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Specific heat of magnetic Ce alloys within a two-component model

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Abstract. We propose a description of the electronic properties of Ce alloys as an inhomogeneous mixture of two components: one containing magnetic Ce ions with an RKKY interaction J_H between them, and the other described as a collection of Kondo impurities with exchange interaction J_K. Both J_H and J_K are assumed to depend on a composition parameter X, with a Gaussian distribution around a value X_0 (near to the expectation value of X), related to the experimental composition parameter x of the alloy. When the concentration of the Kondo impurities is large, the specific heat C displays non-Fermi liquid behavior over a wide temperature range. The main qualitative features of C/T as a function of temperature T observed in several Ce alloys are reproduced using simple $J_H(X)$ and $J_K(X)$ dependences.

PACS. 75.30.Mb Valence fluctuation, Kondo lattice, and heavy-fermion phenomena – 75.40.Cx Static properties (order parameter, static susceptibility, heat capacities, critical exponents, etc.)

1 Introduction

Cerium alloys show a rich variety of magnetic and thermodynamic behaviors depending on the particular physical system in which the Ce atom is embedded. They may display magnetic order, heavy fermion behavior, intermediate valence or non-Fermi liquid behavior [1]. These systems can be described in principle by the periodic Anderson model or the Kondo lattice model including effects of disorder. However, even the simplest case of the homogeneous Kondo lattice remains not well understood after more than 30 years of both theoretical and experimental research.

The competition between magnetic order and single-ion Kondo physics can be qualitative understood on the basis of the Doniach phase diagram [2], in which the effective magnetic RKKY exchange interaction between nearest-neighbors varies as $J_H \sim J_K^2$, being J_K the Kondo interaction, while the Kondo mixture of local and conduction electron spins is characterized by the Kondo temperature, given by:

$$T_K = W \exp\left[-1/(\rho J_K)\right], \tag{1}$$

where W is the band width and ρ is the density of states per spin at the Fermi level. Then, for small J_K the magnetic interaction dominates, while for large enough J_K, the formation of local Kondo singlets inhibits the formation of magnetic order. However, this simple picture cannot explain the non-Fermi liquid behavior observed in several systems, and the magnetic phase diagrams of many Ce-lattice systems [3,4].

Based on the evolution of their magnetic phase boundary, Sereni [4] has classified these alloys into three different types: A) those in which the magnetic ordering temperature T_N (usually corresponding to an antiferromagnetic ordering) tends to zero as a function of a composition parameter x. Exemplary systems for this group are $CeAu_{1-x}Cu_{5+x}$ [5] and $CeIn_{3-x}Sn_x$ [6]. B) those in which, despite the fact that $T_N(x)$ decreases, it is not possible to trace experimentally the transition beyond a certain concentration x_c. This is due to the broadening and disappearance of the specific heat jump (and electrical resistivity kink) at T_N. This is the case of $Ce(Pd_xRh_{1-x})_2Si_2$ [7] among other alloys [4]. C) those in which T_N is nearly independent of x until the transition disappears as in the previous case. An example for this case is $CeCu_{2+x}(Si_{0.9}Ge_{0.1})_{2-x}$ [8].

Besides the previous considerations, the broadening of the specific heat transition in most of these alloys, the increase of the resistivity at intermediate compositions (like in $Ce(Cu_xRh_{1-x})_2Si_2$ [9]), and its temperature dependence [9], point out the importance of disorder in some of these systems. Nevertheless, one has to take into account that a similar evolution of the magnetic phase boundary is observed under pressure, where the effect of disorder is not expected [10]. A phenomenological model with a distribution of Kondo temperatures was able to fit the observed non-Fermi liquid behavior in the field and temperature dependence of magnetic susceptibility and specific heat in

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$UCu_{5-x}Pd_x$ [11]. It has also been shown that a random hybridization between conduction and localized f electrons leads to a finite probability of very small T_K and non-Fermi liquid behavior [12]. Furthermore, several authors have studied models in which Kondo impurities interact with random RKKY interactions between them [13–17]. These "spin-glass" models have led to good agreement with experimental data in alloys at particular compositions close to a quantum critical point [15–17]. It has been argued that a Griffiths phase due to non-percolating giant magnetic clusters is the origin of the observed non-Fermi liquid behavior [15]. A two component model, one of which is homogeneous and the other a set of non-percolating magnetic clusters has explained the temperature and magnetic field dependence of transport and magnetic properties of $Ce(Ru_0{\cdot}5Rh_0{\cdot}5)_2\ Si_2$ [17]. These studies are restricted to compositions near the quantum critical point, where non-Fermi liquid properties are observable. In another work [18], a two-fluid model has been used to describe Mott-Hubbard metal-insulator transitions and local moments in a narrow band. Very recently [19] a two-fluid model has been shown to explain the specific heat, magnetic susceptibility and resistivity of $Ce_{1-x}La_xCoIn_5$. This system is however different from ours in that the concentration of Ce atoms is varied.

