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2009 J. Phys.: Condens. Matter 21 495601

(http://iopscience.iop.org/0953-8984/21/49/495601)

J. Phys.: Condens. Matter **21** (2009) 495601 (4pp) doi:10.1088/0953-8984/21/49/495601

The dilute limit of heavy fermions: evidence of the coherent nature of $CeAl_3$

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Received 26 August 2009, in final form 21 October 2009
Published 12 November 2009
Online at stacks.iop.org/JPhysCM/21/495601

Abstract

Strongly diluted $Ce_xLa_{1-x}Al_3$ alloys have been studied by the low temperature specific heat in order to elucidate the mechanism that determines their ground state. The results for alloys with Ce concentrations of $0.0005 \leqslant x \leqslant 0.1$ are fairly consistent with a $S = 1/2$ Kondo behavior. However, the single-ion scaling is observed only below $x = 0.01$. The true single-ion Kondo temperature is small, 0.2 K, approximately equal to that for dilute $CeAl_2$. It is about 20 times smaller than that for $CeAl_3$, indicating the coherent nature of $CeAl_3$. The single-ion contribution to thermodynamic properties of $CeAl_3$ is negligible even at temperatures as high as 5 K.

1. Introduction

$CeAl_3$, the first discovered [1] and archetypal heavy fermion compound, remains a subject of extensive experimental and theoretical investigations. For years, this material has been considered as an example of a non-magnetic heavy fermion system describable by a single impurity Kondo model, although short-range magnetic correlations [2] have been known to exist below 0.7 K. The results of a more recent alloying study [3] have ignited new interest in the true nature of the ground state. Substitution of a few per cent of non-magnetic La for Ce results in the appearance of strong anomalies, reminiscent of antiferromagnetic ordering, in the thermodynamic properties. In particular, $Ce_{0.8}La_{0.2}Al_3$ shows a well-pronounced peak in the specific heat at 2.3 K, consistent with ordering of magnetic moments of order 0.3 μ_B. However, the elastic neutron scattering [4] for the same composition has not detected a long-range order, setting an upper limit for the ordered moment at 0.05 μ_B. Instead, a broad inelastic peak was found below 3 K. The neutron scattering results have prompted an interpretation in terms of a single-ion anisotropic Kondo effect. However, this interpretation remains controversial and is not corroborated by more recent magnetic field [5] and μSR [6] investigations.

In order to resolve these inconsistencies and gain further insight into the nature of the ground state of $CeAl_3$ we have previously performed thermodynamic studies of $Ce_xLa_{1-x}Al_3$ over an extended range of concentrations x: $0.1 \leqslant x \leqslant 1$ [7]. The overall trends in the low temperature properties observed upon La alloying seemed to be consistent with the Kondo-necklace model [8]. The hexagonal lattice parameter a increases upon the La substitution, possibly leading to weakening of T_K. However, the rate and magnitude of these changes were surprisingly large, considering results for other pseudobinary alloys, such as $Ce_xLa_{1-x}Pb_3$, for which the lattice parameter also increases with an increase of the La content. [9] In $Ce_xLa_{1-x}Pb_3$ specific heat and magnetic susceptibility scale with x, implying constant $T_K \approx 3$ K across the entire range of alloy parameter x. T_K for $Ce_xLa_{1-x}Al_3$ could not be obtained directly from fits to the Kondo model. Therefore, some effective T_K, which we call here T_K^{eff}, was approximated using the measured entropy at some fixed temperature (above any magnetic or magnetic-like anomalies) and comparing it with that for the $S = 1/2$ Kondo model. Such T_K^{eff} spans a large range of values from approximately 4 K for $x = 1$ to about 1 K for $x = 0.2$. Moreover, extrapolation of T_K^{eff} to $x = 0$ yields $T_K^{eff} \approx 0$.

The goal of the present work is to find and characterize the single impurity limit of $Ce_xLa_{1-x}Al_3$ alloys. The anticipated smallness of T_K^{eff} makes such a study feasible, unobscured by the phonon and normal electron background, but only at temperatures considerably lower than 1 K.

