Specific heat and magnetic susceptibility of $Ce_{1-x}La_xAl_3$

R. Pietri and B. Andraka
Department of Physics, University of Florida, P.O. Box 118440, Gainesville, Florida 32611-8440
(Received 11 September 2002; published 27 December 2002)

$Ce_{1-x}La_xAl_3$ alloys, where $0 \leqslant x \leqslant 0.9$, have been studied by x-ray diffraction, magnetic susceptibility, and specific heat. La exerts a negative lattice pressure in hexagonal planes, but has a negligible effect on the distance between them. A decrease of the in-plane hybridization, between Ce and Al ions, causes a decrease of Kondo and magnetic energy scales. The results of the specific heat in magnetic fields and magnetic susceptibility are more consistent with the Kondo-necklace model than with the anisotropic Kondo model.

DOI: 10.1103/PhysRevB.66.224421 PACS number(s): 75.30.Mb, 75.50.Ee, 75.20.Hr, 75.40.Cx

I. INTRODUCTION

$CeAl_3$ is the first identified, canonical heavy fermion system.[1] However, its low temperature thermodynamic and transport properties are far from being completely understood. Strongly enhanced C/T extrapolated to $T=0$ and correspondingly large A, the quadratic temperature coefficient of the resistivity below 1 K, bear witness to very heavy electrons. On the other hand, weak low temperature anomalies in C/T and χ have not been accounted for and were subjects to a number of controversies. The interpretation of these anomalies in $CeAl_3$ and other concentrated Kondo lattice systems range from the ''coherence effect in Kondo lattices'' to weak magnetic order. Recently, it has been proposed that these anomalies might be due to single ion dynamics as described by the anisotropic Kondo model (AKM).[2] The essential feature of this novel explanation is strong anisotropy in the Kondo-exchange parameter J. The AKM explanation was put forward using neutron scattering[2] results for $CeAl_3$ doped with La. Although substituting 20% of La for Ce results in pronounced peaks in C and χ,[3] reminiscent of an antiferromagnetic transition, no magnetic Bragg peaks have been detected within the resolution of $0.05\mu_B$ per Ce atom. Subsequently, the AKM interpretation has been shown to be inconsistent with the magnetic field response of the specific heat for this material.[4] In order to gain further insight into the nature of the low-temperature state of $CeAl_3$, and particularly the relevance of AKM, we have performed the alloying study of $Ce_{1-x}La_xAl_3$ within the whole concentration range from $x=0$ to 1.

II. EXPERIMENTAL AND RESULTS

Polycrystalline samples were prepared by inert atmosphere arc melting of the purest available elements Ce and La from AMES Laboratory and Al from Johnson Matthey (AESAR; 99.999% purity). The stoichiometry was controlled to within 0.1%. The polycrystalline samples were subsequently annealed at 830 °C for two weeks. This annealing procedure has been chosen based on our previous experience with $(Ce,La)Al_3$ and optimized to have negligible contribution from known secondary phases in the low-temperature susceptibility measurements. Lack of detectable secondary phases was additionally confirmed via x-ray diffraction analysis.

Lattice constants were obtained for each composition from 10–15 highest intensity Bragg peaks, using a least-square fitting procedure. As it can be inferred from the Fig. 1, La exerts negative chemical pressure on the Ce lattice. However, the expansion of the lattice is not isotropic, it is mainly in the hexagonal basal plane. The ratio of a/c increases continuously with x, by over 1.5% between the end compounds. This anisotropic La expansion is important in the context of models relaying on magnetic and crystalline anisotropy and will be further discussed.

Magnetic susceptibility was measured for all samples between 2 and 300 K using a Quantum Design SQUID magnetometer. The low temperature results, to 20 K, normalized to a mole of Ce are shown in Fig. 2. No subtraction of the susceptibility for a nonmagnetic analog $LaAl_3$ was performed due to negligible values of the susceptibility of this latter compound in comparison with those for the investigated $(Ce,La)Al_3$ samples. The susceptibility values increase with x for any measured temperature greater than 2.5 K. This trend is an obvious signature of a decreasing strength of RKKY interactions (described by T_{RKKY}) on x. Below 2.5 K and for $x<0.4$, the susceptibility values vary nonmonotonically on x (for a fixed temperature). A small decrease of χ_0 (the susceptibility at the lowest common temperature of the measurement 2 K) is observed between $x=0.1$ and 0.2 (see also Table I). This decrease can be explained by a magnetic

