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Interpretation of experimental results on Kondo systems with crystal field

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Abstract

We present a simple approach to calculate the thermodynamic properties of single Kondo impurities including orbital degeneracy and crystal field effects (CFE) by extending a previous proposal by Schotte and Schotte (1975 *Phys. Lett.* **55A** 38). Comparison with exact solutions for the specific heat of a quartet ground state split into two doublets shows deviations below 10% in the absence of CFE and a quantitative agreement for moderate or large CFE. As an application, we fit the measured specific heat of the compounds CeCu₂Ge₂, CePd₃Si_{0.3}, CePdAl, CePt, Yb₂Pd₂Sn and YbCo₂Zn₂₀. The agreement between theory and experiment is very good or excellent depending on the compound, except at very low temperatures due to the presence of magnetic correlations (not accounted for in the model).

Keywords: Kondo effect crystal field, Ce compounds, Yb compounds

(Some figures may appear in colour only in the online journal)

1. Introduction

In the last decades, heavy fermion systems and intermediate valence compounds have attracted considerable attention because of their fundamental importance in modern solid state physics [1]. Different ingredients contribute to the complexity of these fascinating systems: the presence of strong Kondo interactions, the level structure originated in crystal field effects (CFE) including different hybridization strengths with the conduction band, and possible coherence effects introduced by the periodicity of the lattice and intersite magnetic interactions.

Usually above a certain coherence temperature, several Ce [2, 3] and Yb [4–6] compounds, for example, can be described by an impurity Anderson model or the impurity Kondo model, which is the integer-valent limit of the former when the magnetic configuration dominates. These systems behave as conventional Fermi liquids [7], although with a very large effective mass m^* [8, 9]. Other systems display non-Fermi-liquid behavior [10], but they are outside the scope of this work.

The impurity Anderson model and several variants of it have been solved exactly using the Bethe-ansatz technique [11–19, 22]. Desgranges and Schotte have calculated the specific heat for the spin-1/2 Kondo model solving numerically the resulting system of integral equations [16]. Exact results in the presence of crystal field have been reported by several authors [17–19, 22]. In particular, Desgranges and Schotte calculated the specific heat of a system of two doublets [17].

A limitation of these exact solutions when CFE are present is that the hybridization of different multiplets are considered to be the same, which usually is not the case in real systems. Another drawback is that to calculate thermodynamic quantities, the Bethe-ansatz leads to a set of integral equations, which should be solved numerically, rendering it very difficult to use the exact solutions as a tool to fit experimental data. The numerical renormalization group (NRG) is a very accurate numerical technique which has the advantage over the Bethe-ansatz that there are no restriction for the impurity Hamiltonian [20]. For example, an Anderson model that mixes a doublet with either a singlet or a triplet can be exactly solved [13], but not when both singlet and triplet

are present, while the NRG can treat the complete model and describe the quantum phase transition between singlet and doublet ground states [21]. However, the calculations are numerically demanding. To the best of our knowledge neither exact results nor NRG has been used to fit experimental results in which non-trivial CFE are present.

Recent increases in the available experimental data of physical properties at intermediate temperature ($T > 10$ K) on intermetallic compounds renders necessary the analysis of experimental data with the inclusion of CFE.

In the absence of crystal field, Schotte and Schotte proposed a simplified approach based on the resonant level model to interpret experiments of spin-1/2 Kondo systems in a magnetic field [23]. The theory assumes a linear increase of the splitting of the peaks with magnetic field, which is only approximately true according to Bethe-ansatz results [24]. In spite of this fact, the authors were able to fit the magnetization of Fe impurities in Ag as a function of magnetic field and the magnetic susceptibility as a function of temperature very accurately [23]. For the specific heat, the comparison between this approach with exact solutions shows an excellent agreement [16].

In this work we extend the approach to include CFE and apply the results to interpret the specific heat of several Ce and Yb compounds, for which one expects that single impurity behavior in the Kondo limit (oxidation state near Ce^{3+} or Yb^{3+}) and Fermi-liquid physics applies down to low temperatures. The approximations are described in section 2. The resulting approximate analytical results are compared with available exact results in section 3. In section 4 we apply our approach to four Ce ($CeCu_2Ge_2$, $CePd_3Si_{0.3}$, $CePdAl$ and $CePt$) and two Yb (Yb_2Pd_2Sn and $YbCo_2Zn_{20}$) compounds. We summarize our results in section 5.

2. Approximations

We start from a generalization of the approach proposed by Schotte and Schotte [23] to the case of two doublets split by a crystal field Δ or, alternatively, a quadruplet with different g factors, in both cases with the possible application of a magnetic field. Specifically we postulate the following simplified form of the free energy for two doublets:

$$F_{2d} = -k_B T \int_{-\infty}^{\infty} d\omega \frac{1}{\pi} \left[\frac{\Gamma_0}{(\omega - \Delta_0)^2 + \Gamma_0^2} + \frac{\Gamma_1}{(\omega - \Delta_1)^2 + \Gamma_1^2} \right] \ln \left(e^{\frac{\omega}{2k_B T}} + e^{-\frac{\omega}{2k_B T}} \right), \quad (1)$$

