Ground state in $CeAl_3$: A $Ce_{1-x}La_xAl_3$ study

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By performing La doping on the Ce sites we have demonstrated that the heavy-fermion ground state in $CeAl_3$ is extremely unstable toward local-moment antiferromagnetism. Profound changes in the low-temperature specific heat are already seen at the 1% doping level. We believe that this sensitivity to structural/chemical modifications is responsible for a large number of the mutually contradictory experimental results reported for $CeAl_3$. Further, we propose that the weak C/T structure observed for some $CeAl_3$ samples near 0.4 K has a magnetic origin.

The nature of the ground states among the so-called heavy-fermion materials[1] remains a subject of intense research. Most of the heavy-fermion systems are based on either Ce or U, and these two classes can be considered as yielding two limiting cases of the heavy-fermion behavior. The overall low-temperature behavior (but not superconductivity) of the Ce-based systems can be fairly well accounted for by two mechanisms strongly competing with each other: local-moment-type ordering of $4f$ moments via RKKY-type interactions and the Kondo effect arising as a result of weak charge fluctuations of Ce. The $T=0$ properties are normally dominated by one of these mechanisms. The majority of Ce-based compounds order antiferromagnetically with the value of the ordered moment being a large fraction of μ_B, indicating a local-moment-type ordering, and with the remnant Sommerfeld coefficient γ $[=C/T(T\rightarrow 0)]$ not exceeding 100–200 mJ/K^2 mol [the so-called magnetic Kondo lattices $CeAl_2$ (Ref. 2), $CeCu_2$ (Ref. 3), CeB_6 (Ref. 4), CePdIn (Ref. 5)]. $CeCu_6$ (Ref. 6) is, on the other hand, an example of a system where the Kondo effect prevails and no magnetism is detected down to lowest accessible temperatures. It attains a huge value of γ of almost 1600 mJ/K^2 mol. There is a small class of Ce compounds, with $CeCu_2Si_2$ (Ref. 7) and $CeAl_3$ (Ref. 8) the most outstanding ones, which seem not to fit this classification scheme. Both in $CeCu_2Si_2$ (Ref. 9) and in $CeAl_3$ (Ref. 10) a weak magnetism has been claimed to coexist with large Sommerfeld coefficients of 900 and 1600 mJ/K^2 mol, respectively. Such a coexistence of heavy masses and (usually itinerant) magnetism is a well-established characteristic feature of U-based heavy-fermion metals, e.g., UPt_3 (Ref. 11) and $U_{0.97}Th_{0.03}Be_{13}$ (Ref. 12), and one of the most interesting unsolved issues in the physics of heavy fermions.

However, a recent experimental study seems to suggest presence of multidomain effects in $CeCu_2Si_2$ at low temperatures.[13] One might argue, therefore, that the magnetic order and heavy electron masses occur simultaneously, but in a heterogeneous way. Such an explanation has to be even more seriously considered for $CeAl_3$ whose low-temperature properties are extremely sample dependent. The first direct indications of magnetism in this system came from the muon-spin-resonance (μSR) study by Barth *et al.*[10] Their results suggested a short-range magnetic order, but lack of a long-range order, below about 0.7 K. Subsequent ^{27}Al NMR measurements by Nakamura *et al.*[14] revealed an antiferromagnetic order, with a sizable value of the ordered moment of about $0.3\mu_B$, below 1.2 K. On the other hand, NMR measurements by Wong and Clark,[15] performed on a different sample, have not produced any evidence of magnetism. Some discrepancies exist also in reported thermodynamic studies, like heat capacity and magnetic susceptibility. Most of these studies did not produce clear signatures of magnetic behavior at the lowest temperatures with the exception of those performed on single crystals of $CeAl_3$ by Lapertot *et al.*[16] Their measurements revealed pronounced anomalies in both the specific heat and magnetic susceptibility at temperatures larger than 1 K, strongly indicating large local-moment-type antiferromagnetic ordering. This ordering drastically reduced the Sommerfeld coefficient at the lowest temperatures. All other reported data, to our knowledge, show only very shallow maxima in the specific heat divided by temperature (C/T) around 0.4 K and in the magnetic susceptibility at about 0.6 K.[17,18] Formation of such a maximum (from the high-temperature side) can also be inferred from our specific-heat data shown in Fig. 1. This subtle structure