Concerning the magnetic transition, the specific heat jump of several Ce and Yb compounds has been reproduced [20] using a simple theory for Kondo impurities interacting through an exchange interaction [21]. The specific heat depends on the ratio T_K/T_N, where T_N is the Néel temperature. However, this theory does not lead to a broadening of the specific heat jump.

In this work we describe the alloy as an inhomogeneous system. Fluctuations in the environment around each Ce atom modify the Ce on-site energy with respect to the Fermi level and the interatomic Ce-Ce distances. In our simplified description, a fraction X of the system consists of non-interacting Kondo impurities with an exchange constant J_K. The rest of the system consists of magnetic ions that interact with their nearest neighbors with an exchange constant J_H. The parameter X has a Gaussian distribution around some value X_0 related to the composition parameter x of the alloy. Due to the fact that the detailed interplay between composition x and disorder is not well established, X_0 is not necessarily identical to x. The model is similar to the above mentioned spin glass model. However, we assume that the magnetic ions are always percolating and study the specific heat as a function of X_0.

We assume that J_H decreases with X, while J_K increases, as suggested by experiment. As in a random walk, we assume that the square of the distribution width is $AX_0(1-X_0)$ and A is an adimensional parameter directly related to the disorder in the system. The picture that we have in mind is that the local environment of each Ce (or magnetically unstable rare earth) atom affects the energy of the f level and its hybridization with the conduction band. These two parameters determine whether the magnetic moment survives or is "screened" by the Kondo effect. The proposed model is described in Section 2. Section 3 contains the result and comparison with experiment. Section 4 includes discussion and summary.

2 The model

We describe the free energy of the system per rare earth atom as a weighted average of magnetic and Kondo contributions with a certain distribution:

$$F(X_0) = \int dX\ P(X, X_0) \times [(1-X)F_M(X) + XF_K(X)]. \quad (2)$$

F_M is the contribution of the magnetic ions to the free energy, corresponding to an exchange interaction between nearest-neighbors, and is evaluated using the following Hamiltonian:

$$H_M = \sum_{\langle i,j \rangle} J_H(X)\vec{S}_i \cdot \vec{S}_j, \quad (3)$$

where $\vec{S}_i$ is the spin of the magnetic ion i, assumed 1/2.

F_K is the free energy of an impurity described by the usual Kondo Hamiltonian with exchange interaction $J_K(X)$ and with T_K given by equation (1).

The distribution of X is given by:

$$P(X, X_0) = \theta(X)\theta(1-X)e^{-\frac{(X-X_0)^2}{\sigma^2}}N(X_0)$$
$$\sigma^2 = AX_0(1-X_0), \quad (4)$$

where $N(X_0)$ is a normalization factor to ensure that $\int_0^1 P(X, X_0)dX = 1$ and $\theta(X)$ the step function.

In the usual mean-field treatment of H_M, for a ferromagnet or an up-down antiferromagnet, the spin-flip part of H_M is neglected and the solution is the same as that of an Ising model. Also the antiferromagnetic case for a bipartite lattice (positive J_H) can be mapped into a ferromagnetic case (negative J_H) inverting the spins of one sublattice. To solve H_M we therefore considered a ferromagnetic Ising model in the Bethe-Peierls approximation [22], which allows us to consider a short range order parameter $\alpha = P(++) + P(--) - 2P(+-)$, where $P(++)$ indicates the probability of finding two neighboring spins pointing up. The meaning of the other terms, $P(--)$ and $P(+-)$, is clear. This leads to a better description of the specific heat than the usual mean-field approach, particularly above the transition temperature T_N. This approximation has been used before in several problems, like the description of disordered alloys [23,24] and spin systems [25]. Following Kikuchi [26] and for zero magnetic field, F_M is obtained minimizing the following expression in terms of the

magnetization $m = \langle S_z \rangle$ and the parameter α:

