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Crystal fields and Kondo effect: New results for the magnetic susceptibility

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ABSTRACT

The thermodynamic Bethe ansatz equations for the Coqblin–Schrieffer model have been solved for the first time to obtain the magnetic susceptibility in the presence of crystal fields for non-zero temperatures. For the case of $N=4$ effective ionic states an analytic expression for the limiting values of the pseudo-energies has been found facilitating the numerical solution for various crystal and magnetic field configurations. The single-impurity model applies to a wide range of dense Kondo systems and has been used before to explain apparent non-Fermi-liquid behavior. The flattening off of the susceptibility curves at a substantially higher temperature than the specific heat is shown to be a general feature of the Coqblin–Schrieffer thermodynamics.

1. Introduction

There is an increasing amount of experimental data on heavy fermion compounds, showing a great variety in their behavior, which is still far from being understood. One particular aspect that deserves further clarification is the relative effects of the crystal field and the Kondo scattering terms in the presence of magnetic fields.

The single-impurity Kondo and Anderson models and their generalizations to include orbital degeneracy serve as testing grounds for methods that are aimed at the corresponding lattice problems. The Bethe ansatz solutions to the impurity models in turn provide benchmarks [1–5] for ground state and finite-temperature thermodynamic quantities. The numerical solution to the thermodynamic Bethe ansatz (TBA) equations is able to render the full crossover between local-moment behavior at high temperatures and Fermi-liquid behavior at low temperatures with relatively little numerical effort.

On the experimental side there is on-going interest in the interplay of crystal fields and the Kondo effect [6–10]. The experimentalists' analysis of the measured thermodynamic quantities (for temperatures larger than a magnetic transition as the case may be) has been performed essentially in two steps: The low temperature behavior is fitted to the exact result for the spin-1/2 Kondo model [11]. Here the analytically available result for the resonant level model may be taken as an approximation. The higher temperature region is fitted by the Schottky curve for the non-interacting crystal field Hamiltonian. Recently an attempt has been made [12] to combine the resonant level and crystal field approaches to cover the whole applicable temperature range.

On the theoretical side, the generalization of the single ion Kondo model to a N-fold degenerate ionic configuration, the SU (N) Coqblin–Schrieffer [13] model was solved by Bethe ansatz more than 30 years ago [14]. An overview over the results for dilute mixed-valent and heavy-fermion systems derived from the TBA equations is given in Ref. [15]. An alternative approach to the solution of the Coqblin–Schrieffer model is presented in Ref. [16]. There, formulae are given for the calculation of weak field and low temperature expansions of the free energy of the model. A broad basis for comparison with experiments on the specific heat in zero magnetic field over the whole temperature range has been provided recently by the numerical solution of the TBA equations for the $N=6$ model (Cerium 3^+ ions) with general crystal field configurations [17]. A new high field/low temperature expansion was developed there to calculate the limiting values of the unknown functions as a basis for the numerical solution.

An interesting aspect of the interplay between degeneracy and crystal fields has been raised by Anders and Pruschke [18] who studied the problem by the numerical renormalization group method for the case of $N=4$ and calculated specific heat and magnetic susceptibility to analyze experimental data on $Ce_{1-x}La_xNi_9Ge_4$. These authors argue that the apparent non-Fermi-liquid behavior can be explained by an extended crossover

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regime caused by the crystal field that leads to the flattening off of the susceptibility curves at a substantially higher temperature than the specific heat. Moreover, they claim that this holds only for a narrow range of crystal field splittings.

In contrast to that assertion I show that this behavior is a general feature of the Coqblin–Schrieffer model thermodynamics for arbitrary crystal field splittings.

Following Anders and Pruschke I examine the case of $N=4$ that can hold as an approximation to the physical $N=6$ (Ce^{3+} ions) or $N=8$ (Yb^{3+} ions) case when a low lying quartet or two low lying doublets are separated from the higher multiplets so much that the upper multiplets can be neglected in the low temperature thermodynamics.

I consider three cases of crystal and magnetic field environments that are determined by crystal symmetry and the orientation of the magnetic field. When comparing with experiments the value of the Landè factor g has to be taken as that of the full Hund's rule ionic configuration without crystal fields:

(a) An (effective) spin $J=3/2$ ion in a uniaxial crystal field [19]. Without magnetic field the quartet is split into two doublets separated by an energy difference Δ. The energy levels with magnetic field applied along the z-axis may be labeled from 1 to 4 and are given by:

$$\begin{aligned} E_1 &= -\frac{1}{2}\Delta - \frac{1}{2}g\mu_B H,\\ E_2 &= -\frac{1}{2}\Delta + \frac{1}{2}g\mu_B H,\\ E_3 &= +\frac{1}{2}\Delta - \frac{3}{2}g\mu_B H,\\ E_4 &= +\frac{1}{2}\Delta + \frac{3}{2}g\mu_B H. \end{aligned} \tag{1}$$

(b) A Γ_8 quartet (i.e. cubic environment) with tetragonal distortion [20] with the magnetic field applied along the fourfold axis. The energy levels are given by:

$$\begin{aligned} E_1 &= -\frac{1}{2}\Delta - \frac{1}{2}g\mu_B H\,,\\ E_2 &= -\frac{1}{2}\Delta + \frac{1}{2}g\mu_B H\,,\\ E_3 &= +\frac{1}{2}\Delta - \frac{11}{6}g\mu_B H\,,\\ E_4 &= +\frac{1}{2}\Delta + \frac{11}{6}g\mu_B H\,. \end{aligned} \tag{2}$$