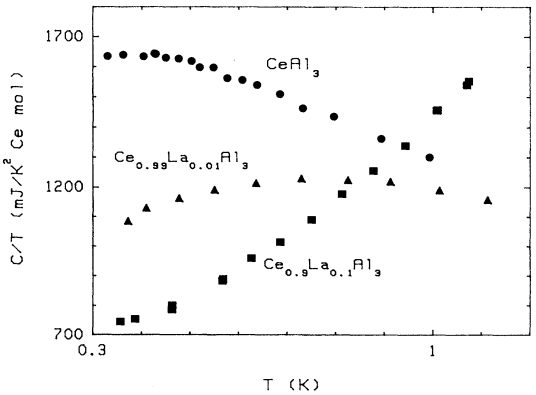

FIG. 1. Temperature dependence of C/T for $CeAl_3$, $Ce_{0.99}La_{0.01}Al_3$, and $Ce_{0.9}La_{0.1}Al_3$ between 0.3 and 1.1 K.

in C/T has attracted considerable interest and has been variously ascribed to either a formation of the coherent state[17] (freezing out local Kondo fluctuations) or freezing out intersite magnetic correlations.[19]

In order to resolve the aforementioned inconsistencies between different experimental studies and identify the origin of the C/T anomaly, we have initiated an alloying study of $CeAl_3$. An alloying approach has been very helpful in clarifying the nature of low-temperature states in a number of Ce-based heavy fermions, mainly because of the existence of a nonmagnetic analog of Ce, La. The scarcity of reported comprehensive alloying studies on $CeAl_3$ can be linked to difficulties with synthesizing the pure compound. $CeAl_3$ forms peritectically with parasitic phases $CeAl_2$ and Ce_3Al_{11}. Some sample homogenization can be achieved by long-time annealing. All our polycrystalline samples annealed for 3 weeks at 830 °C were single phase as far as the x-ray diffraction and magnetic susceptibility are concerned. (Magnetic susceptibility is a particularly useful characterization technique in this case, since both $CeAl_2$ and Ce_3Al_{11} are known to be magnetic.)

The low-temperature specific-heat data for $Ce_{1-x}La_xAl_3$, where $x=0$, 0.01, and 0.1, in the temperature range 0.35–1.1 K are shown in Fig. 1 in the form of C/T versus T. All specific-heat results in this report are normalized to 1 mol of Ce; i.e., the corresponding $LaAl_3$ values have been subtracted and the results divided by $1-x$. Our data obtained on the undoped sample are in excellent agreement with the original data by Andres, Graebner, and Ott.[8] La doping induces drastic changes in the specific heat. Substitution of only 1% of La for Ce reduces C/T at 0.35 K from 1630 to about 1050 mJ/K^2 mol. Since C/T of the doped sample clearly decreases with decreasing T at the lowest temperatures, we expect the relative change of the Sommerfeld coefficient to be even greater than 40% at 0 K. We are not aware of any other Ce-based heavy-fermion system so sensitive to La alloying. For comparison, γ of $Ce_{1-x}La_xCu_6$ alloys (γ of $CeCu_6$ is almost identical to that of $CeAl_3$) is essentially x independent.[20] The large decrease of γ between $CeAl_3$ and $Ce_{0.99}La_{0.01}Al_3$ is accompanied by shifting to higher temperatures (from about 0.4 to 0.75 K) and an increase in the size of the mentioned broad C/T anomaly. We stress that these anomalies for $x=0$ and 0.01 samples can only be identified by maxima in C/T versus T, while C itself is a monotonic function of T at low temperatures. The observed enhancement of the C/T structure and increase of its temperature upon alloying is evidence against the coherence interpretation.

Further La doping continues to strongly modify the specific-heat data. Samples with 5% and more of Ce replaced by La exhibit already clear signatures of thermodynamic transitions in the specific heat (see Fig. 2). Both the specific-heat and magnetic-susceptibility data for these samples are consistent with an antiferromagnetic ordering. The T^3 temperature dependence of the specific heat below 1 K is characteristic of antiferromagnetic spin waves. In Fig. 3, the low-temperature C/T data for $Ce_{0.9}La_{0.1}Al_3$ from Fig. 1 are shown to be proportional to T^2. The Sommerfeld coefficient for this sample is about