$$\tilde{F}_M(m,\alpha) = -\frac{|J_H|z\alpha}{8} - T\left[(z-1)\left\{\frac{1+m}{2}\ln\frac{1+m}{2} + \frac{1-m}{2}\ln\frac{1-m}{2}\right\} - \frac{z}{2}\left\{\frac{\alpha+2m+1}{4} \times \ln\frac{\alpha+2m+1}{4} + \frac{\alpha-2m+1}{4} \times \ln\frac{\alpha-2m+1}{4}\right\} + \frac{1-\alpha}{2}\ln\frac{1-\alpha}{2}\right], \quad (5)$$

where z is the coordination number, which we have taken as 6, corresponding to the simple cubic arrangement of Ce atoms in $CeIn_{3-x}Sn_x$ [6].

From the minimization conditions $\partial\tilde{F}/\partial m = 0$ and $\partial\tilde{F}/\partial\alpha = 0$ for $m \neq 0$ but $m \to 0$, one obtains an analytical expression for the transition temperature in both cases (ferromagnetic for $J_H < 0$ or antiferromagnetic for $J_H > 0$):

$$T_N = \frac{|J_H(X)|}{2\ln(z/(z-2))}. \quad (6)$$

The magnetic contribution to the specific heat is

$$C_M = -\frac{|J_H(X)|z}{8}\frac{\partial\alpha}{\partial T}. \quad (7)$$

The free energy of the impurity Kondo model F_K is known from the Bethe ansatz exact solutions [27,28]. In particular, the specific heat has been calculated by Desgranges and Schotte [29] and by Rajan, Lowenstein and Andrei [30]. The former authors have shown that the result is quite similar to that of a resonant level model of width T_K. Then, in order to simplify the numerical integration in equation (2) we take this form for the Kondo contribution to the specific heat [31]:

$$C_K = \frac{k_B}{\pi}\frac{T_K}{T}\left[1 - \frac{T_K}{2\pi T}\psi'\left(\frac{1}{2} + \frac{T_K}{2\pi T}\right)\right], \quad (8)$$

where $\psi'(x)$ is the derivative of the digamma function. The total specific heat is given by the weighted average equation (2) with the free energies replaced by corresponding specific heat contributions.

3 Results

We have applied this model to describe the ground state properties of some Ce systems belonging to the groups identified as A and B, according to the classification introduced in Section 1. A characteristic of the systems included in group A is the linear decrease of T_N with X_0. Taking into account equation (6) this suggest the following dependence of $J_H(X)$:

$$J_H(X) = \begin{cases} J_H^0\left(1 - \frac{X}{X_c}\right) & \text{if } X \leq X_c \\ 0 & \text{if } X > X_c. \end{cases} \quad (9)$$

Table 1. Parameters of the model for a system belonging to case A (see Fig. 1).

Parameter	Value
X_c	0.65
J_H^0	8.00 K
J_K^0	0.68 eV
J_K^1	0.728 eV
A	0.25
W	6 eV
ρ	1/6 eV^{-1}

The meaning of X_c is the concentration beyond which no magnetic Ce ions exist. In addition, we assume:

$$J_K(X) = J_K^0 + (J_K^1 - J_K^0)X, \quad (10)$$

as previously postulated for U alloys [11].

Having in mind the system $CeIn_{3-x}Sn_x$, we take the parameters listed in Table 1. The concentration x=1 corresponds to the non-magnetic $CeIn_2Sn$ composition.

For these parameters one has $T_N = 10.2$ K (for $X_0 = 0$) and $T_K = 10.3$ K (for $X_0 = 1$). We want to stress that the qualitative aspect of the result is not sensitive to the parameters as long as $T_K(1)/T_N(0) \approx 1$. This ratio controls the relative weight of both contributions to the specific heat and turns out to be the most relevant parameter. The temperature dependence of the resulting specific heat is shown in Figure 1 for several values of X_0. For $X_0 = 0$ one has a well defined magnetic transition. As X_0 increases, the specific heat jump broadens due to disorder. For X_0 substantially larger than X_c or $X_0 \approx 1$, the magnetic contribution to the specific heat becomes small and the inhomogeneity leads to a temperature range in which C/T displays an approximate $\ln T$ behavior, characteristic of a non-Fermi liquid, in agreement with previous studies for U systems [11].

For example, for $X_0 = 0.8$ (see Fig. 2) the linear behavior of C/T vs. $\ln T$ extends between 1 and 10 K approximately. However, we must warn the reader that in several of these alloys, the $\ln T$ behavior is related to the proximity to a quantum critical point, which is not described by our approach.