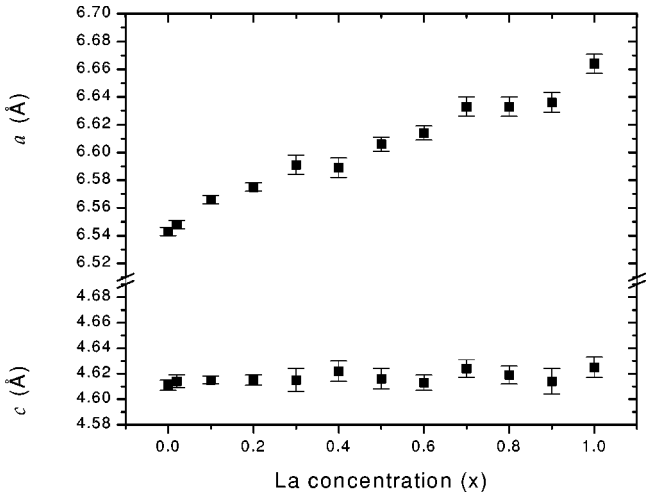

FIG. 1. Lattice constants of $Ce_{1-x}La_xAl_3$.

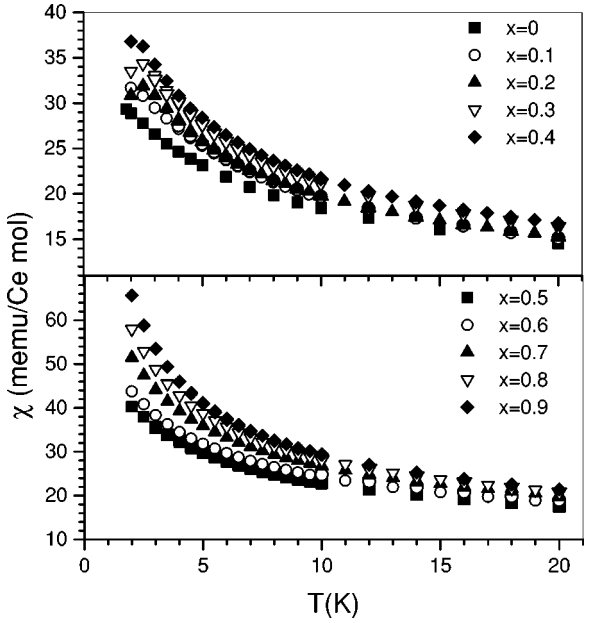

FIG. 2. Low-temperature magnetic susceptibility of $Ce_{1-x}La_xAl_3$.

ordering occurring near 2.3 K for $x=0.2$ and 0.3. The susceptibility curves corresponding to $x=0$ and 0.4 exhibit some flattening at the lowest temperatures, suggesting anomalies below 2 K. A wide maximum has been previously seen in the susceptibility of the pure compound, somewhere between 0.3 and 0.5 K.[1]

According to a Kondo-lattice model of Doniach,[5] these results indicate that $CeAl_3$ corresponds to a nearly critical value of the exchange parameter J, separating magnetic, and nonmagnetic systems. Expansion of the lattice by larger La causes a decrease of J and therefore a decrease of both relevant energy scales T_{RKKY} and T_K. Due to a much stronger dependence of T_K than T_{RKKY} on J this leads to a magnetically ordered state. The reduction of T_K upon La alloying is also consistent with the high temperature susceptibility. The susceptibility for all samples, but $x=0.9$, at sufficiently high temperatures can be approximately described by a Curie-Weiss law. A fit performed consistently between 150 and 300 K yields μ_{eff} in the range 2.44 and $2.59\mu_B$/Ce, with most of the values in the vicinity of $2.54\mu_B$/Ce. This latter value is close to the Hunds's rule effective moment of $4f^1$ ion. The scattering of measured μ_{eff} is due to a rather narrow temperature range of the fit and particularly due to a low value of the upper temperature limit with respect to the crystal field splitting. Thus, these measurements provide an evidence for a stable trivalent configuration of Ce ions for all concentrations. The corresponding paramagnetic Curie-Weiss temperature is negative with the absolute value (Θ_{CW}) having a tendency to decrease with x. Since in a single impurity Kondo model Θ_{CW} is proportional to T_K,[6] the overall behavior of Θ_{CW} is consistent with a decrease of T_K with x.

