

Crystal fields and Kondo effect: Specific heat for Cerium compounds



H.-U. Desgranges

Scientifically unaffiliated, Albert-Kusel-Str. 25, Celle, Germany

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ABSTRACT

The thermodynamic Bethe ansatz equations for the $N=6$ Coqblin-Schrieffer model with crystal fields have been solved numerically. The realistic case of three Kramers doublets with arbitrary splittings has been studied for the first time. The specific heat has been calculated for representative combinations of the ionic energy splittings providing ample material for comparison with experimental results for Cerium impurities and compounds.

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1. Introduction

The single ion Kondo model and its generalization to a N -fold degenerate ionic configuration, the $SU(N)$ Coqblin-Schrieffer [1] model, has been used successfully to describe the thermodynamic properties of dense Kondo systems [2,3,4]. Apparent non-Fermi-liquid like behavior has been explained (within an $N=4$ approximation) as stemming from the interplay of Kondo effect and crystal field splitting [5,6].

The change of the effective spin-degeneracy N due to the interplay between Kondo and crystal field effects has been studied experimentally by investigating various Cerium based pseudo-ternary intermetallic substitution series [7]. Specific heat data have been fitted by combining exact $N=2$ Bethe ansatz or resonant level model results with crystal field Schottky terms [8].

Within the exact solution [9,10] of the Coqblin-Schrieffer model by Bethe ansatz the specific heat was calculated already for three special cases of crystal field configurations: (a) the case that the $N=6$ multiplet is split into a Γ_6 doublet and a Γ_8 quartet by small cubic crystal fields [11], (b) the case that a low lying quartet is further split into two doublets while the highest doublet can be neglected, resulting in an effective $N=4$ model [12], and (c) the case that the $N=6$ multiplet is split into three equidistant Kramers doublets [13] (cf. Fig. 1).

In the two latter cases it was possible to treat the full range of crystal field splittings showing in the specific heat the separation for large crystal fields into an effective spin-1/2 ($N=2$) Kondo peak at low temperatures and a Schottky-type peak at high

temperatures. In all three cases a shoulder like structure develops for low to intermediate crystal fields. In the case of a low lying Γ_8 quartet the shoulder appears at the high temperature side of the peak.

In the present work the above cases have been generalized to the case of three Kramers doublets with arbitrary splittings. Also case (a) has been reexamined numerically and extended to higher crystal field strengths.

These new results allow a quantitative comparison with experimental data that makes it possible to identify deviations from single-ion behavior. They also show how the interplay between crystal fields and Kondo effect reduces the effective spin-degeneracy N .

2. Model and thermodynamic 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 $C_{k,r}^\dagger$ where the exchange interaction is given by a permutation operator:

$$H = \sum_{k,r} k C_{k,r}^\dagger C_{k,r} + J \sum_{k,r;k',r'} |r\rangle\langle r'| C_{k',r'}^\dagger C_{k,r} + \sum_r E_r |r\rangle\langle r| \quad (1)$$

For integrability of the model a linear dispersion of the conduction electron energy is assumed as well as a small exchange coupling J independent of r . The Bethe ansatz solution requires also an ad hoc cut-off D that enters the Kondo temperature (non-universally defined here as) $T_K \sim D \exp(-1/N|J|)$.

The thermodynamic properties of the model are calculated from certain pseudo-energy functions $\varepsilon_n^{(r)}(\lambda)$, $N=1, 2, \dots, \infty$, $1 \leq r \leq N-1$ that are determined by the Bethe ansatz equations [9].

E-mail address: H-Ulrich.Desgranges@nexgo.de

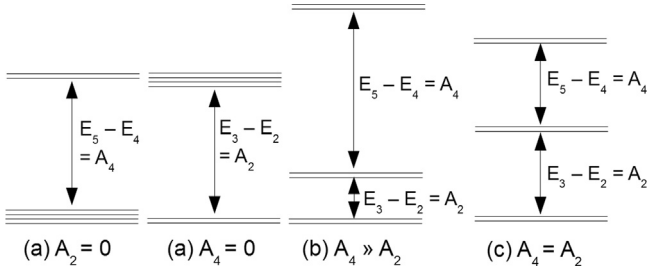


Fig. 1. The energy levels for the ionic ground state of Ce^{3+} ions in cubic crystal fields: case (a) and in non-cubic crystal fields considered in cases (b) $A_4 \gg A_2 \equiv A$ and (c) $A_4 = A_2 \equiv A$.