where Γ_i represents the half-width at half-maximum of the spectral density for the doublet i , $\Delta_1 = \Delta + s$, where $s \leq \Gamma_0$ is a small shift that can be disregarded for the moment, $\Delta_0 = B_0 + s$ and $B_0 = g_0 \mu_B \tilde{B}$ is the Zeeman magnetic splitting of the doublet ground state by the magnetic field \tilde{B} . The Kondo temperature T_K is proportional to the width of the ground-state doublet, Γ_0 , as explained in detail in section 3. Note that in the absence of hybridization effects (i.e. $\Gamma_i = 0$), except for

an irrelevant additive constant, F_{2d} reduces to

$$F_{2d}^0 = -k_B T \ln \left(e^{\frac{B_0/2}{k_B T}} + e^{-\frac{B_0/2}{k_B T}} + e^{\frac{\Delta+B_0/2}{k_B T}} + e^{-\frac{\Delta+B_0/2}{k_B T}} \right), \quad (2)$$

which corresponds to the free energy of two doublets separated by an energy Δ , both split by a magnetic field in the same fashion. Although the latter fact is not realistic, for the usual cases in which $\Delta \gg B_0$, the individual levels of the excited doublet have a similar population for all temperatures and their magnetic splitting becomes irrelevant. The same situation occurs for $\Gamma_1 \gg B_0$. Thus we expect that equation (1) is a reasonable approximation in general.

An alternative scenario to which equation (1) can be applied is a quadruplet split by a magnetic field. In that case the corresponding energies are $\pm g_0 \mu_B \tilde{B}/2$ and $\pm g_1 \mu_B \tilde{B}/2$ and one should consider $\Gamma_1 = \Gamma_0$, $\Delta_1 = (g_0 + g_1) \mu_B \tilde{B}/2$ and $\Delta_0 = (g_0 - g_1) \mu_B \tilde{B}/2$.

The integral in equation (1) with a cutoff D can be expressed in terms of the Gamma function $\Gamma(x)$:

$$F_{2d} = 2k_B T \text{Re} \sum_{j=0}^1 \left\{ \ln \Gamma \left(1 + \frac{\Gamma_j + i\Delta_j}{\pi k_B T} \right) - \ln \Gamma \left(1 + \frac{\Gamma_j + i\Delta_j}{2\pi k_B T} \right) \right\} - \left(\frac{\Gamma_0 + \Gamma_1}{\pi} + 2k_B T \right) \ln 2 + \frac{\Gamma_0 + \Gamma_1}{\pi} \left(1 - \ln \frac{D}{k_B T} \right). \quad (3)$$

In practice, we find that for small bare splitting Δ , it is convenient to increase the position of both doublets by a shift s with $0 < s \leq \Gamma_0$. This can be understood as follows. For the $SU(2)$ model, the approximation of Schotte and Schotte seems to be inspired by the fact that the electron spectral density has a resonance centered at the Fermi energy, in such a way that in the Kondo limit, with total electron occupation 1 at the impurity, both spins have occupation 1/2. This becomes clear in Fermi-liquid approaches, in which the resonance near the Fermi energy can be accurately described [25, 26]. However, when the hybridization between the impurity and conduction electrons is the same for both doublets and $\Delta = 0$, the model has $SU(4)$ symmetry [27–33], each fermion should have an occupation near 1/4, and this means that the resonance is displaced above the Fermi energy [31, 32]. For general hybridizations and zero magnetic field, integrating the spectral densities (in a similar way as in the slave-boson mean-field approximation [32]), one finds that to enforce a total occupation 1 (as corresponding to Ce and Yb impurities in the Kondo limit) in a mean-field approach, the shift s should satisfy

$$\frac{2}{\pi} \left[\arctan \frac{\Gamma_0}{s} + \arctan \frac{\Gamma_1}{s + \Delta} \right] = 1, \quad (4)$$

which is equivalent to

$$\Delta_0 \Delta_1 = \Gamma_0 \Gamma_1, \quad (5)$$

where we have used that $\Delta_0 = s$ for $B = 0$. The extension of this heuristic approach to finite magnetic field is beyond

the scope of the present work. In any case the above equation shows that s is negligible for large Δ .

In Ce compounds, the Hund's rules ground state with total angular momentum $j = 5/2$ is split into a quartet and a doublet, or three doublets depending on the point group determined by the symmetry around the Ce atom. Therefore, for a comparison with experiment, a third doublet should be included. Note that including a third term between brackets in equation (1) would mean that eight (not six) broadened levels are considered (as it is clear taking all $\Gamma_i = 0$). Therefore, a straightforward extension of this equation to include three doublets is not possible. However, if the width of the levels Γ_i is much smaller than the splitting Δ_2 between the third and the first doublet, we can take at high temperatures the simple Schottky expression F_S , which corresponds to all $\Gamma_i = 0$:

$$F_S = -k_B T \ln \left(2c_0 + 2c_1 e^{-\frac{\Delta_1}{k_B T}} + 2c_2 e^{-\frac{\Delta_2}{k_B T}} \right), \quad (6)$$

$$c_i = \cosh(g_i \mu_B \tilde{B}/2).$$

A similar reasoning can be followed for more doublets. This leads to the following proposal to describe the free energy for three doublets, or a quartet ground state and an excited doublet:

$$F = F_{2d} - F_{2d}^0 + F_S. \quad (7)$$

For small temperatures F_{2d} dominates, while the remaining two terms become important when $k_B T$ reaches values near Δ_2 . This will become apparent in section 4. Note that this form ensures the correct limit ($k_B \ln 6$) for the entropy as $T \rightarrow \infty$. For a ground-state doublet and an excited quadruplet, F_{2d} and F_{2d}^0 should be replaced by the corresponding expressions for one doublet in which the terms containing Δ_1 are absent. Extension of equation (7) to include more doublets (like, e.g., in the case of Yb systems with $J = 7/2$) with width much smaller than its excitation energy is straightforward.