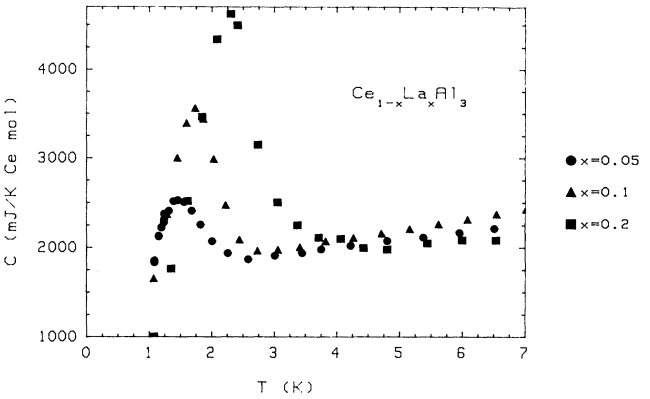

FIG. 2. Temperature dependence of the specific heat for $Ce_{1-x}La_xAl_3$, where $x=0.05$, 0.1, and 0.2, between 1 and 7 K.

620 mJ/K^2 mol, still large, but more than 60% smaller than for the pure compound. Magnetic-susceptibility versus temperature curves (χ vs T; see Fig. 4) for $x=0.1$ and 0.2 samples also have maxima, but at temperatures about 20% larger than the corresponding maxima in the specific heat. Since 1.8 K is the lowest temperature we can reach with our magnetometer, we could not detect similar anomalies in χ for samples with La content less than 10%. (Recall that a broad maximum in χ for the pure compound occurs also at higher temperature than the temperature of the C/T maximum.) The $x=0.2$ sample has been checked for any thermal and magnetic hysteretic effects. No such effects have been found, consistent with an antiferromagnetic nature for the observed transitions.

The entropies associated with the magnetic transitions are large fractions of R ln2. The measured entropy for the $x=0.1$ sample at 2.7 K (just above the peak in C) is about $0.6R$ ln2 per mole of Ce. The corresponding value for $x=0.2$ is about $0.7R$ ln2 at 3.7 K. This second number carries a large uncertainty since the specific heat for $x=0.2$ was measured only down to 1 K; data below 1 K were extrapolated from those above 1 K assuming the temperature dependence of antiferromagnetic spin waves. Large entropies removed via ordering strongly imply the ordering of local moments. The values of the ordered

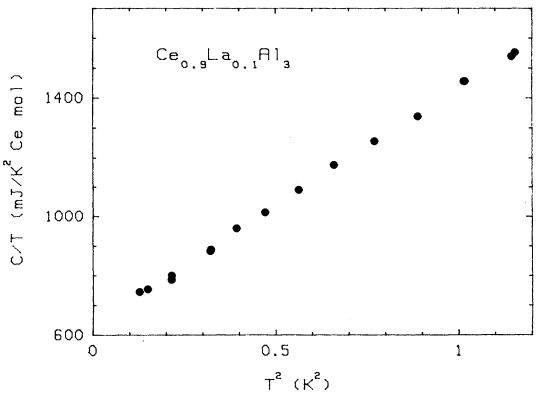

FIG. 3. C/T vs T^2 for $Ce_{0.9}La_{0.01}Al_3$ below 1.1 K.

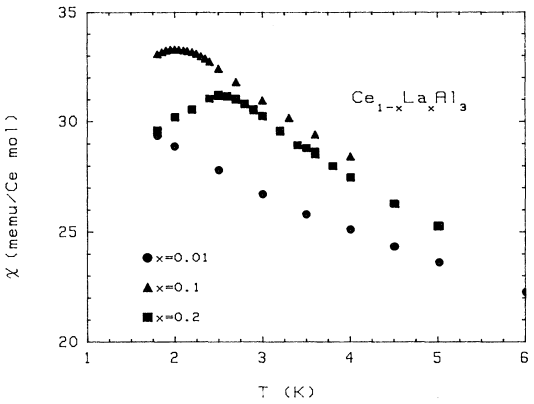

FIG. 4. Low-temperature magnetic susceptibility for $Ce_{1-x}La_xAl_3$, where $x=0.01$, 0.1, and 0.2.