Our previous study has shown that the weak anomaly in C/T^3 becomes more distinctive and moves to higher temperatures upon doping with La. These changes are seen for doping levels as small as 1%. This weak structure evolves smoothly into a pronounced peak, not only in C/T, but also in C for concentrations corresponding to 5% or more of La. Since these peaks have appearances of typical antiferromagnetic transitions, we have suggested the antiferromagnetic ordering interpretation, which is also consistent with the above described susceptibility data. These pronounced peaks in C/T are shown in Fig. 3. C/T values have been obtained by subtracting the phonon contribution approximated from the $LaAl_3$ data and normalized to a mole of Ce.

C/T at $T=0$ (γ), shown in Fig. 4, has been extrapolated from the lowest temperature C/T versus T^2 data. The main source of the uncertainty, about 10% for $x<0.8$ and somewhat larger for $x\geqslant 0.8$ (20%), is a narrow temperature range of the fit and the fact that the data do not strictly follow this assumed temperature dependence. In fact, the specific heat results for $CeAl_3$ by Brodale *et al.*[7] indicate C/T to be linear in T between 0.06 and 0.25 K. Assuming C/T linear in T at the lowest temperatures does not appreciably affect the final results. γ initially decreases with x and then increases for $x>0.2$. A similar initial decrease with x was observed in $Ce_{1-x}La_xCu_2Si_2$ (Ref. 8) and $U_{1-x}M_xBe_{13}$ (Ref. 9) (sometimes considered as a U-Kondo lattice) and interpreted in terms of the destruction of the coherent heavy fermion state upon dilution. Such a decrease of γ on x is in fact consistent with general arguments concerned with the formation of a heavy fermion state from the single impurity limit. These arguments are also related to the famous exhaustion principle. When the number of Kondo centers increases, the Kondo screening changes character from independent impu-

TABLE I. Magnetic susceptibility and specific heat parameters for $Ce_{1-x}La_xAl_3$ alloys.

La x	χ_0 (2 K) (m emu/Ce mol)	μ_{eff} (μ_B)	Θ_{CW} (K)	$S_m(3\ \mathrm{K})/(R\ln 2)$	T_K(K)
0	28.9	2.53	29	0.59	4.0
0.1	31.7	2.57	33	0.62	3.4
0.2	30.9	2.52	29	0.65	3.0
0.3	33.5	2.54	25	0.64	3.2
0.4	36.8	2.59	25	0.66	2.8
0.5	40.3	2.53	23	0.70	2.3
0.6	43.8	2.58	24	0.73	2.0
0.7	51.5	2.44	11	0.81	1.1
0.8	57.9	2.53	18	0.83	1.0

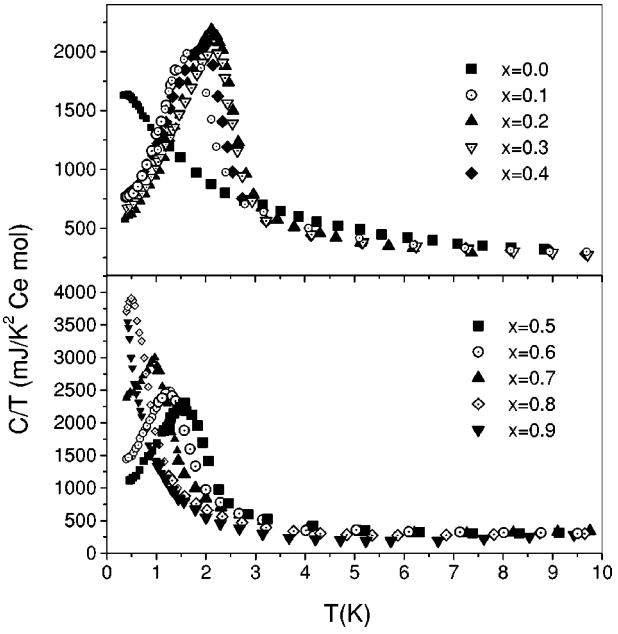

FIG. 3. C/T versus T for $Ce_{1-x}La_xAl_3$.

rity screening to the dynamical process in which all conduction electrons participate simultaneously in the screening of each Kondo impurity. Such a state can only develop at sufficiently low temperatures and is characterized by a Kondo temperature significantly lower than that corresponding to the single impurity.[10]