The specific heat and magnetic susceptibility of the system can be obtained differentiating equation (7) [23]. Here for later use, we give the expression of the specific heat at zero magnetic field ($\tilde{B} = 0$):

$$C = C_{2d} - \frac{1}{k_B T^2} \left[\frac{\Delta^2 e^{-\frac{\Delta}{k_B T}}}{(1 + e^{-\frac{\Delta}{k_B T}})^2} \right] + C_S, \quad (8)$$

where the specific heat for only two doublets or a quartet $C_{2d} = -T \partial^2 F_{2d} / \partial T^2$ becomes

$$C_{2d} = -\frac{k_B}{2(\pi k_B T)^2} \mathbf{Re} \sum_{j=0}^1 \left\{ (\Gamma_j + i\Delta_j)^2 \times \left[4\psi' \left(\frac{\Gamma_j + i\Delta_j}{\pi k_B T} \right) - \psi' \left(\frac{\Gamma_2 + i\Delta}{2\pi k_B T} \right) \right] \right\} + \frac{\Gamma_0 + \Gamma_1}{\pi T}, \quad (9)$$

where ψ' is the derivative of the digamma function and C_S is the Schottky expression for the specific heat obtained deriving equation (6):

$$C_S = \frac{1}{k_B T^2} [(\Delta_1)^2 e^{-\frac{\Delta_1}{k_B T}} + (\Delta_2)^2 e^{-\frac{\Delta_2}{k_B T}} + (\Delta_2 - \Delta_1)^2 e^{-\frac{\Delta_2 + \Delta_1}{k_B T}}] \cdot ((1 + e^{-\frac{\Delta_1}{k_B T}} + e^{-\frac{\Delta_2}{k_B T}})^2)^{-1}. \quad (10)$$

For later use, we give here the coefficient γ of the first term in the low-temperature expansion $C = \gamma T + O(T^2)$ of the specific heat:

$$\gamma = \frac{\pi k_B^2}{3} \sum_{j=0}^1 \frac{\Gamma_j}{\Delta_j^2 + \Gamma_j^2}. \quad (11)$$

3. Comparison with exact solutions

While several works discuss the solution of the Bethe-ansatz equations with CFE [17–19, 22], to the best of our knowledge, the solution in a wide range of temperatures has been reported only by Desgranges and Rasul [17]. These authors calculated the specific heat as a function of temperature for a quartet split into two doublets by an energy Δ and zero magnetic field. For $\Delta = 0$, this Kondo model has $SU(4)$ symmetry, which is reduced to $SU(2)$ as soon as $\Delta > 0$. This $SU(4) \rightarrow SU(2)$ model, and the corresponding (more general) Anderson one, has become popular recently in the context of nanoscopic systems [27–31, 33, 32]. It describes, for example, quantum dots in carbon nanotubes, [27, 28, 30–32] and silicon nanowires [33, 32] in the presence of a magnetic field and interference effects in two-level systems [29, 34].

Before comparing the results of [17] with ours, it is convenient to discuss briefly the meaning of the Kondo temperature in systems with CFE.

3.1. The Kondo temperature

We define the Kondo temperature T_K as the binding energy of the ground-state singlet, as done for example in a perturbative-renormalization-group study of the Kondo model with CFE [35] or variational (non-perturbative) methods [6, 31]. Alternative definitions, like for example from the width of the lowest peak in the spectral density [31, 32], temperature dependence of transport properties [32, 36] or the linear term in the specific heat [17], give the same result within a factor of the order of 1, but the leading exponential dependence on the parameters is the same. In the extreme limits in which either no CFE are present or they are so large that only the ground-state multiplet matters, the Kondo temperature is given by the usual expression for an $SU(N)$ Kondo model:

$$T_K^{SU(N)} = D \exp(-2\rho J/N), \quad (12)$$

where N is the degeneracy of the ground state, D half the bandwidth, J the exchange interaction and ρ the conduction density of states at the Fermi level.

For the case of a quartet split into two doublets (the $SU(4) \rightarrow SU(2)$ model mentioned above), using a simple variational function, it has been found that the Kondo

Table 1. Parameters Γ_i , Δ_1 used in the fit of figure 1 in units of $T_K^{\text{DR}}/3$. The first column corresponds to the Kondo temperature given by equation (13) and the last to the shift determined by equation (5).

Δ	$0.6T_K$	Γ_0	Γ_1	Δ_1	Δ_0
0	1/3	1/3	1/3	1/3	1/3
1	0.173	0.237	0.4	0.94	0.1009
2	0.118	0.14	0.47	1.75	0.0376
4	0.0806	0.078	0.55	3.49	0.0123

temperature as a function of the splitting Δ can be written as [31]

$$\frac{T_K(\Delta)}{T_K(0)} = \sqrt{1 + \delta/d + \delta^2} - \delta, \quad (13)$$

$$\delta = \frac{\Delta}{2T_K(0)}, \quad d = \frac{D}{2T_K(0)},$$

where, of course, $T_K(0) = T_K^{\text{SU}(4)}$ and from the above equations $T_K(\infty) = T_K^{\text{SU}(2)}$.