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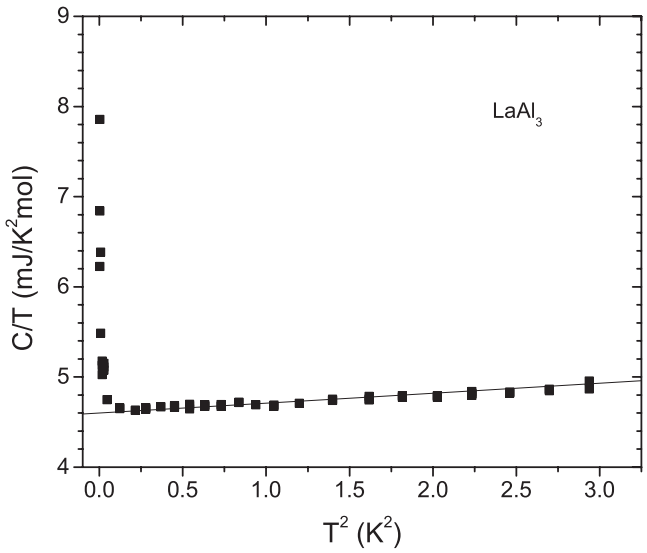

Figure 1. C/T versus T^2 for the $LaAl_3$ sample. The straight line corresponds to conduction electron and phonon contributions. The possible origin of the low temperature tail is discussed in the text.

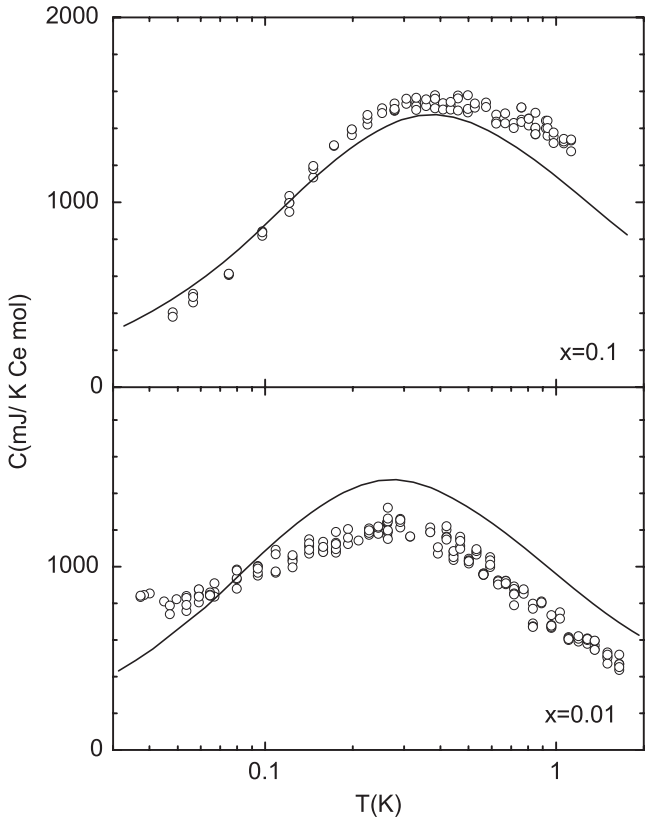

Figure 2. f-electron specific heat of moderately dilute $Ce_xLa_{1-x}Al_3$ alloys with $x = 0.1$ (upper panel) and 0.01 (lower panel). The solid lines are theoretical curves for the $S = 1/2$ Kondo model, as described in the text.

2. Experimental and results

Polycrystalline samples were prepared by arc melting using a multiple step procedure. First, master ingots corresponding to $x = 0$ and 0.1 were synthesized. Alloys corresponding to $x < 0.1$ were made by successively melting together a more concentrated alloy and $x = 0$, such that the ratio of the starting masses of the two alloys was always smaller than 20. Since the weight losses during the melting and annealing were very small and Al is more volatile than Ce and La, we expect a negligible discrepancy between the nominal and actual concentrations. All samples were annealed at 830 °C for two weeks. No secondary phases were detected by x-ray diffraction techniques.

In order to account for non-f-electron contribution to the specific heat of $(Ce{\cdot}La)Al_3$ alloys, a piece of a master $LaAl_3$ sample was measured. The results, in the form of C/T versus T^2, are shown in figure 1. Above 0.3 K and below 2 K, the data can be approximated by the following expression: $C/T = \gamma T + \beta T^2$, where $\gamma = 4.6$ mJ K^{-2} mol^{-1} and $\beta = 0.11$ mJ K^{-4} mol^{-1}. The linear coefficient is about 6% smaller than that previously reported [10]. Also, there is a tail at the lowest temperatures of the measurements, below 0.2–0.3 K. Note that this tail is clearly seen in the C/T versus T^2 format, while not apparent in a C versus T format. C decreases with decreasing temperature down to the lowest temperature of the measurement, of approximately 60 mK. This point is of some importance since the results for Ce-containing alloys presented in figures 2 and 3 are in the form of C versus T.

