Magnetic Correlations and the Anisotropic Kondo Effect in $Ce_{1-x}La_xAl_3$

E. A. Goremychkin,[1] R. Osborn,[1] B. D. Rainford,[2] T. A. Costi,[3,4] A. P. Murani,[4] C. A. Scott,[2] and P. J. C. King[5]

[1]*Argonne National Laboratory, Argonne, Illinois 60439-4845*

[2]*Department of Physics, University of Southampton, Southampton, SO17 1BJ, United Kingdom*

[3]*Institut für Theorie der Kondensierten Materie, Universität Karlsruhe, 76128 Karlsruhe, Germany*

[4]*Institut Laue Langevin, F-38042 Grenoble Cédex, France*

[5]*ISIS Pulsed Neutron and Muon Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, United Kingdom*

(Received 30 November 2001; published 12 September 2002)

By combining the results of muon spin relaxation and inelastic neutron scattering in the heavy fermion compounds $Ce_{1-x}La_xAl_3$ ($0.0 \leq x \leq 0.2$), we show that static magnetic correlations are suppressed above a characteristic temperature, T^*, by electronic dissipation rather than by thermal disorder. Below T^*, an energy gap opens in the single-ion magnetic response in agreement with the predictions of the anisotropic Kondo model. Scaling arguments suggest that similar behavior may underlie the "hidden order" in URu_2Si_2.

DOI: 10.1103/PhysRevLett.89.147201 PACS numbers: 75.40.Cx, 71.27.+a, 76.75.+i, 78.70.Nx

Although $CeAl_3$ was the first material to be designated a heavy fermion compound [1], the nature of the low temperature ground state has never been resolved [2–5]. An anomaly in the electronic specific heat coefficient, γ, at $T^* \approx 0.5$ K, was shown by muon spin relaxation (μSR) experiments to coincide with the development of static magnetic correlations [3], but no evidence for magnetic order was found by neutron diffraction. It is possible that the ordered moment is too small to be observable by neutron scattering from polycrystalline samples. If so, $CeAl_3$ would be reminiscent of other heavy fermion compounds exhibiting "hidden order," such as URu_2Si_2 [6,7], in which the magnetism is too weak to explain the entropy associated with the observed transition.

The specific heat anomaly that is observed in pure $CeAl_3$ grows in both temperature and magnitude with lanthanum doping. Andraka *et al.* [8] have shown that T^*, defined by the maximum in C/T, increases to 2.2 K in $Ce_{1-x}La_xAl_3$ when $x = 0.2$. Nevertheless, in an earlier study, we were still unable to observe magnetic Bragg peaks in high intensity neutron diffraction [9]. Instead, we proposed that the specific heat peak results from a crossover in the single-ion dynamics that is explained by the anisotropic Kondo model (AKM) [10]. In highly anisotropic systems, such as $Ce_{1-x}La_xAl_3$, the AKM predicts that, at high temperature, the spin dynamics will be purely relaxational but that, at low temperature, an energy gap, representing a tunneling transition between two anisotropically hybridized states, will open up in the magnetic response. It is the development of this spin gap that produces the observed specific heat anomaly at T^*. Various scaling relations predicted by the AKM were in good agreement with our neutron data.

However, Pietri *et al.* [11] concluded that the field dependence of the specific heat peaks was inconsistent with the AKM and probably signified a magnetic transition [12]. It is therefore still an open question whether the unusual spin dynamics in $Ce_{1-x}La_xAl_3$ are evidence of a novel single-ion Kondo regime, as we originally proposed [9], or whether they are the consequence of a magnetic phase transition affected by Kondo interactions.

In this Letter, we present new μSR and inelastic neutron scattering results on the $Ce_{1-x}La_xAl_3$ series, with $x = 0.0$, 0.05, 0.1, and 0.2, that demonstrate unambiguously that magnetic order is not responsible for the specific heat maxima. For low values of x, we observe with muons a well-defined magnetic order parameter. However, in contrast to the expected behavior at a conventional magnetic phase transition, the temperature dependence of the order parameter is extremely weak below T^* and shows no correlation with the spin gap, which falls to zero at T^*. Our results show that the magnetic correlations are suppressed above T^* by the increased density of low-frequency Kondo spin fluctuations caused by the closing of the gap, rather than by thermal disorder. We discuss similarities with URu_2Si_2, which is also highly anisotropic, and show that the predictions of the AKM are in good agreement with its experimental properties.