Using the non-crossing approximation, the width of the peak nearest to the Fermi energy of the spectral density has been found to be accurately described by equation (13) within a constant factor near 0.6 [31].

3.2. The specific heat for two doublets

The exact Bethe-ansatz solution of the specific heat of the Kondo model for a quartet split into two doublets has been reported by Desgranges and Rasul [17]. In figure 1 we compare their results with our simplified proposal for the specific heat, equation (9). The authors define their Kondo temperature T_K^{DR} by the condition that, in the $SU(4)$ case $\Delta = 0$, the term linear in temperature T in the specific heat for $T \rightarrow 0$ is $\gamma = k_B\pi/T_K^{\text{DR}}$. In our case $SU(4)$ symmetry and equation (5) imply $\Delta_0 = \Delta_1 = \Gamma_0 = \Gamma_1$. For these parameters, equation (11) gives $\gamma = k_B\pi/(3\Gamma_1)$. Comparing this result with the corresponding one of Desgranges and Rasul fixes $\Gamma_0 = T_K^{\text{DR}}/3$. Except for this, there are no fitting parameters for zero splitting in our approach. Taking into account this fact, we find that the agreement is very satisfactory. Our approach underestimates the maximum in the specific heat by about 10%, but the overall trend and the low-temperature part are well reproduced. The comparison is, however, much better when the splitting Δ reaches T_K or higher values. In fact, for large Δ , the lower peak corresponds to the ordinary Kondo model with one doublet, for which the approach works very well [16].

As soon as $\Delta > 0$, we use three parameters to fit the exact results: both Γ_i and Δ_1 , with the position of the lower doublet $\Delta_0 = s$ determined by the condition (5). As discussed below, the resulting parameters are consistent with expectations from known results on the $SU(4) \rightarrow SU(2)$ symmetry breaking. The fitting parameters are displayed in table 1, together with the corresponding shift.

The first column of table 1 is an estimate of Γ_0 based on the expected dependence of the Kondo temperature

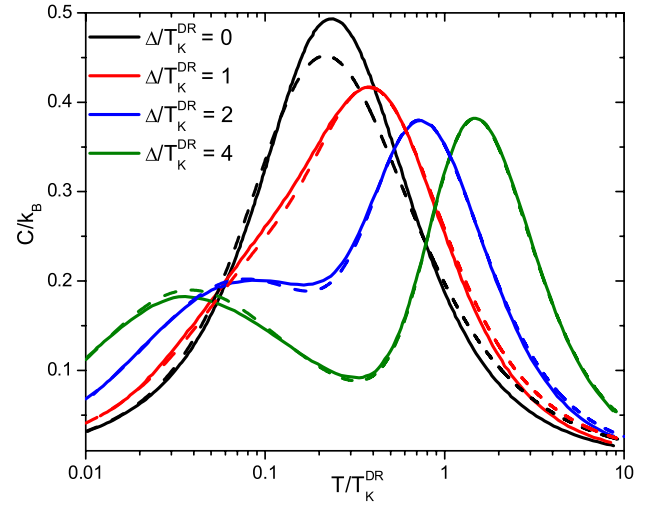


Figure 1. Impurity contribution to the specific heat for a Kondo model with two doublets. Full lines correspond to exact results of [17] and dashed lines to our approach. The absolute maximum displaces to higher temperatures with increasing Δ .

with splitting, equation (13). Results using the non-crossing approximation show that the width of the peak near the Fermi energy in the spectral density is proportional to T_K for all Δ [31]. The proportionality factor for the charge transfer energy used was found to be 0.606. We assume $\Gamma_0 = 0.6T_K$. Using this relation for $\Delta = 0$, the ratio $T_K^{\text{SU}(4)}/T_K^{\text{DR}}$ is obtained, and for the other values of Δ , equation (13) was used, with a bandwidth $2D = 10T_K^{\text{DR}}$. Larger values of D lead to lower values of T_K but have little effect on the values for $\Delta \geq 4T_K^{\text{DR}}$. As seen in table 1, the estimate of the width of the lowest peak in the spectral density agrees with Γ_0 within 30%, while the values of Γ_0 for different values of Δ vary by more than a factor of 4. This is a strong indication that the value of Γ_0 that results from the fit is proportional to the binding energy of the ground-state singlet.

Concerning Γ_1 , one observes a moderate increase as Δ increases, a fact also shared by the spectral density studied before [31]. One way to understand this fact is to consider the spectral density of the simplest $SU(2)$ Anderson model in the Kondo regime, under an applied magnetic field B (which, for the peak at higher energies, is a simpler analog of the $SU(4)$ model under a magnetic or crystal field). Clearly, the width of the resonance is proportional to $T_K^{\text{SU}(2)}$ for $B = 0$. As B increases, the Kondo effect is progressively destroyed and for very large B one expects that the width of the peak in the spectral density is just the resonant level width, which is larger than T_K . This is consistent with Bethe-ansatz results [24]. These results also show that the position of the peak is lower than the magnitude of the Zeeman term, but tends to it for large B , in agreement with the fact that our fit gives $\Delta_1 < \Delta$ for $\Delta > 0$. Calculations of the spectral density in the $SU(4) \rightarrow SU(2)$ case, show peaks above and below the Fermi energy (depending on the component), with excitation energies smaller than Δ [31], a fact also consistent with the fitting results.