Another feature of the curve is that for $X \leq X_c$, after an initial rapid decrease of the maximum value of C/T as a function of X_0, it remains approximately constant upon further increase of X_0.

These general features of C/T agree very well with experimental observations performed on Ce-systems belonging to group A, even with a semiquantitative agreement (see Fig. 1). A specific feature of $CeIn_{3-x}Sn_x$ which is not explained by our model is the presence of two peaks for $x \geq 0.3$. The smallest one is due to a weak first order transition. The explanation of these details is beyond the scope of the present work.

A general feature of the systems classified in groups B and C is the disappearance of the maximum of C/T at a finite non-zero temperature. These features are in clear

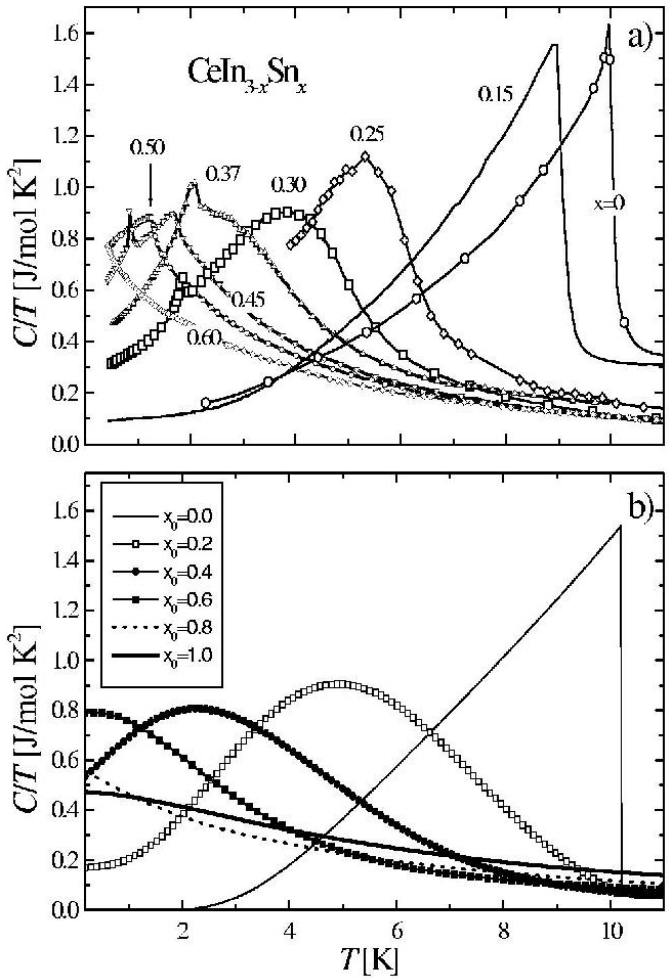

Fig. 1. Specific heat divided by temperature as a function of temperature for several compositions. a) experiments on $CeIn_{3-x}Sn_x$ [6]. b) our results for parameters corresponding to group A (see Tab. 1).

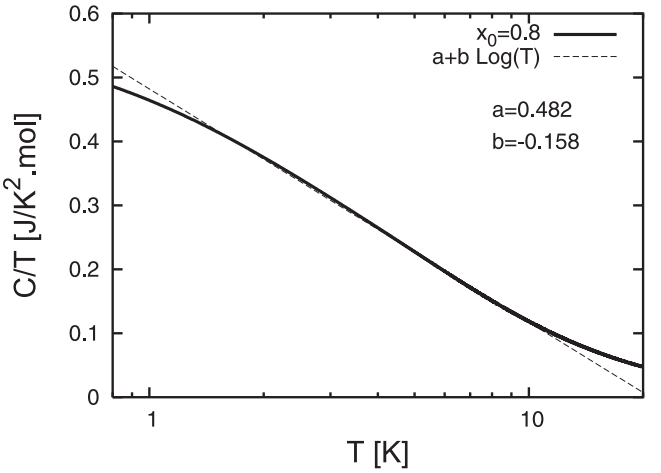

Fig. 2. Specific heat divided by temperature as a function of $\ln T$ for $X_0 = 0.8$. Dashed line is a linear fit of a mesh of points taken between 1 K and 10 K.