The samples of $Ce_{1-x}La_xAl_3$ with $x = 0.0$, 0.05, 0.1, and 0.2 were prepared by arc melting stoichiometric quantities of the constituent elements, followed by annealing at 850 °C for four weeks. Neutron diffraction confirmed that all samples were single phase. The μSR measurements were performed at the ISIS pulsed muon facility, Rutherford Appleton Laboratory, U.K., using the MUSR spectrometer. Samples with $x = 0.0$, 0.05, and 0.1 were measured in a dilution refrigerator at temperatures down to 50 mK and the other in a standard helium cryostat down to 1.6 K. The neutron scattering experiments were performed at the Institut Laue Langevin, Grenoble, France, on the time-of-flight spectrometer IN6, using an incident energy of 3.1 meV. Two samples with $x = 0.0$ and $x = 0.05$ were measured in the dilution refrigerator down to milliKelvin temperatures.

In a magnetically ordered phase, muons precess in the static internal field of the sample, which, in zero-field

μSR, leads to well-defined oscillations of the muon spin depolarization with a frequency that is proportional to the magnetic order parameter. In the present experiment, we modeled the muon depolarization by the sum of two components, one magnetic and the other nuclear.

$$G(t) = A_m[\tfrac{2}{3}\cos(2\pi\nu t + \phi)\exp(-\lambda_T t) + \tfrac{1}{3}\exp(-\lambda_L t)] + A_n G_{\mathrm{KT}}(t), \quad (1)$$

where A_m and A_n are the magnetic and nuclear amplitudes, ν is the precession frequency and ϕ is its phase, λ_T and λ_L are the transverse and longitudinal damping coefficients, and $G_{\mathrm{KT}}(t)$ is the Kubo-Toyabe function that accounts for depolarization by ^{27}Al nuclei [13]. The need for two components could mean either that there are two muon sites in these samples, one dominated by nuclear and the other by magnetic relaxation, or that the samples are magnetically inhomogeneous. At the lowest temperatures, the magnetic oscillations account for about 70% of the depolarization in all the samples we measured, in agreement with earlier μSR results [3] and close to the volume fraction of magnetically correlated regions derived from NMR data [5].

In our earlier μSR measurements on samples with $x \geq 0.2$, we did not observe any oscillations, but Fig. 1 shows that they are indeed present at lower values of x. They are particularly well-defined in pure $CeAl_3$, but they become increasingly damped with increasing x. Although our data are in good agreement with earlier results [3,13], the improved statistical quality of the present measurements shows that the oscillations follow the damped sine wave of Eq. (1), rather than the Bessel function proposed by Amato [13]. This indicates that the ordering does not involve a modulation of the magnitude of the magnetic moment [14].

The longitudinal and transverse damping rates are approximately equal at temperatures well below T^*. This rate increases dramatically with x, from 1.6 μs^{-1} at $x = 0.0$ to 12.5 μs^{-1} at $x = 0.2$, so that muon oscillations are no longer observable for $x > 0.1$ and the magnetic depolarization can be modeled by a simple exponential decay. This behavior shows that lanthanum substitution suppresses the well-defined magnetic order seen in pure $CeAl_3$, whereas the specific heat anomalies, shown in the insets in Fig. 1, become much more pronounced with lanthanum substitution. These contrasting trends are the first indication that the specific heat peaks are not associated with conventional magnetic phase transitions.