4. Application to real systems

In this section, we apply our approach to interpret the specific heat measured on four Ce and two Yb compounds at zero applied magnetic field. These systems have an oxidation state of the magnetic atom near Ce^{3+} or Yb^{3+} (they are in the Kondo regime) and seem to display Fermi-liquid single-ion behavior down to low temperatures. The Ce compounds ($CeCu_2Ge_2$, $CePd_3Si_{0.3}$, $CePdAl$ and $CePt$ with increasing Kondo temperature T_K) order at low temperatures. Above this ordering temperature, one expects that the system can be described by a generalized impurity Kondo model, for which our approach was developed. The Yb compounds that we considered (Yb_2Pd_2Sn and $YbCo_2Zn_{20}$) do not order down to very low temperatures.

As is known, the possibility of ordering depends on the magnitude of the exchange interaction J between localized spins and conduction electrons. For small J the indirect Ruderman–Kittel–Kasuya–Yosida (RKKY) exchange interaction between localized spins is much larger than T_K and the system orders, while for large J single-ion Kondo physics dominates down to zero temperature and the system does not order. This is the basis of the so-called Doniach phase diagram [37]. For only one doublet, the critical ordering temperature T_N as a function of J has been calculated using the exact magnetic susceptibility of the impurity system and treating the RKKY interaction at a mean-field level [38]. T_N first increases quadratically with J , reaches a maximum and then decreases until it vanishes at a quantum critical point $J = J_c$. Near this point obviously $T_N \ll T_K$, whereas for very small J , $T_N \gg T_K$. In general we expect that our theory is valid for $T > T_N$, even if $T_N > T_K$ as for the case of $CeCu_2Ge_2$ discussed below.

4.1. $CeCu_2Ge_2$

The structure of $CeCu_2Ge_2$ is tetragonal. Compounds with this structure were intensively investigated after the discovery of superconductivity in $CeCu_2Si_2$ [39]. The specific heat of the Ge compound is reported in figure 1 of [40].

In figure 2 we fit the magnetic contribution to specific heat data. The tetragonal symmetry, in particular the point group symmetry D_{4h} around the Ce^{3+} ions, implies that the $j = 5/2$ ground-state multiplet splits into three doublets. Thus, we can apply equations (8)–(10). In principle, our expression for the specific heat has four fitting parameters (Γ_0 , Γ_1 , Δ_1 and Δ_2). The shift $\Delta_0 = s$ calculated with equation (5) is very small and does not provide any significant change in the fit. We have neglected it for all the Ce compounds studied. In practice, however, we have used only the Γ_i as fitting parameters, taking the same values of Δ_i as in the Schottky expression with three doublets, equation (10), provided in [40] to compare with the experimental results. This expression overestimates the peak near 70 K by about 20% (see figure 1 of [40]) and underestimates the specific heat between 12 and 25 K. Instead, as is apparent in figure 2 above 12 K (where the experimental curve has a kink), our fit is excellent and the difference between experiment and the figure is less than the

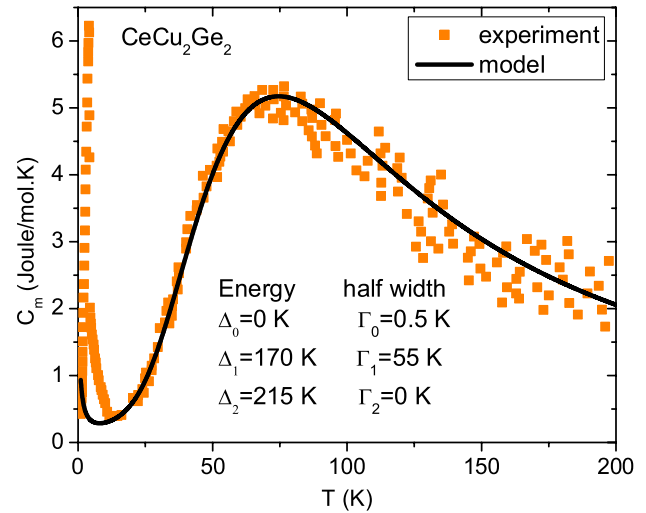


Figure 2. Magnetic contribution to the specific heat as a function of temperature of $CeCu_2Ge_2$. Squares: experimental results [40]. Full line: our approach.

experimental error. Thus, the introduction of the widths Γ_0 and Γ_1 by our approach leads to a significant improvement of the fitting expression with almost the same computational cost.

The system orders antiferromagnetically at $T_N = 4.15$ K. Below 12 K, our fit deviates from experiment. This is probably due to the onset of antiferromagnetic correlations between Ce^{3+} ions which cannot be captured in an approach based on a single impurity like ours. We have a similar limitation in the fits described below. Since the data at very low temperatures deviates from experiment, the reader might ask, how sensitive the fit is to changes in Γ_0 which, as discussed in section 3, is proportional to the Kondo temperature T_K . If Γ_0 is increased from 0.5 to 1 K, the specific heat C increases by about 15% in the region between 12 and 25 K. If $\Gamma_0 = 2$ K, C nearly doubles for $T = 12$ K and lies above the experimental data for $T < 30$ K.