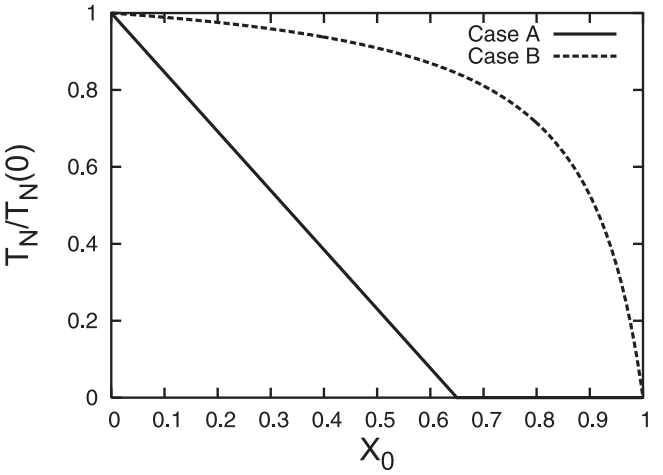

Fig. 3. Magnetic critical temperature as a function of X, for a system with nearest-neighbor interaction J_H given by equation (9) with $X_c = 0.65$ (case A, full line) and equation (11) with $X_c = 1$ (case B, dashed line).

contrast with those of group A where, when approaching X_c, the value of the temperature for which C/T is maximum depends linearly with X_0 and reaches $T = 0$ at $X_0 = X_c$. If the experimental phase diagrams of groups B and C were interpreted in terms of an homogeneous system, either the second order transition line should fall abruptly between two neighboring compositions, or the transition becomes first order with a very narrow two-phase field. However, in our picture of an inhomogeneous system, the phase boundary is not well defined, since for any intermediate X_0 there is a possible coexistence of microscopic regions of the alloy with order parameter $m = 0$ and $m \neq 0$.

To model a homogeneous system in which T_N falls abruptly to zero at X_c, we have modified equation (9) and assumed:

$$J_H(X) = \begin{cases} J_H^0 \left(\frac{1-X/X_c}{1-BX}\right) & \text{if } X \leq X_c \\ 0 & \text{if } X > X_c \end{cases} . \qquad (11)$$

This leads to the dependence of T_N vs. X_0 shown in Figure 3. We also have changed the parameters as indicated in Table 2, and in this case we have $T_N(0) = 37.0$ K and $T_K(1) = 13.7$ K.

The resulting specific heat is shown in Figure 4. One can see that the maximum in C/T decreases slightly with X_0 until, for $0.8 < X_0 < 0.9$, the relative maximum near T_N disappears and C/T shows a monotonic behavior. These results are in qualitative agreement with experiments on systems belonging to group B [3,4,7]. For the specific system chosen for the comparison, the two-peak structure clearly visible in the theory is only weakly present for $x = 0.15$ and $x = 0.2$. The large value of C/T for $T \to 0$ can be reduced by increasing T_K, but this leads to an increase of C/T for large T. The arrows in Figure 4 show the position of the critical temperature T_N for an ideal homogeneous system.