This conclusion is strengthened by the detailed temperature dependence of the muon spin relaxation, which is illustrated by the behavior of $x = 0.05$ in Fig. 2. The most striking result is the nearly temperature-independent oscillation frequency up to temperatures above T^*. Therefore, the magnetic order parameter does not change significantly over the entire temperature

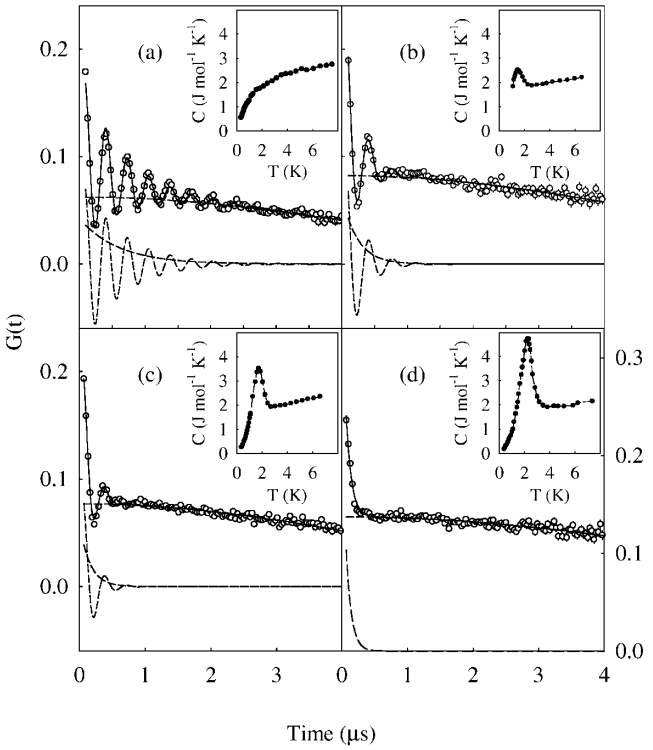

FIG. 1. Zero field muon spin depolarization in $Ce_{1-x}La_xAl_3$ with (a) $x = 0$ at 50 mK, (b) $x = 0.05$ at 100 mK, (c) $x = 0.1$ at 50 mK, and (d) $x = 0.2$ at 1.6 K (note the different scale). The solid lines are fits to Eq. (1), whose three components (transverse and longitudinal magnetic, and nuclear) are shown as dashed lines. The insets show the specific heat data of Ref. [8].

range of the specific heat anomaly, unlike a conventional second-order magnetic phase transition, in which the order parameter should fall to zero. Instead, λ_T begins to diverge at T^*, i.e., there is a broadening of the distribution of internal fields, while λ_L starts to fall as the quasistatic correlations become dynamic. This is consistent with earlier muon data from pure $CeAl_3$ [3,13].

We will now compare this trend with the inelastic excitation seen by neutrons (Fig. 3). In pure $CeAl_3$, the response is almost entirely quasielastic. There is a small inelastic peak at 0.8 meV that represents only 2% of the total spectral weight. It is well known that there is a strong sample dependence to the properties of $CeAl_3$, which probably results from an extreme sensitivity to internal strains [9,15]. We believe that the inelastic peak may arise from small strained regions of the sample and do not discuss it further. Although the remaining response is quasielastic, it has a non-Lorentzian form. In Fig. 3, we have fitted the data to the sum of two quasielastic Lorentzian line shapes (see discussion later). In all the other samples, the magnetic response is well described by a Lorentzian line shape centered at $\pm\Delta$ below T^* and a quasielastic Lorentzian line shape above T^* [9].

Although the magnetic response of pure $CeAl_3$ is quasielastic, it becomes inelastic with increasing x, and the