However, a rather narrow concentration range in which γ decreases with x in $Ce_{1-x}La_xAl_3$, and the fact that in addition to the aforementioned results for $Ce_{1-x}La_xCu_2Si_2$ there are no other alloying data published showing a similar concentration dependence of γ on La substitution, make the ''coherent Ce lattice'' interpretation very unlikely. In fact we argue that in our case the experimental γ is not a good measure of T_K, and we attempt to extract it from the specific heat in the paramagnetic state. For all investigated alloys the entropy removed between $T=T_0$ and 0 was calculated; where T_0 has been arbitrarily set to 3 K, thus larger than the

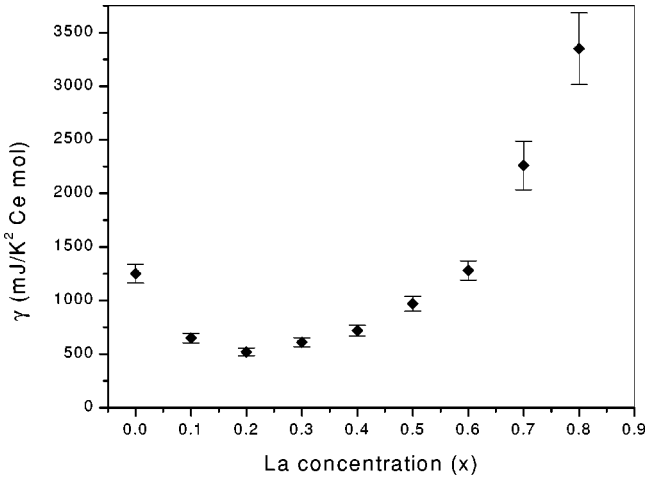

FIG. 4. γ versus x for $Ce_{1-x}La_xAl_3$.

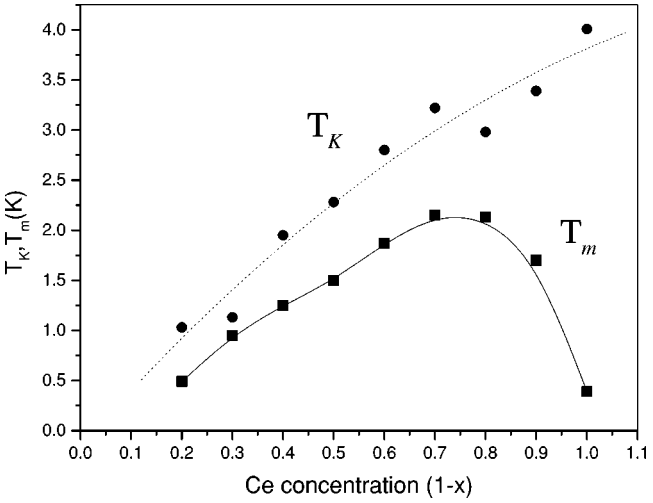

FIG. 5. T_m and T_K versus 1-x (Ce-concentration) for $Ce_{1-x}La_xAl_3$. See text for the definition of T_m and T_K.

temperature of the anomaly for any x. This entropy S_0 is shown in Table I. From the value of S_0 we calculate the Kondo temperature assuming $S_0=S_K(T_0)$, where S_K is the Kondo entropy for spin 1/2. Although the entropy S_0 can be mostly magnetic, our procedure is justified by the following argument. The entropy removed between $T=\infty$ and T_0 (S_1) is primarily via the Kondo effect and thus constitutes a good measure of T_K. Since $S_0+S_1=R\ln 2$, S_0 is also a good measure of T_K. A similar argument was presented by Varma.[11] The extracted T_K as a function of 1-x (Ce concentration) is shown in Fig. 5. Increasing T_0 to 4 K does not change a qualitative behavior of $T_K(x)$. On the other hand, $T_0=5$ K (or larger) results in a much larger scattering of $T_K(x)$. [This is because $T_K(T)$ is only weakly temperature dependent for T much larger than T_K.] Obviously, this procedure neglects the contribution due to higher lying crystal field levels. However, we believe that this contribution at temperatures lower than 3 K is small; moreover, it should not vary significantly between different compositions.