In the scaling limit $J \rightarrow 0$, $D \rightarrow \infty$, T_K kept fixed these read (with $\varepsilon_0^{(r)} = -\infty$):

$$\begin{aligned} -\ln\{1 + \exp[-\varepsilon_n^{(r)}(\lambda)/T]\} &= -\sin(r\pi/N) \exp[\lambda] \delta_{n,1} \\ + \sum_{q=1}^{N-1} S_q^r * (\ln\{1 + \exp[\varepsilon_{n+1}^{(q)}(\lambda)/T]\} + \ln\{1 + \exp[\varepsilon_{n-1}^{(q)}(\lambda)/T]\} \\ - s^{-1} * \ln\{1 + \exp[\varepsilon_n^{(q)}(\lambda)/T]\}), \end{aligned} \quad (2)$$

where $s * f(\lambda)$ 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:

$$S_q^r(\omega) = \frac{\sin h(\min(q, r)\pi\omega/N) \sin h((N - \max(q, r))\pi\omega/N)}{\sin h(\pi\omega) \sin h(\pi\omega/N)} \quad \text{and} \\ s^{-1}(\omega) = 2 \cosh(\pi\omega/2).$$

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

$$F = -T \sum_{r=1}^{N-1} \int_{-\infty}^{\infty} \frac{\sin(r\pi/N) \ln\{1 + \exp[\varepsilon_1^{(r)}(\lambda)/T]\} d\lambda}{\{\cosh[\lambda - \ln(T_K/T)] - \cos(r\pi/N)\} 2\pi} \quad (3)$$

The thermodynamic properties in the absence of external fields depend only on the ratio T/T_K . $T_K \equiv T_K(N)$ can be related by the universal Wilson number [14] to the conventionally defined Kondo temperature. It is connected with the linear specific heat coefficient $\gamma = C/T$ for $T \rightarrow 0$ through $T_K(N) = (N-1) \pi / (3\gamma)$.

The numerical solution of the type of Eq. (2) has become standard practice since their first occurrence [15] with the spin-1/2 ($N=2$) Kondo model, provided that the limiting values $\varepsilon_n^{(r)}(\lambda)$ for $\lambda \rightarrow \pm \infty$ are known. For $n \geq 2$ the equations can be written in the following form [10]:

$$\begin{aligned} \varepsilon_n^{(r)}/T &= s * \ln\{1 + \exp[\varepsilon_{n+1}^{(r)}(\lambda)/T]\} + s * \ln\{1 + \exp[\varepsilon_{n-1}^{(r)}(\lambda)/T]\} \\ &- s * \ln\{1 + \exp[-\varepsilon_n^{(r+1)}(\lambda)/T]\} - s * \ln\{1 + \exp[-\varepsilon_n^{(r-1)}(\lambda)/T]\}. \end{aligned} \quad (4)$$

In the limit $\lambda \rightarrow -\infty$ the integral equations reduce to the following algebraic recurrence relations (with the notation: $g_r^{(r)} \equiv \ln\{1 + \exp[\varepsilon_n^{(r)}(-\infty)/T]\}$, $b_n^{(r)} \equiv -\ln\{1 - \exp[-g_n^{(r)}]\}$):

$$\begin{aligned} g_n^{(r)} - \frac{1}{2} (g_{n+1}^{(r)} + g_{n-1}^{(r)}) &= b_n^{(r)} - \frac{1}{2} (b_{n+1}^{(r)} + b_{n-1}^{(r)}), \\ g_0^{(r)} &= 0, \quad b_n^{(0)} = b_n^{(N)} = 0 \\ \lim_{n \rightarrow \infty} g_{n+1}^{(r)} - g_n^{(r)} &= A_r/T. \end{aligned} \quad (5)$$

where the generalized fields A_r ($A_r \geq 0$) are related to the energy levels E_r of the ionic ground state in the particular crystal field configuration: $A_r = E_{r+1} - E_r$, $1 \leq r \leq N-1$, cf. Fig. 1.

An analytic solution to Eq. (5) is known only in the magnetic field case ($A_r = g_{\mu_B} H$ for all r). In the above cases (b) and (c) a numerical solution was accomplished by an interval halving method [13]. This was facilitated by the fact that in both cases only one field parameter $A_2 \equiv A$ has to be taken into account (cf. Fig. 1, $A_1 = A_3 = A_5 = 0$), and that due to the symmetry $r \rightarrow N-r$ of Eq. (5) the problem reduces to a two-dimensional one in case (b) and a three-dimensional in case (c). In the general case of unequal

Kramers splittings $A_4 \neq A_2$ the problem is five-dimensional and this method appears not to be feasible.

In order to overcome this problem a new strong field (or low temperature) expansion has been devised for the case (c) that has then been generalized to the new case (d) of three Kramers doublets with unequal splittings ($A_4 \neq 0$, $A_2 \neq 0$) and to case (a) ($A_2 = 0$ or $A_4 = 0$). The physical backing for this expansion comes from the observation that for large values of the crystal field splitting the system can essentially be described as an effective spin-1/2 ($N=2$) Kondo system (or an effective spin-3/2 ($N=4$) system for the case (a) with $A_2 = 0$).