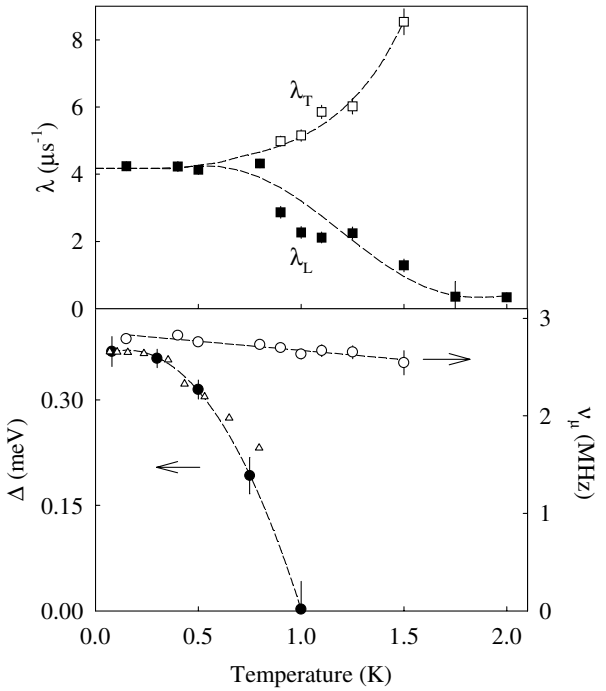

FIG. 2. Temperature dependence of the muon spin depolarization analyzed using Eq. (1) and the excitation energy measured with inelastic neutron scattering. The open and solid squares denote the transverse and longitudinal damping coefficients, λ_T and λ_L (below 1 K, $\lambda_T = \lambda_L$), the open circles denote the precession frequency, ν, and the solid circles denote the excitation energy of the magnetic response, Δ. The triangles are the theoretical values of Δ derived from an inelastic Lorentzian fit to the NRG calculations of $S(\omega)$. The dashed lines are guides to the eye.

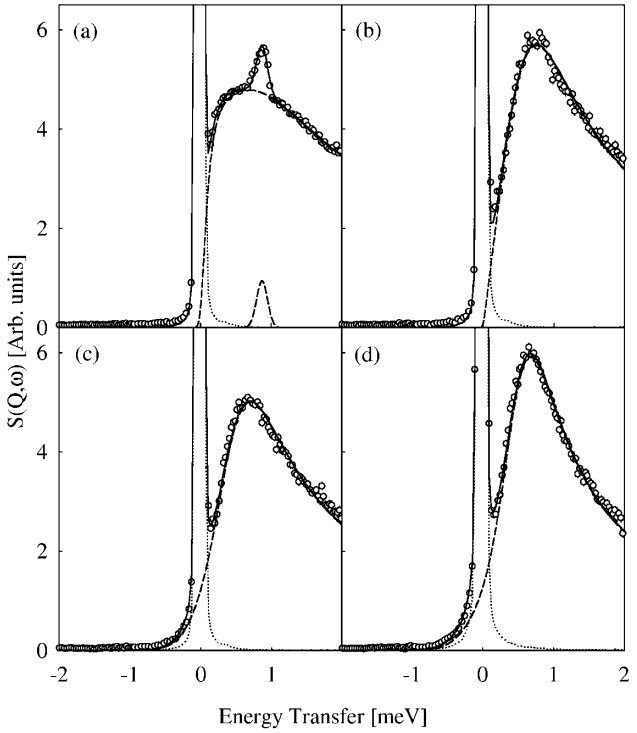

FIG. 3. Inelastic neutron scattering from $Ce_{1-x}La_xAl_3$ with (a) $x = 0.0$ at $T = 80$ mK, (b) $x = 0.05$ at $T = 80$ mK, (c) $x = 0.1$ at $T = 1.6$ K, and (d) $x = 0.2$ at $T = 1.6$ K. The solid line is the sum of the magnetic response (dashed lines) and the elastic background (dotted line).

excitation is progressively better defined at $T \ll T^*$. At $x = 0.05$ ($T^* = 0.8$ K), Δ is 0.37(3) meV and the half-width is 0.66(2) meV at 80 mK, whereas, at $x = 0.2$ ($T^* = 2.2$ K), Δ increases to 0.47(1) meV and the half-width is 0.42(1) meV measured at 1.6 K. The development of this inelastic response with x correlates well with the growth of the specific heat peak, in contrast to the behavior of the muon oscillations.

Figure 2 shows the temperature dependence of the energy, Δ, of this inelastic excitation. The fits show that the energy falls to zero at T^*, as if the gap were proportional to an order parameter. Above T^*, the spin dynamics are overdamped. It is important to note that the entire magnetic response becomes inelastic below T^*. There is no evidence of a two-component response as would be seen if the spin dynamics were spatially inhomogeneous as suggested by μSR and NMR [3,5]. Therefore, although there is evidence that the static magnetic correlations develop inhomogeneously, the dynamical transition involves all the cerium ions.