Figure 5 shows also the position of the maximum in C/T, T_m, for the same compositions. This figure is highly reminiscent of that corresponding to the Doniach's (Kondo lattice) model if T_m is associated with the magnetic phase transition. Thus, the zero field alloying results for $(Ce,La)Al_3$ provide support for the conventional Kondo-effect behavior and magnetic nature of the low-temperature anomaly. Note that assuming an alternative description of the alloys in terms of the anisotropic (single-impurity) Kondo model (AKM) leads to a rather unusual phase diagram in which T_K has a nonmonotonic dependence on x. According to AKM,[12] T_K is a function of two components of J, such that $T_K \propto J_\perp^{1/J_z}$. Thus, in principle, one can obtain a nonmonotonic dependence of T_K on x if $d(J_\perp)/dx$ and $d(J_z)/dx$ have opposite signs. However, this scenario is unlikely considering the lattice constant data. Therefore, the alloying results seem to be much more consistent with a conventional Kondo-lattice model than with AKM. The fact that La-alloying affects not only the f-electron conduction electrons coupling J but also the average distance between f moments introduces an addi-

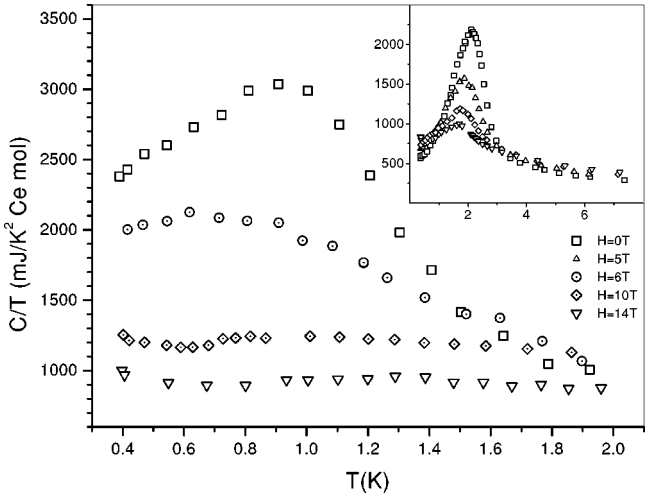

FIG. 6. C/T versus T for $Ce_{0.3}La_{0.7}Al_3$ in $H=0$, 6, 10, and 14 T. The inset shows C/T versus T for $Ce_{0.8}La_{0.3}Al_3$ in $H=0$, 5, 10, and 14 T (from Ref. 4.)

tional complication. Substituting nonmagnetic ions for magnetic ones leads to a decrease of the average distance between magnetic ions R, such that $T_{\mathrm{RKKY}} \propto R^{-3} J^2 \propto (1-x) J^2$. Figure 5 suggests that this dilution effect might be important for $x > 0.3$. In this concentration range, T_m is approximately linear in $(1-x)$ and intercepts $T_m = 0$ at x close to 1.

In our previous paper we have presented a more direct evidence for the inapplicability of AKM to $(Ce,La)Al_3$ alloys by performing the measurement of the specific heat of $Ce_{0.8}La_{0.2}Al_3$ in magnetic fields.[4] (See also the inset to Fig. 6.) The reported increase of γ and decrease of T_m in fields were clearly inconsistent with AKM. We have expanded this investigation to a much more dilute $Ce_{0.3}La_{0.7}Al_3$, which has an enhanced a/c, and therefore larger magnetic anisotropy, with respect to that for $x=0.2$. Both the dilution mechanism and the increase of the magnetic anisotropy are expected to make AKM effects more pronounced. The electronic part of the specific heat, normalized to a mole of Ce, is shown in the main pane of Fig. 6 for 0, 6, 10, and 14 T. As opposed to the data for $x=0.2$ (inset to Fig. 6), we do not observe an increase of C/T on H in the investigated temperature and field regime. The magnetic field has a strong influence on the size and sharpness of the anomaly. Because of this latter effect, it is rather difficult to estimate the change of T_m for the fields studied. Our best estimate is that T_m is reduced by about 20% for 6 T and the anomaly is completely washed out for 10 and 14 T. Weak maxima seen in C/T for 10 and 14 T, at higher temperatures, can be ascribed to the behavior corresponding to $S=1/2$ impurity in fields.[13] Again, the reduction of T_m and the dramatic change of the specific heat values in fields, particularly around T_m, are inconsistent with AKM and strongly point to the magnetic nature of the anomaly. A much stronger response of the low temperature specific heat of $Ce_{0.3}La_{0.7}Al_3$ to the magnetic field than that for $Ce_{0.8}La_{0.2}Al_3$ is consistent with significantly smaller relevant energy scales of the former system, such as T_K and T_{RKKY}, with respect to applied fields ($\mu_{\mathrm{eff}}H$). This difference in energy scales can also explain apparently different dependence of lowest temperature C/T values on H. Most probably, an increase of C/T on H can also be observed in $Ce_{0.3}La_{0.7}Al_3$ but at smaller (than 0.3 K) temperatures and for sufficiently low fields. On the other hand, the analysis of the depression of the lowest temperature C/T in fields $H=6$ T and higher, using a Kondo-resonance broadening model,[14] yields $\mu_{\mathrm{eff}} \approx 1\mu_B$, a value whose magnitude is consistent with the ground state doublet.

