model we present here we can reach the following conclusions:

(a) Intermediate valence occurs when the difference between the energies of two configurations of different integer number of particles equals the chemical potential ($E(n) - E(n-1) \cong E_F$ if the energies are measured from the bottom of the band).

(b) The finite susceptibility at zero temperature is a direct consequence of the width of the levels, thus confirming the conjecture by Hirst[7] and the authors of references 1 and 2. Kondo effects may be present in some of the cases, but they are not necessary to explain the saturation of magnetization at low temperature.

(c) The narrowing of the levels at integer valencies is a many body effect. In fact, in order to get the correct expression for the susceptibility at integer valencies ($\epsilon_0 \gtrless \theta + \Delta$ in equation 12) we have to assume that $\Delta \to 0$ as either $P^{(1)}$ or $P^{(2)}$ go to zero.

(d) The results can be explained on the basis of an admixture of the levels of two configurations with integer number of particles.

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