As discussed in Ref. [9], the excitation cannot arise from a conventional molecular field splitting of the ground state doublet, because such a transition is forbidden by dipole selection rules for a $|\pm\frac{3}{2}\rangle$ Kramers doublet [16]. It can only arise if the doublet is split by off-diagonal matrix elements producing two nonmagnetic singlets, as proposed by Rainford *et al.* [17] in a heuristic analysis of another anisotropic heavy fermion system, $CeRu_2Si_{2-x}Ge_x$. The fact that Δ does not track the magnetic moment, which is nearly temperature-independent over the entire temperature range, provides further confirmation that the excitation is not coupling directly to a molecular field.

To summarize the experimental conclusions, it is clear that the static magnetic correlations are not responsible for the thermodynamic anomalies, but that these anomalies are nevertheless directly correlated with the opening of a spin gap. Just such behavior is predicted by the anisotropic Kondo model. The AKM is formally equivalent to a dissipative two-state system or spin boson model [10,18–20], in which a tunneling transition between two singlets is broadened by coupling to Ohmic dissipation. When mapped onto the AKM, the transverse Kondo exchange produces the energy splitting, while the axial Kondo exchange produces the dissipation. When the anisotropy is sufficiently strong, defined by the dimensionless parameter α being less than $1/3$, there is a specific heat peak at a characteristic temperature at which the dynamics cross over from quasielastic to inelastic. We estimated in Ref. [9] that $Ce_{0.8}La_{0.2}Al_3$ falls in this regime with $\alpha \approx 0.1$. If we apply the same scaling

arguments for the $x = 0.05$ sample, $\alpha \approx 0.2$, but becomes 0.3, i.e., close to the critical value, at $x = 0.0$.

Figure 2 also shows the results of a numerical renormalization group (NRG) calculation of $S(\omega)$ [21]. By fitting an inelastic Lorentzian line shape to the theoretical calculations as a function of temperature, we obtain good agreement with the experimental data up to more than $T^*/2$. At higher temperatures, as the dynamics become progressively overdamped, the theoretical line shape becomes non-Lorentzian, reminiscent of the unusual line shape of the quasielastic response in pure $CeAl_3$. Nevertheless, at $x = 0.05$, the agreement is quantitatively good up to 0.7 K and qualitatively describes the observed transition from inelastic to quasielastic dynamics.

In conclusion, we have observed clear evidence for static magnetic correlations in μSR from compounds of $Ce_{1-x}La_xAl_3$ with $x \leq 0.1$. However, they become progressively more damped with increasing x, whereas peaks in the specific heat become more pronounced. Inelastic neutron scattering shows that these peaks are associated with the opening of a gap in the single-ion spin dynamics consistent with the predictions of the AKM, confirming our earlier conjecture that it is a crossover in the local dynamics rather than cooperative magnetic ordering that is responsible for the thermodynamic behavior.

We believe that these conclusions for $Ce_{1-x}La_xAl_3$ can provide some insight into the hidden order in URu_2Si_2 [6]. Both systems have strong Ising-like anisotropy, with substantial thermodynamic anomalies that are associated with the opening of a gap in the spin dynamics [22,23]. There is evidence that the static magnetic correlations develop inhomogeneously in both systems [5,24]. Furthermore, for URu_2Si_2 there is extremely good agreement between experimental results and the AKM predictions. According to the AKM, $\alpha = \gamma T^*/k_B N_A$, where the electronic specific heat coefficient, $\gamma = 50$ mJ mol^{-1} K^2 [25] and the temperature of the maximum in the specific heat, $T^* = 17.5$ K, so that $\alpha \approx 0.1$. URu_2Si_2 is therefore in the regime where there is an energy gap below T^* and a large concomitant thermodynamic anomaly. The AKM value of the energy gap is $\Delta = \pi^2 k_B^2 \alpha/3\gamma \approx 5.0$ meV, close to the experimental value of 5.5 meV [26]. Finally, the magnetic susceptibility at $T = 0$ is estimated to be $\mu_B^2 N_A/2\Delta = 3 \times 10^{-3}$ emu mol^{-1}, compared to the experimental value of 2.5×10^{-3} emu mol^{-1} [25].

This remarkable quantitative agreement strongly suggests that the anisotropic Kondo model provides an appropriate description of the single-ion properties of URu_2Si_2. The theoretical challenge presented by these results is to incorporate this conclusion into future models of the hidden order parameter.