III. CONCLUSIONS

In summary, the described La-alloying results of $CeAl_3$ are consistent with the Kondo-lattice model in the following sense. The increase of the lattice parameter a upon a partial substitution of La for Ce causes a decrease of the f-electron-conduction-electron coupling (J) which leads to a decrease of both Kondo and magnetic energy scales. Note that this study implies the importance of in-hexagonal-planes hybridization on the low-temperature properties and fails to provide any insight on how the spacing between hexagonal planes (c) affects the ground state. Thus, these results do not preclude the importance of the magnetic and structural anisotropy aspect on the ground state of $CeAl_3$, as argued by both Goremychkin *et al.*[2] and Corsepius *et al.*[15] Extensive alloying and pressure investigations of other hexagonal Ce-based Kondo lattices $CePd_2Al_3$ (Ref. 16) and $CeCu_5$ (Ref. 17) have shown that the anisotropy plays an important role. In these two latter systems, the in-plane hybridization is responsible for the magnitude of the Kondo temperature while the spacing between hexagonal planes seems to affect the Neel temperature only. Thus, a similar alloying and uniaxial pressure study of $CeAl_3$, in which the lattice constant c is primarily varied, would provide a complementary information on the nature of the ground state of $CeAl_3$.

ACKNOWLEDGMENT

This work has been supported by the U.S. Department of Energy, Grant No. DE-FG02-99ER45748.

[1] K. Andres, J.E. Graebner, and H.R. Ott, Phys. Rev. Lett. **27**, 1779 (1975).

[2] E.A. Goremychkin, R. Osborn, B.D. Rainford, and A.P. Murani, Phys. Rev. Lett. **84**, 2211 (2000).

[3] B. Andraka, C.S. Jee, and G.R. Stewart, Phys. Rev. B **52**, 9462 (1995).

[4] R. Pietri, K. Ingersent, and B. Andraka, Phys. Rev. Lett. **86**, 1090 (2001).

[5] S. Doniach, *Valence Fluctuations and Related Narrow Band Phenomena* (Plenum Press, New York, 1977), p. 169; S. Doniach, Physica B **91**, 231 (1977).

[6] See, for example, J. Callaway, *Quantum Theory of the Solid State*

(Academic Press, New York, 1991), p. 448.
[7] G.E. Brodale, R.A. Fisher, N.E. Phillips, and J. Flouquet, Phys. Rev. Lett. **56**, 390 (1986).
[8] C.S. Jee, B. Andraka, J.S. Kim, and G.R. Stewart, Phys. Rev. **43**, 2656 (1991).
[9] J.S. Kim, B. Andraka, C.S. Jee, S.B. Roy, and G.R. Stewart, Phys. Rev. **41**, 11 073 (1990).
[10] A.J. Millis, Physica B **259-261**, 1169 (1999).
[11] C.M. Varma, Phys. Rev. Lett. **55**, 2723 (1985).
[12] T.A. Costi, Phys. Rev. Lett. **80**, 1038 (1998).
[13] The Kondo $S=1/2$ solution does not exhibit a maximum in C/T for $H=0$. However, a weak maximum appears in C/T for sufficiently large fields, corresponding to $\mu_{\mathrm{eff}}H/k_BT_K \approx 2$ and larger; R. Pietri, B. Andraka, and K. Ingersent (unpublished).
[14] K. Satoh, T. Fujito, Y. Maeno, Y. Onuki, and K. Komatsubara, J. Magn. Magn. Mater. **76-77**, 128 (1988).
[15] S. Corsepius, M. Lenkewitz, and G.R. Stewart, J. Alloys Compd. **259**, 29 (1997).
[16] S.A. Mentink, G.J. Nieuwenhuys, A.A. Menovsky, J.A. Mydosh, H. Tou, and Y. Kitaoka, Phys. Rev. **49**, 15759 (1994).
[17] M. Lorenzen, M. Hanfland, E. Bauer, F.-W. Schaper, and A. Eichler, Physica B **259-261**, 20 (1999).