4.2. $CePd_3Si_{0.3}$

$CePd_3$ has a cubic structure and behaves as an intermediate valence system. Doping with B or Si expands the lattice and drives the system to the Kondo regime [41]. To fit the specific heat, we have chosen $CePd_3Si_{0.3}$, because the subtraction of the phonon contribution has been done by measuring the specific heat of a La compound with a similar Si content, $LaPd_3Si_{0.2}$. The specific heat of both compounds has been measured by one of us [42]. The low-temperature behavior for $LaPd_3Si_{0.2}$ has been fitted with an $aT + bT^3$ dependence to obtain the Debye temperature of a simple Debye model for the phonon contribution to the specific heat [43]. Then, the Debye expression for this contribution is subtracted from the corresponding data for $CePd_3Si_{0.3}$ to obtain the magnetic contribution C_m to the specific heat of this compound. The result is represented in figure 3 together with our fit.

Since the point group around a Ce ion is O_h , we have used a ground-state doublet and an excited quadruplet for the

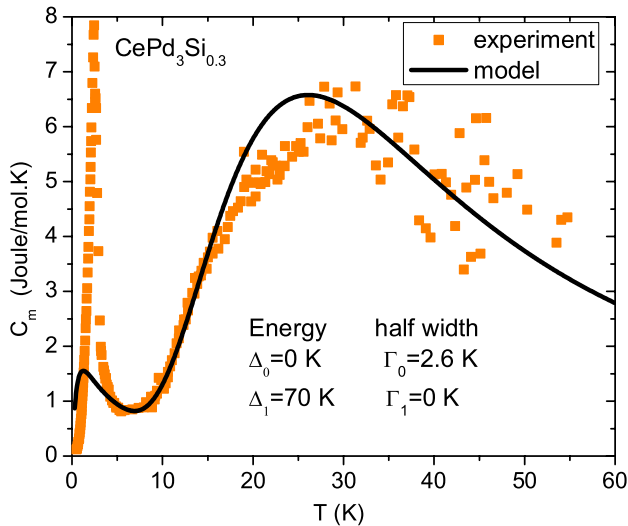


Figure 3. Magnetic contribution to the specific heat as a function of temperature for $\text{CePd}_3\text{Si}_{0.3}$. Squares: experimental results [42]. Full line: our approach.

fit, as described in section 2. Since we are not able to introduce a width to the excited quadruplet within our approach, we have only two fitting parameters, the width of the ground-state doublet Γ_0 and the position of the quadruplet Δ_1 . The fit is very good for temperatures between 5 and 18 K. For $T < 5$ K, as for the other compounds, the disagreement with experiment is due to the effects of magnetic correlations. Above 30 K, the dispersion of the experimental data is too large to allow us to extract firm conclusions, but the agreement is reasonable. Instead in the intermediate regime $18 \text{ K} < T < 27 \text{ K}$ the fit lies above the experimental data. This is likely due to the lack of broadening of the quadruplet in our approach. Some effects of disorder due to random distribution of Si atoms at the center of the cubic cage built by eight Ce^{3+} ions might also play a role.

4.3. CePdAl

CePdAl is a heavy fermion system which crystallizes in the hexagonal ZrNiAl structure and orders antiferromagnetically at $T_N = 2.7 \text{ K}$ [44]. The specific heat is reported in figure 4 of [44] together with a fit using a Schottky expression with three doublets, equation (10). This fit falls clearly below the experimental data for $T < 50 \text{ K}$.

Our fit using equations (8)–(10) is displayed in figure 4 together with the experimental data. At $T > 130 \text{ K}$, where the experimental data seem to have more dispersion, our fit falls slightly below the experimental data, which nevertheless show more dispersion at high temperatures. The fit fails, of course, near T_N because it is based on a single-ion approach, which cannot describe magnetic order. At intermediate temperatures $T_N < T < 130 \text{ K}$, our fit is excellent.

Considering the whole range of temperatures, our fit is again superior to the Schottky expression with a similar computational effort.

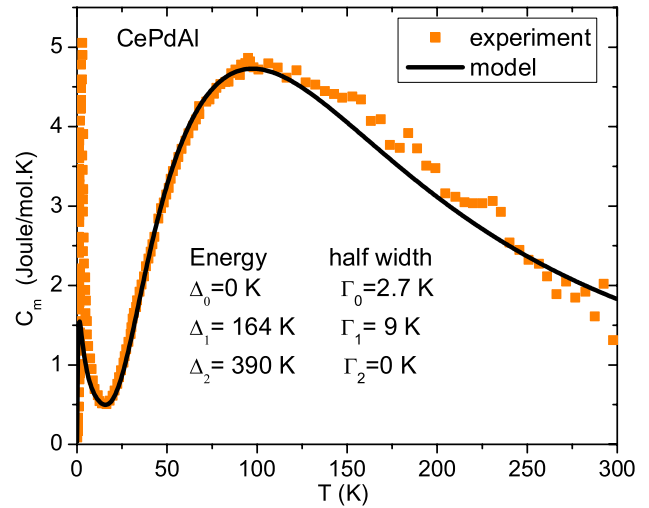


Figure 4. Magnetic contribution to the specific heat as a function of temperature for CePdAl. Squares: experimental results [44]. Full line: our approach.

4.4. CePt

The crystal symmetry of CePt is orthorhombic. Thus, it is another material in which the Ce^{3+} ions lie in low symmetry sites and the $j = 5/2$ multiplet is split into three doublets. The magnetic contribution to the specific heat C has been measured in [45]. The data together with a Schottky calculation (equation (10)) are presented in figure 2 of this reference. As for CeCu_2Ge_2 , this expression overestimates C near the peak at about 75 K and underestimates it below 30 K. There is also a funny structure between 250 and 300 K in which the experimental data lie above the Schottky expression.