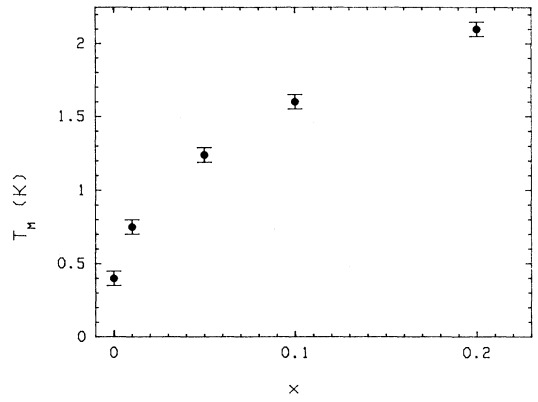

FIG. 5. Temperature position of the maximum in $C/T(T_M)$ vs x.

moments have been approximated using a molecular-field formula[21] derived for a single up and down antiferromagnet and are about $0.26\mu_B$/Ce and $0.34\mu_B$/Ce for $x=0.1$ and 0.2, respectively. Both these numbers are close to the ones occasionally claimed for the pure compound.[14,16]

What is the connection between the weak C/T anomalies found in $x=0$ and 0.01 samples and the distinct C anomalies seen for $x\geq 0$ samples? In Fig. 5 we show temperature position of the C/T maxima (T_M) for all the investigated samples. There is some difference between T_M and a temperature corresponding to the maximum in the specific heat (T_N) for $x\geq 0.05$ (T_M is smaller than T_N). This difference is the largest for $x=0.05$, about 0.2 K, and decreases with x such that it almost disappears for $x=0.2$. Figure 5 demonstrates that T_M varies monotonically and smoothly with x, implying the same source of the C/T maximum in the pure $CeAl_3$ sample and of those found in the specific heat for our La-doped samples. Thus our data provide evidence, for the first time, for a magnetic nature of the subtle C/T anomaly in the specific heat of the pure compound. Furthermore, our data are consistent with the existence of local moment domains. Formation of such domains can be readily understood in view of an incredible sensitivity of $CeAl_3$ toward creation of local magnetic moments as evidenced by the results on the La-doped samples. Structural defects, similar to those produced by low-level doping, can be anticipated considering the above discussed difficulties with making highly homogeneous samples of $CeAl_3$ due its peritectic formation. The DO19 structure of $CeAl_3$ is known to be prone to stacking-type defects.[22]

The final question which we address is about the mechanism of such an astounding destruction of heavy electron masses, not seen in other Ce-based heavy fermions, and creating local moments. There are two obvious consequences of replacing Ce ions by La. First, we remove some of the magnetic moments; second, we modify interatomic distances (which, in turn, can create local strains in the sample). La alloying acts as a negative lattice pressure and can cause a decrease in the effective exchange parameter J via a decrease of the hybridization strength between the f states of Ce and the ligand states. Within the theoretical scenario based on the Kondo-necklace model, the J value for $CeAl_3$ would have to be close to the critical one, separating a nonmagnetic and magnetic ground state.[23]

Another explanation invokes magnetic frustration. Ce ions in the basal plane of this hexagonal, Ni_3Sn-type, crystal structure form a triangular lattice which does not support an antiferromagnetic order in these planes. Removing some of the magnetic moments, by substituting La for Ce, would relax the triangular lattice constraint. This second explanation relies on the assumption that the in-plane exchange interactions, which correspond to the second-nearest neighbor (Ce-ion separation in the planes is 6.545 Å), are dominant. Such a scenario is plausible considering the arrangement of Al ions. There are no Al ions between the nearest-neighbor Ce ions (4.43 Å, belonging to two adjacent basal planes), while any two nearest Ce ions in the basal plane are separated by an Al ion. In order to find out which of these two discussed mechanisms is responsible for the observed distraction of heavy masses and formation of local moments, we intend to perform a low-level Y-doping study. Y atoms are smaller than Ce, and therefore the first of the discussed mechanisms cannot be applicable.

In summary, we have demonstrated that the heavy-fermion state in $CeAl_3$ is unstable toward local-moment antiferromagnetism. The extreme sensitivity of $CeAl_3$ to minor chemical and structural alterations accounts for discrepancies between various reported experimental results. The C/T anomaly has a magnetic origin and can be explained by the presence of small antiferromagnetic domains associated with sample imperfections. There is no evidence for homogeneous coexistence of a heavy-fermion state and magnetic order in $CeAl_3$.