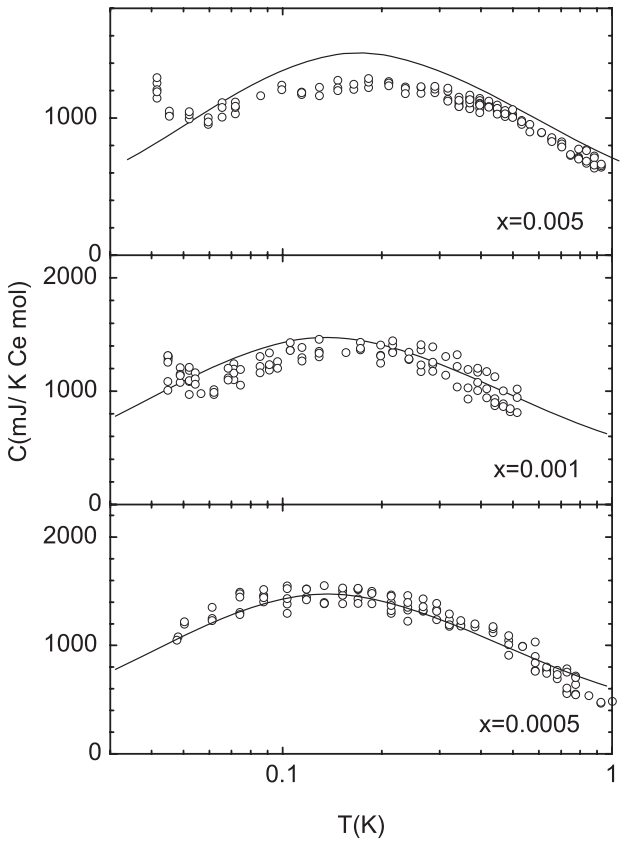

Figure 3. f-electron specific heat of extremely dilute $Ce_xLa_{1-x}Al_3$ alloys with $x = 0.005$ (top), 0.001 (center), and 0.0005 (bottom). The solid lines are theoretical curves for the $S = 1/2$ Kondo model, as described in the text.

There are two possible sources for this low temperature tail: magnetic impurities and the nuclear quadrupolar specific heat of lanthanum and aluminum nuclei. Although the purest available elements were used to synthesize the samples, such as lanthanum and cerium from Ames National Laboratory, and 6N aluminum from Johnson Matthey, these elements contain magnetic impurities (including Gd and Fe) of at least a single-digit ppm levels. The quadrupolar nuclear contribution is expected for atomic nuclei with spins I larger than $1/2$ in non-cubic environments at millikelvin temperatures. In indium, for instance, this nuclear contribution [11] to specific heat amounts to about 0.4 mJ K^{-1} mol^{-1} at 50 mK. (The electric quadrupole moment, Q, of ^{115}In is 0.83 barns.) This value is twice the excess specific heat of $LaAl_3$ at the same temperature. Since $LaAl_3$ contains four moles of non-$I = 1/2$ nuclei, ^{139}La with Q of 0.22 barns [12] and ^{27}Al with $Q = 0.15$ barns [12], we expect a comparable quadrupolar nuclear contribution to the case of indium. This excess specific heat in $LaAl_3$ can be expressed by the following formulae, $\Delta C = A_n/T^2$, where $A_n = 0.0009$ mJ K mol^{-1}.

Figures 2 and 3 show the specific heat of $Ce_xLa_{1-x}Al_3$ alloys after subtracting the specific heat due to normal electrons and phonons, approximated by the $LaAl_3$ data, $\gamma T + \beta T^3 + A_n/T^2$, and dividing by x. Both sets of data exhibit broad maxima reminiscent of a Kondo-type specific heat. The maximum occurs at a lower temperature for the $x = 0.01$ case. The solid lines are theoretical curves [13] for the $S = 1/2$ Kondo model corresponding to T_K of 0.55 and 0.4 K for $x = 0.1$ and 0.01, respectively. The experimental points show some systematic deviations from the theoretical curves. In particular, there is an excess specific heat for $x = 0.1$ at temperatures larger than 0.5 K that cannot be eliminated by a reasonable adjustment of the background subtraction. The specific heat values for $x = 0.01$ are about 20% lower than the fit, except at the lowest temperatures.