The data are represented in figure 5 together with our fit using equations (8)–(10). As before, the values of Δ_1 and Δ_2 were chosen the same as those proposed in [45] from the fit using the Schottky expression and only two Γ_i were varied. The fit is excellent except near or below the ordering temperature (6.2 K) and near the above-mentioned high-temperature structure.

We also display the contributions proportional to Γ_0 , Γ_1 and the remaining term, which can be interpreted loosely³ as the contribution of each doublet to C . Specifically, the dashed (dot-dashed) line corresponds to the terms containing Γ_0 (Γ_1) in the expression of C_{2d} (equation (9)), while the dot-dot-dashed curve is the correction due to the third doublet and corresponds to the two remaining terms of equation (8).

4.5. Yb₂Pd₂Sn

No magnetic transition is found above $T = 0.5 \text{ K}$ in this compound [46] and therefore it is believed to be a non-magnetic compound with $J > J_c$ in the Doniach

³ The partition function and not the free energy is additive in terms of the contributions of different states which mutually exclude each other. Therefore, the contribution of each doublet to the specific heat is not well defined.

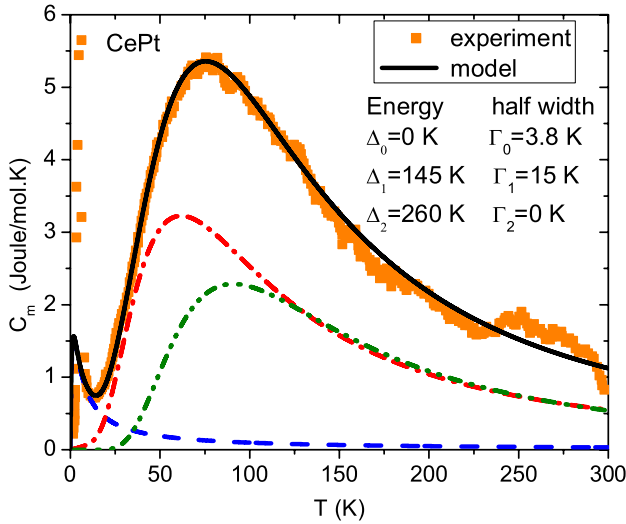


Figure 5. Magnetic contribution to the specific heat as a function of temperature for CePt. Squares: experimental results [45]. Full line: our approach. Dashed, dot-dashed and dot-dot-dashed curves correspond to the contribution of the different doublets (see text and footnote 3).

phase diagram [38]. It crystallizes in a tetragonal structure. Therefore, the $j = 7/2$ ground state of Yb is split into four doublets. Then, we can describe its specific heat with equations (8) and (9), with equation (10) generalized to contain an additional doublet at energy Δ_3 .

In contrast to the above Ce compounds, in both Yb compounds that we considered, the splitting of the first excited doublet is not small compared to the widths of the two lowest lying levels, and therefore the shift s (which coincides with Δ_0 in the absence of magnetic field) cannot be neglected. In fact, using Δ_0 given by equation (5) leads to a substantial improvement of the fits as compared to $\Delta_0 = 0$.

The magnetic contribution to the specific heat (after subtracting the specific heat of $\text{Lu}_2\text{Pd}_2\text{Sn}$) has been reported by Kikuchi *et al* [46]. The authors also show in their figure 2 an interpretation of the data based on the sum of a Kondo $1/2$ contribution plus a crystal-electric-field contribution with three doublets, which clearly fall much below the data near 30 K. They suggest that taking the Kondo effect of excited states into account would improve the description of the data. This is indeed what we have done for the first excited state.

The comparison between these experiments and our theory is shown in figure 6. The values of the different Δ_i are consistent with inelastic neutron scattering data of a similar compound $\text{Yb}_2\text{Pd}_2\text{In}$ with In instead of Sn [47]. The agreement is very good except above 100 K, where some entropy is lacking in our approach. Presumably this is due to the broadening of the two higher levels, particularly the highest one, which are absent in our approach. These broadenings would contribute to the entropy at smaller temperatures than the position of the respective peaks at Δ_2 and Δ_3 . In spite of this shortcoming, our fit is much better to the curve presented in figure 2 of [46] in the whole temperature range.

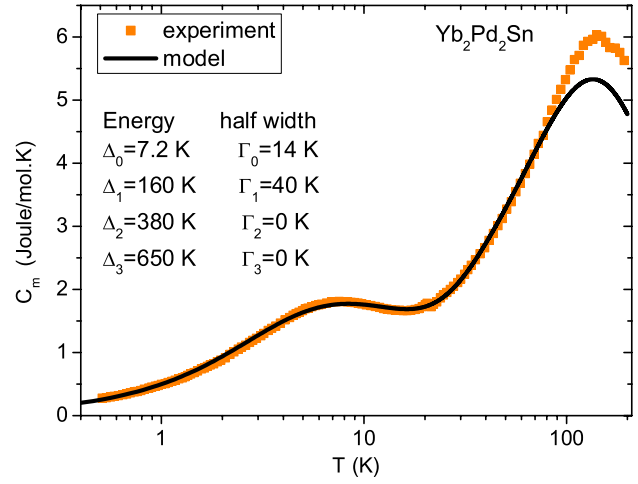


Figure 6. Magnetic contribution to the specific heat as a function of temperature for $\text{Yb}_2\text{Pd}_2\text{Sn}$. Squares: experimental results [46]. Full line: our approach.

