Magnetic Correlations and the Anisotropic Kondo Effect in Ce$_{1-x}$La$_x$Al$_3$

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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$^2$. An anomaly in the electronic specific heat coefficient, $\gamma$, at $T^* \approx 0.5$ K, was shown by muon spin rotation ($\mu$SR) 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$_2$Si$_2$,$^4$ in which the magnetism is too weak to explain the entropy associated with the observed transition.

The thermodynamic anomaly that is observed in pure CeAl$_3$ grows in both temperature and magnitude with lanthanum doping. $T^*$ increases to 2.2 K in Ce$_{1-x}$La$_x$Al$_3$ when $x = 0.2$, and there is a substantial peak in the specific heat with an entropy approaching $R \ln 2$ (1). Nevertheless, in an earlier study, we were still unable to observe magnetic Bragg peaks in high intensity neutron diffraction$^5$. 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)$^6$. In highly anisotropic systems, such as Ce$_{1-x}$La$_x$Al$_3$, 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.

Although we were able to conclude that the spin dynamics were consistent with the AKM$^3$, we had no explanation for the presence of static magnetic correlations below $T^*$ seen in $\mu$SR. Furthermore, Pietri et al. (10) concluded that the field-dependence of the specific heat peaks, though unusual, was inconsistent with the AKM and probably signified a magnetic transition (11). It is important to clarify the link between the development of static magnetic correlations and the appearance of an energy gap in the spin dynamics, in order to establish the origin of the thermodynamic anomalies and to assess the validity of a single-ion explanation such as the AKM.

In this paper, we present new $\mu$SR and inelastic neutron scattering results on the Ce$_{1-x}$La$_x$Al$_3$ series, with $x = 0.0, 0.05, 0.1, 0.2$, 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, but $T^*$ does not mark the temperature at which the magnetic moments become thermally disordered, as in a conventional magnetic phase transition. Rather, $T^*$ is the temperature at which the magnetic order is suppressed by electronic dissipation. Moreover, there is no correlation between the temperature dependence of the spin gap and the magnetic order parameter, as there must be at a classical magnetic phase transition. We discuss similarities with URu$_2$Si$_2$, another highly anisotropic compound, in which the magnetic order appears to be a parasitic phenomenon (11), but with a Néel temperature $T_N$ slightly less than the “hidden order” transition, i.e., $T_N \leq T^*$ in the case of URu$_2$Si$_2$, whereas $T_N > T^*$ in Ce$_{1-x}$La$_x$Al$_3$ for $x < 0.2$.

The samples of Ce$_{1-x}$La$_x$Al$_3$ 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 sample were single phase. The $\mu$SR measurements were performed at the ISIS pulsed muon facility, Rutherford Appleton Laboratory, UK, 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 fridge down to milliKelvin temperatures.

In a magnetically ordered phase, muons precess in the static internal field of the sample, which, in zero-field \( \mu \)SR, 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.

\[
G(t) = A_m \left[ \frac{2}{3} \cos(2\pi \nu t + \phi) \exp(-\lambda_T t) + \frac{1}{3} \exp(-\lambda_L t) \right] + A_n G_{KT}(t)
\]

where \( A_m \) and \( A_n \) are the magnetic and nuclear amplitudes, \( \nu \) is the precession frequency and \( \phi \) is its phase, \( \lambda_T \) and \( \lambda_L \) are the transverse and longitudinal damping coefficients, and \( G_{KT}(t) \) is the Kubo-Toyabe function that accounts for depolarization by \( ^{27}\text{Al} \) nuclei \cite{note12}. 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 \( \mu \)SR results \cite{note3} and close to the volume fraction of magnetically correlated regions derived from NMR data \cite{note3}.

In our earlier \( \mu \)SR measurements on samples with \( x \geq 0.2 \), we did not observe any oscillations, but Fig. \ref{fig1} 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 \cite{note3,note12}, the improved statistical quality of the present measurements shows that the oscillations follow the damped sine wave of Eq. \ref{eq1}, rather than the Bessel function proposed by Amato \cite{note12}. This indicates that the ordering does not involve a modulation of the magnitude of the magnetic moment \cite{note23}.