The specific heat data for the more dilute alloys of $x = 0.005$, 0.001, and 0.0005, shown in the upper and middle panels of figure 3, exhibit even better agreement with the Kondo specific heat. The data for all three alloys have broad maxima at about the same temperature. The magnitude of these maxima is consistent with the $S = 1/2$ Kondo model and T_K of about 0.2–0.25 K. Kondo curves corresponding to $T_K = 0.2$ K are also shown for comparison. Note that the subtraction of the hyperfine specific heat (A_n/T^2) is needed to observe the Kondo-like maximum in the most dilute alloy, $x = 0.0005$. This subtraction was less important for all other alloys investigated.

3. Discussion

Figure 4 shows T_K for alloys investigated in this work. T_K was obtained from fits of the specific heat to the single-ion $S = 1/2$ Kondo model. The inset presents T_K^{eff} versus x for the entire alloy parameter space. T_K^{eff} for the concentrated range ($x > 0.1$) was derived in the previous study [7] and is not the single impurity T_K since the specific heat cannot be approximated by the single impurity model. In the dilute range, T_K^{eff} and T_K are equivalent.

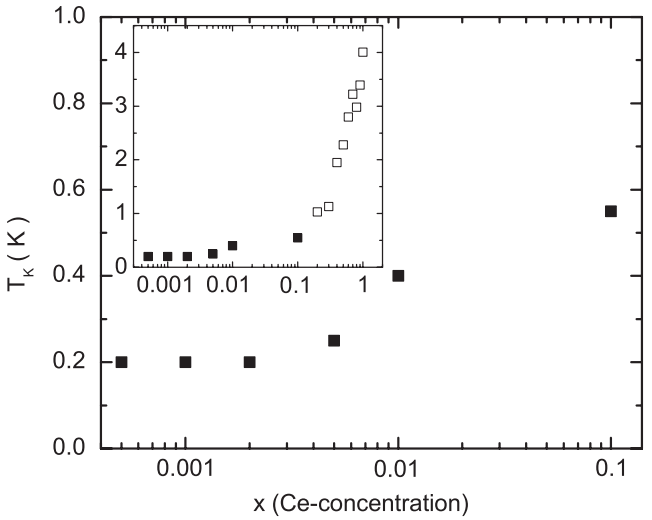

Figure 4. T_K versus x for $Ce_xLa_{1-x}Al_3$ obtained from the $S = 1/2$ Kondo fits. The inset shows T_K^{eff} for the whole concentration range, open symbols for x between 0.2 and 1 representing the results of [7]. Note that the method of determining T_K^{eff} was different, although consistent with the convention used in the present investigation.

It is interesting that although the normalized f-electron specific heat shows a significant variation below $x = 0.1$ it can be approximated by the single impurity model. It is very unlikely that this variation is caused by changes of parameters entering the model. For instance, changes in the lattice constants for these concentrations are below the resolution of our x-ray diffraction analysis while Ce and La have the same number of valence electrons.

Our results imply, however, that the true single-ion scaling takes place at concentrations of f-electron ions well below 1%. Such low concentrations are expected from the arguments of Noziéres [14]. For the single-ion Kondo screening to be effective, the concentration of Kondo centers has to be small, since—at a given temperature T—only a fraction T/T_F of conduction electrons is available for the Kondo effect, where T_F is the unnormalized Fermi temperature of order 10^3 K. This sets a limit of $x \approx 0.001$ for the upper concentration of Kondo centers, roughly consistent with the value of x below which we observe the saturation of T_K. However, one would expect that increasing the concentration of Kondo centers would make the Kondo screening more difficult, resulting in a decrease of T_K. Our experiment shows otherwise, arguing against the single-ion mechanism responsible for changes of T_K.

It is also remarkable that T_K for very dilute alloys ($x \to 0$) of 0.2 K is equal to that of strongly La-diluted [15] $CeAl_2$. The crystal structure, coordination numbers, and the length of bonds are clearly different in the two alloy systems. Ce in the hexagonal structure of $LaAl_3$ has six nearest neighbor Al atoms at a distance of 3.27 Å and six nearest neighbor La atoms at a distance of 4 Å, whereas Ce in the cubic $LaAl_2$ is surrounded by twelve Al atoms at a distance of 3.36 Å and is separated from the four nearest La atoms by 3.50 Å.