(c) A configuration considered in ref. [18] and [21] where the relative g-factor g_{rel} between the two doublets is determined to fit the experiments for $Ce_{0.5}La_{0.5}Ni_9Ge_4$ and is equal to $\sqrt{2}$. The energy levels are given by:

$$\begin{aligned} E_1 &= -\frac{1}{2}\Delta - \frac{1}{2}g\mu_B H\,,\\ E_2 &= -\frac{1}{2}\Delta + \frac{1}{2}g\mu_B H\,,\\ E_3 &= +\frac{1}{2}\Delta - \frac{1}{2}g_{rel}g\mu_B H\,,\\ E_4 &= +\frac{1}{2}\Delta + \frac{1}{2}g_{rel}g\mu_B H\,. \end{aligned} \tag{3}$$

The rest of this publication is organized as follows: In Section 2 the model is introduced and the TBA equations are formulated. The results for the limiting values needed to solve these non-linear integral equations are given in Section 3. An overview over the numerical results on the magnetic susceptibility for high and low temperatures is given in Section 4 exemplarily for case (a). From these results the zero temperature values of the magnetic susceptibilities for the three cases considered are extracted and shown as functions of the splitting Δ. In Section 5 results for representative values of the crystal field splittings are provided for all three cases to compare with experimental data. The apparent non-Fermi-liquid behavior is shown to be a general feature of the Coqblin–Schrieffer thermodynamics. The behavior of the limiting values of the unknown functions of the TBA equations at large values of the equation index n is given in the Appendix.

2. Model and TBA equations

The Coqblin–Schrieffer Hamiltonian can be written in terms of the N ionic crystal field states$|r\rangle$ with energy levels E_r and the usual notation for conduction electron operators $C^{\dagger}_{k,r}$. The exchange interaction is simply a permutation operator acting on the quantum labels of the particles.

$$H = \sum_{k,r} k\, C^{\dagger}_{k,r}C_{k,r} + J\sum_{k,r;\ k',r'} |r\rangle\langle r'|C^{\dagger}_{k',r'}C_{k,r} + \sum_r E_r|r\rangle\langle r| \tag{4}$$

For integrability of the model a linear dispersion of the conduction electron energy is assumed as well as the smallness of the exchange coupling J independent of r. The Bethe ansatz solution introduces an ad hoc cut-off D that enters the Kondo temperature $T_K \sim D\exp(-1/N|J|)$ in a non-universal way [11]. In the scaling limit $J\to 0$, $D\to\infty$, T_K is kept fixed and is the only scale of the model whose value may be fitted to the experiments.

In the language of the Anderson model the conditions on the crystal fields reduce to the requirement that the size of the splittings E_{r+1}-E_r be negligible compared to both the bare f-level position and the conduction-electron bandwidth. The splittings may then be large or small compared with the Kondo temperature.

The thermodynamic properties of the model are calculated from certain pseudo-energy functions $\varepsilon_n^{(r)}(\lambda)$, $n=1,\ 2,...,\ \infty$, $1\le r\le N$-1 that are determined by the TBA equations [14] (with $\varepsilon_0^{(r)} = -\infty$):

$$\begin{aligned} &-\ln\{\,1+\exp[\,-\varepsilon_n^{(r)}(\lambda)/T]\,\}\\ &= -\sin(r\pi/N)\exp[\lambda]\delta_{n,1} + \sum_{q=1}^{N-1} S_q^r * (\ln\{1+\exp[\varepsilon_{n+1}^{(q)}(\lambda)/T]\}\\ &+\ln\{1+\exp[\varepsilon_{n-1}^{(q)}(\lambda)/T]\} - s^{-1} * \ln\{1+\exp[\varepsilon_n^{(q)}(\lambda)/T]\}). \end{aligned} \tag{5}$$

Here $s*f(\lambda)$ denotes the convolution $s*f(\lambda) = \int_{-\infty}^{\infty} s(\lambda-\lambda')f(\lambda')\,d\lambda'$, and the kernels S_q^r are given by their Fourier transforms:

$$S_q^r(\omega) = \frac{\sinh(\min(q,r)\pi\omega/N)\sinh((N-\max(q,r))\pi\omega/N)}{\sinh(\pi\omega)\sinh(\pi\omega/N)}$$

and

$$s^{-1}(\omega) = 2\cosh(\pi\omega/2).$$

The free energy at temperature T is given by the following expression:

$$F = -T\sum_{r=1}^{N-1}\int_{-\infty}^{\infty}\frac{\sin(r\pi/N)\ln\left\{1+\exp\left[\varepsilon_1^{(r)}(\lambda)/T\right]\right\}d\lambda}{\left\{\cosh\left[\lambda - \ln(T_K/T)\right] - \cos(r\pi/N)\right\}2\pi} \tag{6}$$

The thermodynamic properties depend only on the ratio T/T_K and on the external fields scaled by T_K. The definition of the Kondo temperature $T_K \equiv T_K(N)$ used here connects it with the linear specific heat coefficient in the absence of all fields $\gamma_0 = C/T$ for $T\to 0$ through $T_K(N) = (N\text{-}1)\pi/(3\gamma_0)$.

By introducing $g_n^{(r)}(\lambda) \equiv \ln\{1+\exp[\varepsilon_n^{(r)}(\lambda)/T]\}$ Eq. (5) can be written for $n\ge 2$ in the following form (with $g_n^{(0)} = g_n^{(N)} \equiv \infty$):