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[1]G. R. Stewart, Rev. Mod. Phys. **56**, 755 (1984); N. Grewe and F. Steglich, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner, Jr. and L. Eyring (Elsevier, Amsterdam, 1991), Vol. 14, Chap. 97, p. 343.
[2]C. D. Bredl, F. Steglich, and K. D. Schotte, Z. Phys. B **29**, 327 (1978).
[3]E. Gratz, E. Bauer, B. Barbara, S. Zemirili, F. Steglich, C. D. Bredl, and W. Lieke, J. Phys. F **15**, 1975 (1985).
[4]C. D. Bredl, J. Magn. Magn. Mater. **63&64**, 355 (1987).
[5]H. Fujii, Y. Uwatoko, M. Akayama, K. Satoh, Y. Maeno, T. Fujita, J. Sakurai, H. Kamimura, and T. Okamoto, Jpn. J. Appl. Phys. **26**, 549 (1987); B. Andraka, C. Quitmann, J. S. Kim, and G. R. Stewart, Bull. Am. Phys. Soc. **32**, 685 (1987).
[6]G. R. Stewart, Z. Fisk, and M. S. Wire, Phys. Rev. B **30**, 482 (1984).
[7]F. Steglich, J. Aarts, C. D. Bredl, D. Meschede, W. Franz, and H. Schafer, Phys. Rev. Lett. **43**, 1892 (1979).
[8]K. Andres, J. E. Graebner, and H. R. Ott, Phys. Rev. Lett. **35**, 1979 (1975).
[9]H. Nakamura, Y. Kitaoka, Y. Yamada, and K. Asayama, J. Magn. Magn. Mater. **76&77**, 517 (1989); Y. J. Uemura, W. J. Kossler, X. H. Yu, H. E. Schone, J. R. Kempton, C. E. Stronach, S. Barth, F. N. Gygax, B. Hitti, A. Schenck, C. Baines, W. F. Lankford, Y. Onuki, and T. Komatsubara, Phys. Rev. B **39**, 4726 (1989).
[10]S. Barth, H. R. Ott, F. N. Gygax, B. Hitti, E. Lippelt, A. Scheck, C. Baines, B. van den Brandt, T. Konter, and S. Mango, Phys. Rev. Lett. **59**, 2991 (1987).
[11]G. Aeppli, E. Bucher, A. I. Goldman, G. Shirane, C. Broholm, and J. K. Kjems, J. Magn. Magn. Mater. **76&77**, 385 (1988).
[12]R. H. Heffner, J. L. Smith, J. O. Willis, P. Birrer, C. Baines, F. N. Gygax, B. Hitti, E. Lippelt, H. R. Ott, A. Schenck, E. A. Knetch, J. A. Mydosh, and D. E. MacLaughlin, Phys. Rev. Lett. **65**, 2816 (1990).
[13]R. H. Heffner, A. Amato, R. Feyerherm, F. N. Gygax, A. Schenck, C. Geibel, F. Steglich, and D. E. MacLaughlin, Bull Am. Phys. Soc. **39**, 1992 (1994).
[14]H. Nakamura, Y. Kitaoka, K. Asayama, and J. Flouquet, J. Magn. Magn. Mater. **76&77**, 465 (1988).
[15]W. H. Wong and W. G. Clark, J. Magn. Magn. Mater. **108**, 175 (1992).
[16]G. Lapertot, R. Calemczuk, C. Marcenant, J. Y. Henry, J. X. Boucherle, J. Flouquet, J. Hammann, R. Cibin, J. Cors, D. Jaccard, and J. Sierro, Physica B **186-188**, 454 (1993).
[17]C. D. Bredl, S. Horn, F. Steglich, B. Luthi, and R. M. Martin, Phys. Rev. Lett. **52**, 1982 (1984).
[18]A. Benoit, A. Berton, J. Chaussy, J. Flouquet, J. C. Lasjaunias, J. Odin, J. Palleau, J. Peyrard, and M. Ribault, in *Valence Fluctuations in Solids,* edited by L. M. Falicov, H. Hanke, and M. B. Maple (North-Holland, Amsterdam, 1981), p. 283.
[19]S. Doniach, in *Theoretical and Experimental Aspects of Valence Fluctuations and Heavy Fermions,* edited by L. C. Gupta and S. K. Malik (Plenum, New York, 1987), p. 179.
[20]Y. Onuki and T. Komatsubara, J. Magn. Magn. Mater. **63&64**, 281 (1987).
[21]J. Peyrard, Ph.D. thesis d'Etat, Universite de Grenoble, France, 1980.
[22]B. R. Coles, J. Magn. Magn. Mater. **15-18**, 1225 (1980).
[23]N. B. Brandt and V. V. Moshalkov, Adv. Phys. **33**, 373 (1984).