The concentration variation of the specific heat of $Ce_xLa_{1-x}CoIn_5$, another well studied Ce-alloy system, has been successfully accounted for using the so-called two fluid

model [16]. In this model the specific heat (and magnetic susceptibility) is a sum of two contributions; a single impurity C_{KI}, fully determined by the single impurity T_K that does not depend on x, and a coherent contribution C_{HF}. The relative weight of these contributions is a function of temperature. $C = [1 - f(T)]C_{KI} + f(T)C_{HF}$. For T much smaller than the coherence temperature T^* of a system, the coherent part is dominant ($f \approx 1$). f decreases with increasing T/T^*. In $Ce_xLa_{1-x}CoIn_5$, T^* depends approximately linearly on x. T^* is the largest for $x = 1$ and decreases to 0 for $x \to 0$.

This two fluid model analysis seems to be appropriate, although difficult, for $Ce_xLa_{1-x}Al_3$. It is appropriate because of similarly small variations of the lattice constants and identical valences of Ce and La. It is difficult because we expect the coherent part (C_{HF}) to change its character across the system from non-magnetic to magnetic to non-magnetic again as a function of x. Because of the smallness of T_K, we cannot use the magnetic susceptibility data (χ is much more strongly affected by impurities than C at very low temperatures). However, if we assume that T_K (characterizing the single impurity contribution) does not depend on x and that T_K is $\approx$0.2 K, we arrive at the conclusion that the specific heat of $CeAl_3$ in the most interesting temperature range, say below 5 K, is entirely due to intersite (coherent) effects. This is because C_{KI} at 5 K for T_K of 0.2 K is by an order of magnitude smaller than the measured specific heat.

Acknowledgments

This work has been supported by the US Department of Energy, Grant No. DE-FG02-99ER45748. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-0084137, by the State of Florida, and by the DOE. We thank K Ingersent for providing the numerical $S = 1/2$ Kondo fits.

References

[1] Andres K J, Graebner J E and Ott H R 1975 *Phys. Rev. Lett.* **27** 1779
[2] Barth S, Ott H R, Gygax F N, Hitti B, Lippelt E, Schenck E, Baines C, van den Brandt B, Konter T and Mango S 1987 *Phys. Rev. Lett.* **59** 2991
[3] Andraka B, Jee C S and Stewart G R 1995 *Phys. Rev.* B **52** 9462
[4] Goremychkin E A, Osborn R, Rainford B D and Murani A P 2000 *Phys. Rev. Lett.* **84** 2211
[5] Pietri R, Ingersent K and Andraka B 2001 *Phys. Rev. Lett.* **86** 1090
[6] MacLaughlin D E, Rose M S, Young B L, Bernal O O, Heffner R H, Nieuwenhuys G J, Pietri R and Andraka B 2003 *Physica* B **326** 387
[7] Pietri R and Andraka B 2002 *Phys. Rev.* B **66** 224421
[8] Doniach S 1977 *Valence Instabilities and Related Narrow-Band Phenomena* ed R D Parks (New York: Plenum) p 169
[9] Lin C L, Wallash A, Crow J E, Mihalisin T and Schlottmann P 1987 *Phys. Rev. Lett.* **58** 1232
[10] Edelstein A S, Fisher R A and Phillips N A 1987 *J. Appl. Phys.* **61** 3177
[11] Tang Y H, Adams E D, Uhlig K and Bittner D N 1985 *J. Low Temp. Phys.* **60** 351
[12] Carter G C, Bennett L H and Kahan D J 1977 *Metallic Shifts in NMR* (*Prog. Mater. Sci.* vol 20) (Oxford: Pergamon)
[13] Rajan T V, Lowenstein J H and Andrei N 1982 *Phys. Rev. Lett.* **49** 497
Ingerent K, unpublished
[14] Noziéres P 1985 *Ann. Phys., Paris* **10** 19
[15] Bader S D, Phillips N E, Maple M B and Luengo C A 1975 *Solid State Commun.* **16** 1263
[16] Nakatsuji S, Pines D and Fisk Z 2004 *Phys. Rev. Lett.* **92** 016401