We thank G. Zarand and D. E. MacLaughlin for helpful discussions. This work was performed with the support of the U.S. Department of Energy, Office of Science, under Contract No. W-31-109-ENG-38.

[1] K. Andres, J. E. Graebner, and H. R. Ott, Phys. Rev. Lett. **35**, 1779 (1975).
[2] C. D. Bredl, S. Horn, F. Steglich, B. Lüthi, and R. M. Martin, Phys. Rev. Lett. **52**, 1982 (1984).
[3] S. Barth, H. R. Ott, F. N. Gygax, B. Hitti, E. Lippelt, A. Schenck, and C. Baines, Phys. Rev. B **39**, 11 695 (1989).
[4] W. H. Wong and W. G. Clark, J. Magn. Magn. Mater. **108**, 175 (1992).
[5] J. L. Gavilano, J. Hunziker, and H. R. Ott, Phys. Rev. B **52**, R13 106 (1995).
[6] N. Shah, P. Chandra, P. Coleman, and J. A. Mydosh, Phys. Rev. B **61**, 564 (2000).
[7] P. Chandra, P. Coleman, J. A. Mydosh, and V. Tripathi, Nature (London) **417**, 831 (2002).
[8] B. Andraka, C. S. Jee, and G. R. Stewart, Phys. Rev. B **52**, 9462 (1995).
[9] E. A. Goremychkin, R. Osborn, B. D. Rainford, and A. P. Murani, Phys. Rev. Lett. **84**, 2211 (2000).
[10] T. A. Costi, Phys. Rev. Lett. **80**, 1038 (1998).
[11] R. Pietri, K. Ingersent, and B. Andraka, Phys. Rev. Lett. **86**, 1090 (2001).
[12] We believe that the discrepancies reported in Ref. [11] are due to the neglect of crystal field effects in their calculations rather than a failure of the AKM. We will address this in more detail in a future publication.
[13] A. Amato, Rev. Mod. Phys. **69**, 1119 (1997).
[14] Amato's model was designed to explain the origin of the large value of ϕ seen in all μSR experiments on $CeAl_3$, including our own. This remains an unresolved problem.
[15] G. E. Brodale, R. A. Fisher, N. E. Phillips, and J. Flouquet, Phys. Rev. Lett. **56**, 390 (1986).
[16] R. Osborn, E. A. Goremychkin, B. D. Rainford, I. L. Sashin, and A. P. Murani, J. Appl. Phys. **87**, 5131 (2000).
[17] B. D. Rainford, A. J. Neville, D. T. Adroja, S. J. Dakin, and A. P. Murani, Physica (Amsterdam) **223B & 224B**, 163 (1996).
[18] T. A. Costi and G. Zaránd, Phys. Rev. B **59**, 12 398 (1999).
[19] S. Chakravarty and J. Rudnick, Phys. Rev. Lett. **75**, 591 (1995).
[20] A. J. Leggett, S. Chakravarty, A. T. Dorsey, M. P. A. Fisher, A. Garg, and W. Zwerger, Rev. Mod. Phys. **59**, 1 (1987).
[21] T. A. Costi and C. Kieffer, Phys. Rev. Lett. **76**, 1683 (1996).
[22] C. Broholm, H. Lin, P. T. Matthews, T. E. Mason, W. J. L. Buyers, M. F. Collins, A. A. Menovsky, J. A. Mydosh, and J. K. Kjems, Phys. Rev. B **43**, 12 809 (1991).
[23] W. J. L. Buyers, Z. Tun, T. Petersen, T. E. Mason, J.-G. Lussier, B. D. Gaulin, and A. A. Menovsky, Physica (Amsterdam) **199B & 200B**, 95 (1994).
[24] K. Matsuda, Y. Kohori, T. Kohara, K. Kuwahara, and H. Amitsuka, Phys. Rev. Lett. **87**, 087203 (2001).
[25] T. T. M. Palstra, A. A. Menovsky, J. van den Berg, A. J. Dirkmaat, P. H. Kes, G. J. Nieuwenhuys, and J. A. Mydosh, Phys. Rev. Lett. **55**, 2727 (1985).
[26] U. Walter, C.-K. Loong, M. Loewenhaupt, and W. Schlabitz, Phys. Rev. B **33**, 7875 (1986).