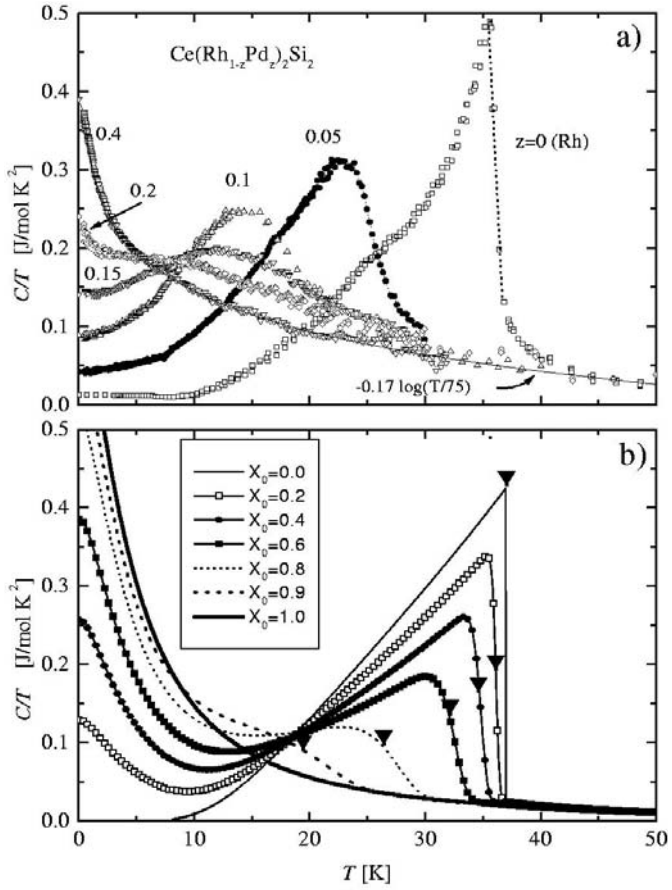

Fig. 4. Same as Figure 1 for parameters corresponding to group B. The experimental system is $Ce(Pd_xRh_{1-x})_2Si_2$ [7]. The arrows show T_N given by the full line of the previous figure for $X = X_0$.

Table 2. Parameters of the model for the case B (see Fig. 4).

Parameter	Value
X_c	1.00
J_H^0	20.00 K
B	0.9
J_K^0	0.75 eV
J_K^1	0.0 eV
A	0.03
W	6 eV
ρ	1/6 eV^{-1}

Some features seem to be essential to obtain the characteristic behavior of group B: i) the curvature in $J_H(X)$. A linear dependence leads to an excessively fast shift of the maximum in C/T at low values of X_0, like in Figure 1. ii) a lower ratio $T_K(1)/T_N(0)$. This produces a steeper Kondo contribution to C/T (decreasing with increasing T), which leads to the disappearance of the C/T maximum for large enough X. A weaker disorder is also necessary to decrease the value of C/T for $X > 0$ near $T_N(X = 0)$. iii) a constant value of T_K as composition is varied (i.e. $J(X) = J_K^0$). This feature is consistent with the fact that the magnetic entropy (obtained integrating $C(T)/T$) for the highest T shown in the figure is independent of concentration [4].

A remarkable experimental feature in the alloys of group B is that the tail in C/T after the jump (or the bump) is practically independent of composition. In our case, the increase in this tail due to the larger contribution of non-magnetic Kondo ions overcomes approximately the decrease of the effect of short-range magnetic correlations as X_0 increases. This partial compensation takes place in our model if $T_K(1)/T_N(0)$ is in the range $1/4 < T_K(1)/T_N(0) < 1/2$ approximately.

4 Discussion and summary

We have proposed an inhomogeneous model to describe the thermodynamics of some Ce alloys near their region of magnetic instability. The model contains a fraction of Ce atoms which interact magnetically among them, and the rest which behave as Kondo impurities with magnetic moments compensated by the spin of conduction electrons.

The model explains naturally the observed broadening of the specific heat jump, and the "disappearance" of the magnetic transition in some alloys. Since the transition between an ordered and a disordered phase cannot terminate at a point of non-zero finite parameters, the above mentioned disappearance seems very difficult to explain within a homogeneous picture. As pointed out before [11], disorder plus a linear dependence of the Kondo interaction with composition leads to non-Fermi liquid behavior of thermodynamic properties.

In addition, the main qualitative features of the observed specific heat in Ce alloys classified into group A [3,4,6] are described by the model. The relevant parameter for this description is $T_K(1)/T_N(0) \approx 1$.

In order to explain the independence of the tail of C/T with composition observed in alloys of group B, the model requires that the Néel and Kondo temperatures of respective extreme compositions should fall not too far from $T_K(1)/T_N(0) \approx 1/3$ and, in addition, some restrictions on the degree of disorder and the dependence of J_H with composition.

In spite of this shortcoming, we believe that the model contributes to the understanding of alloys containing Ce and possibly Yb, U or other magnetically unstable rare earths. A more quantitative theory requires a more detailed microscopic knowledge of the effect of disorder on the exchange parameters J_H and J_K, and assumptions of our model.

For example we have assumed a constant nearest-neighbor exchange interaction J_H decreasing with the amount of Kondo compensating atoms. A more realistic description seems to be to keep the same J_H but to eliminate magnetic ions at random. This makes contact with the "spin-glass" description of the non-Fermi liquid phenomena [13–17]. The concept of a Griffiths phase is based on the existence of isolated magnetic clusters, originally proposed by Griffiths for Ising ferromagnets with

nearest-neighbor interactions [32]. Here we assume that magnetism extents to the whole system. This is consistent with the long-range nature of the RKKY interaction. Although our assumptions are likely to be an over simplification of the actual effect of disorder, comparison with experiment is encouraging and suggests that the relevant mechanisms are included in this model.

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