We look exemplarily at the cases (c) and (d) describing three Kramers doublets. Writing $A_4 = x A$, $A \equiv A_2$ ($x > 0$), for $A/T \rightarrow \infty$ we observe the decoupling of Eq. (5) due to $b_n^{(2)} \rightarrow 0$, $b_n^{(4)} \rightarrow 0$ for $A/T \rightarrow \infty$. The solution to (5) is then

$$\begin{aligned} g_n^{(t)}(A/T \rightarrow \infty) &= 2 \ln(n+1), \quad t = 1, 3, 5 \\ g_n^{(s)}(A/T \rightarrow \infty) &= n A_s/T - \frac{1}{2} \{g_n^{(s+1)}(A/T \rightarrow \infty) + g_n^{(s-1)}(A/T \rightarrow \infty)\}, \\ & \quad s = 2, 4 \end{aligned} \quad (6)$$

We now introduce the deviations from the strong field limit as

$$g_n^r = g_n^r(A/T \rightarrow \infty) + u_n^{(r)}, \quad 1 \leq r \leq 5 \quad (7)$$

and rewrite Eq. (5) in terms of $u_n^{(r)}$:

$$\begin{aligned} u_n^{(t)} - \frac{1}{2} \{u_{n+1}^{(t)} + u_{n-1}^{(t)}\} + \ln\{1 - k_n[\exp(-u_n^{(t)}) - 1]\} \\ = \frac{1}{2} \ln\{1 - (n+1)^2 \exp(-n A_{t+1}/T - u_n^{(t+1)})\} \\ + \frac{1}{2} \ln\{1 - (n+1)^2 \exp(-n A_{t-1}/T - u_n^{(t-1)})\}, \quad t = 1, 3, 5 \\ u_n^{(s)} - \frac{1}{2} \{u_{n+1}^{(s)} + u_{n-1}^{(s)}\} + \ln\{1 - (n+1)^2 \exp(-n A_s/T - u_n^{(s)})\} \\ = \frac{1}{2} \ln\{1 - k_n[\exp(-u_n^{(s+1)}) - 1]\} + \frac{1}{2} \ln\{1 - k_n[\exp(-u_n^{(s-1)}) - 1]\}, \\ s = 2, 4 \\ \text{with } A_0 \equiv A_6 \equiv \infty \text{ and } k_n = [n(n+2)]^{-1}. \end{aligned} \quad (8)$$

Eq. (8) allows for a systematic expansion of $u_n^{(r)}$ in powers of $\exp(-A/T)$ and are also amenable to a numerical treatment by iteration.

From this expansion we have come to the following formulae for the general case (d) confirmed by numerical evaluation:

$$\begin{aligned} g_n^{(t)} &= 2 \ln[n+1 + \alpha^{(t)}] + O(\exp(-(n+1) \text{Min}(A_s)/T)), \quad t = 1, 3, 5 \\ \alpha^{(1)} &= \frac{-2 \exp(-A_2/T)}{1 - \exp(-A_2/T)} + \frac{-2 \exp(-(A_2 + A_4)/T)}{1 - \exp(-(A_2 + A_4)/T)} \\ \alpha^{(3)} &= \frac{-2 \exp(-A_2/T)}{1 - \exp(-A_2/T)} + \frac{-2 \exp(-A_4/T)}{1 - \exp(-A_4/T)} \\ \alpha^{(5)} &= \frac{-2 \exp(-A_4/T)}{1 - \exp(-A_4/T)} + \frac{-2 \exp(-(A_2 + A_4)/T)}{1 - \exp(-(A_2 + A_4)/T)} \\ g_n^{(s)} &= n A_s/T - \frac{1}{2} \{g_n^{(s+1)} + g_n^{(s-1)}\} + f_s(A_2/T, A_4/T) \\ & \quad + O(\exp(-(n+1) \text{Min}(A_s)/T)), \quad s = 2, 4 \\ f_2(A_2/T, A_4/T) &= -4 \ln[1 - \exp(-A_2/T)] + 2 \ln[1 - \exp(-A_4/T)] \\ & \quad - 2 \ln[1 - \exp(-(A_2 + A_4)/T)] \\ f_4(A_2/T, A_4/T) &= 2 \ln[1 - \exp(-A_2/T)] - 4 \ln[1 - \exp(-A_4/T)] \\ & \quad - 2 \ln[1 - \exp(-(A_2 + A_4)/T)] \end{aligned} \quad (9)$$

We can determine $g_n^{(r)}$ numerically if we first truncate Eq. (8) at some large value m , solve them for $u_{m-1}^{(r)}$, then insert $g_{m+1}^{(r)}$ and $g_m^{(r)}$ according to (9) via (7) and compute all $u_n^{(r)}$ with $0 \leq n \leq m-1$ down the chain; $u_0^{(r)}$ computed this way will in general not be equal to 0. Next we set $u_0^{(r)} = 0$ and use the computed $u_n^{(r)}$ with $1 \leq n \leq m-1$ as starting values that we insert into the original form of the truncated Eq. (8) and calculate $u_n^{(r)}$, $1 \leq n \leq m$ up the chain. We take the obtained values of $u_n^{(r)}$ as new starting values for the

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