The longitudinal and transverse damping rates are approximately equal at temperatures well below \( T^* \). This rate increases dramatically with \( x \), from 1.6 \( \mu s^{-1} \) at \( x = 0.0 \) to 12.5 \( \mu s^{-1} \) 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 to Fig. \ref{fig1}, 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. \ref{fig2}. 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 range of the specific heat anomaly, unlike a conventional second-order magnetic phase transition, in which the order parameter should fall to zero. Instead, \( \lambda_T \) begins to diverge at \( T^* \), i.e. there is a broadening of the distribution of internal fields, while \( \lambda_L \) starts to fall as the quasistatic correlations become dynamic. This is consistent with earlier muon data from pure CeAl\(_3\) \cite{note3,note12}.

We will now compare this trend with the inelastic excitation seen by neutrons (Fig. \ref{fig3}). 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 \cite{note3}. 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-Lorenzian form. In Fig. \ref{fig3}, we have fitted the data to the sum of two quasielastic Lorenzian lineshapes (see discussion later). In all the
other samples, the magnetic response is well described by a Lorenzian lineshape centered at $±\Delta$ below $T^*$ and a quasielastic Lorenzian lineshape above $T^*$.

Although the magnetic response of pure CeAl$_3$ is quasielastic, it becomes inelastic with increasing $x$, and the excitation is progressively better defined at $T \ll T^*$. At $x = 0.05$ ($T^* = 0.8$ K), $\Delta$ is 0.37(3) meV and half-width 0.66(2) meV at 80 mK, whereas, at $x = 0.2$ ($T^* = 2.2$ K), $\Delta$ increases to 0.47(1) meV and 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, $\Delta$, 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 $\mu$SR and NMR [8, 9]. Therefore, although there is evidence that the static magnetic correlations develop inhomogeneously, the dynamical transition involves all the cerium ions.

As discussed in Ref. [8], 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 $|±\frac{3}{2}\rangle$ Kramers doublet [14]. It can only arise if the doublet is split by off-diagonal matrix elements producing two non-magnetic singlets, as proposed by Rainford et al [14] in a heuristic analysis of another anisotropic heavy fermion system, CeRu$_2$Si$_2$-xGe$_x$. The fact that $\Delta$ 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 [8, 10, 11, 12, 13], 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 $\alpha$ 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. [8] 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 $S(\omega)$ [14]. By fitting an inelastic Lorenzian lineshape 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 lineshape becomes non-Lorenzian, reminiscent of the unusual lineshape 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 $\mu$SR from compounds of Ce$_{1-x}$La$_x$Al$_3$ 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.
FIG. 3: Inelastic neutron scattering from Ce$_{1-x}$La$_x$Al$_3$ 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).

We believe that these conclusions for Ce$_{1-x}$La$_x$Al$_3$ can provide some insight into the “hidden order” in URu$_2$Si$_2$ [8]. Both systems have strong Ising-like anisotropy, with substantial thermodynamic anomalies that are associated with the opening of a gap in the spin dynamics [20, 21]. There is evidence that the static magnetic correlations develop inhomogeneously in both systems [20, 21]. We have applied the same AKM scaling relations as in Ref. [8], using the following experimental values for URu$_2$Si$_2$: the electronic specific heat coefficient and the magnetic susceptibility at $T \to 0$, $\gamma = 50$ mJmol$^{-1}$K$^2$ and $\chi = 2.5 \times 10^{-3}$ emu mol$^{-1}$, respectively [22], the excitation energy determined from inelastic neutron scattering, $\Delta = 5.5$ meV [23], and the temperature of the maximum in the specific heat, $T^* = 17.5$ K. We derive $\alpha \approx 0.1$ self-consistently, i.e., it is in the regime where the AKM predicts a dynamical transition and large concomitant thermodynamic anomaly.

It remains to be seen if a lattice version of the AKM can model the dispersion of the magnetic excitations observed by inelastic neutron scattering [24]. Nevertheless, the single-ion model accounts for the main features of URu$_2$Si$_2$ listed above, suggesting that the AKM may form the basis of a resolution of the “hidden order” problem.

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[24] We believe that the discrepancies reported in Ref. [10] 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.
[25] Amato’s model was designed to explain the origin of the large value of $\phi$ seen in all $\mu$SR experiments on CeAl$_3$, including our own. This remains an unresolved problem.