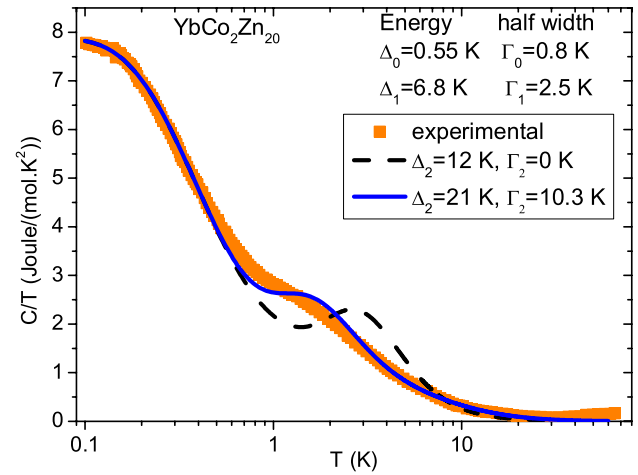


Figure 7. Magnetic contribution to the specific heat divided by temperature as a function of temperature for $\text{YbCo}_2\text{Zn}_{20}$. Squares: experimental results [48]. Dashed line: our approach. Full line: modification to simulate a width of the quadruplet (see text).

4.6. $\text{YbCo}_2\text{Zn}_{20}$

This heavy fermion compound is characterized by an extremely large value of C/T at low temperatures. The magnetic contribution to the specific heat has been measured by Takeuchi *et al* [48] and the results are reproduced by square symbols in figure 7. The compound is cubic and therefore the $J = 7/2$ states of Yb are split into two doublets (Γ_6 and Γ_7) and a Γ_8 quadruplet. Our fit indicates that the latter lies at higher energy. Following our approach we used then equations (8) and (9), but with C_S replaced by the corresponding term obtained by differentiating the free energy F_S for all $\Gamma_i = 0$, which in this case is

$$F_S = -k_B T \ln(2 + 2e^{-\frac{\Delta_1}{k_B T}} + 4e^{-\frac{\Delta_2}{k_B T}}). \quad (14)$$

The resulting fit is shown by the dashed line of figure 7. Clearly, the fit is very good at temperatures below 1 K, but

fails between 1 and 10 K, slightly above the energy of the quadruplet. We believe that the cause of this discrepancy is the lack of broadening of this quadruplet in our theory. To test this, we have replaced the last term of equation (14) by a sum of four terms with equidistant energies $E_k = \Delta_2 - \Gamma_2(k - 3/2)$, $k = 0-3$, which simulates the effect of the broadening (although naturally the queues of the distribution are lost). This improves the experimental curve, except at small temperatures as described above.

In contrast, the agreement at low temperatures, in which the experimental C/T is rather flat, is a success of our approach. The shift Δ_0 given by equation (5) is essential to reproduce this behavior. Using $\Delta_0 = 0$ leads to a too fast decay of C/T with increasing temperature.

Concerning the extremely high value of the linear term of the specific heat $\gamma = 7.8 \text{ J (mol K}^2\text{)}^{-1}$, our result using equation (11) and the parameters of the fit (given in the figure) indicate that 5.3% of the observed γ is due to the first excited doublet.

5. Summary and discussion

We have presented a simple approach to describe the thermodynamics of Kondo impurities with several levels, extending a previous proposal of Schotte and Schotte [23]. In the absence of an applied magnetic field, a comparison with available exact results indicates that the approach describes properly the specific heat of systems with two doublets, and accurately as long as the splitting is equal to or larger than the Kondo temperature. The parameters of the fit are related to fundamental quantities which describe the spectral density of the system. In particular Γ_0 is related to the Kondo temperature.

Application to specific heat measurements of several compounds with low symmetry around the Ce^{3+} ions (CeCu_2Ge_2 , CePdAl and CePt) provides an excellent fit at temperatures above those at which magnetic correlations between different Ce^{3+} ions become important. For the cubic system $\text{CePd}_3\text{Si}_{0.3}$, our fit deviates above the experimental results in a narrow range of intermediate temperatures. This might be due to the limitations of our approach, which does not include a broadening of excited quadruplets, or to effects of disorder. In the case of the Yb compound $\text{YbCo}_2\text{Zn}_{20}$, in which the position of the excited quadruplet is of the order of its broadening, the effect of the lack of the latter becomes evident in the fit. An artificial splitting of this quadruplet improves the fit, but this does not represent the actual physics of the hybridization of excited states with conduction electrons. In contrast, the low-temperature part, which shows an unusually flat C/T , is very well reproduced by our approach. Finally for $\text{Yb}_2\text{Pd}_2\text{Sn}$, which has the largest T_K and a crystal field splitting of four doublets, our fit is very good except at high energies, where it is likely that the effect of broadening of excited states also plays a role.

For all the above systems our fit was superior to alternative theoretical curves if available, and the computational cost is very modest.

We conclude that the present approach provides a flexible tool to properly interpret experimental results at temperatures larger than those corresponding to the onset of either coherence effects of the lattice or magnetic correlations.

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Note added. Recently we became aware of the work in [49], in which Desgranges extends the exact Bethe-ansatz results of [17] to the case of three doublets, all of them with the same hybridization to the conduction states.

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