

## Magnetically inhomogeneous ground state of CeAl<sub>3</sub>: An NMR study

J. L. Gavilano, J. Hunziker, and H. R. Ott

*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich–Hönggerberg, CH-8093 Zürich, Switzerland*

(Received 2 February 1995; revised manuscript received 10 July 1995)

We report <sup>27</sup>Al nuclear-magnetic-resonance (NMR) studies on partly oriented powder of CeAl<sub>3</sub> in the temperature range between 0.03 and 10 K. Below 2 K the NMR line shape shows a broad structure, increasing in relative intensity with decreasing temperature. In part of the sample the nuclear magnetization relaxes via a single  $T_1$ , following a Korringa law below 0.6 K. The remaining fraction of nuclei relaxes via a distribution of lower relaxation rates. These two-component NMR spectra manifest a gradual and spatially inhomogeneous development of magnetic correlations in regions with strongly reduced Ce-ion moments.

CeAl<sub>3</sub> has for a long time been considered as a typical heavy-electron metal whose itinerant electrons form a simple Fermi-liquid ground state with strongly renormalized parameters.<sup>1,2</sup> Previous thermal and transport measurements have given no hint of any cooperative phase transition down to temperatures below 1 mK,<sup>2,3</sup> but a  $\mu$ SR study has indicated that frustrated quasistatic magnetic correlations appear below 2 K in CeAl<sub>3</sub>, becoming partly coherent below 0.7 K.<sup>4,5</sup> Different conclusions have been drawn from two different NMR studies. Nakamura and co-workers<sup>6</sup> claimed a phase transition to an antiferromagnetic state occurred at 1.2 K, and more recently Wong and Clark<sup>7</sup> found no indication of a phase transition to a magnetically ordered state down to 0.5 K. The properties of CeAl<sub>3</sub> are known to be extremely sensitive to sample preparation techniques and chemical composition. Therefore, we have performed NMR measurements on samples prepared from the same material used in the previous  $\mu$ SR studies and well characterized by transport and thermal properties.<sup>8</sup> We find that at low temperatures spatially inhomogeneous magnetic correlations among strongly reduced Ce moments develop in CeAl<sub>3</sub> coexisting with normal paramagnetic regions.

CeAl<sub>3</sub> crystallizes in the hexagonal Ni<sub>3</sub>Sn-type structure with the Ce ions on equivalent sites of hexagonal symmetry. The corresponding ground state of the Ce 4*f* electrons is doubly degenerate,  $J_z = \pm |\frac{3}{2}\rangle$ , and the doublets  $\pm |\frac{5}{2}\rangle$  and  $\pm |\frac{1}{2}\rangle$  are at 60 and 87 K.<sup>9</sup> The susceptibility has a large anisotropy,  $\chi$  being larger along the *c* axis. We have used this property to orient our sample by applying large fields at temperatures below 1 K. The Al ions are on equivalent sites with only two orthogonal mirror planes. The six Zeeman energy levels of the Al nuclei, combine into a very complicated NMR powder spectrum due to an anisotropic Knight shift and quadrupolar interactions with no axial symmetry.

The NMR sample was prepared by carefully powdering a well-characterized piece of CeAl<sub>3</sub> in a <sup>4</sup>He atmosphere. Most of the grains have linear dimensions of less than 50  $\mu$ m. The powder was placed inside the coil of a tuned tank circuit in the interior of the mixing chamber of a dilution refrigerator. The NMR signal at a given field was obtained by integrating the spin-echo signal, and the NMR spectra were monitored by stepwise changing the magnetic field at

the chosen frequency. In what follows we use the term “integrated intensity” to refer to areas under the spectrum. The spin-lattice relaxation rate was measured by destroying the nuclear magnetization with a long comb of rf pulses and observing the recovery as a function of time. Previously, we attempted to irradiate only the central part of the NMR spectrum. This procedure, also used by Nakamura and co-workers,<sup>6</sup> yielded no indication of a phase transition below 4 K. The fits of the expected multiple-exponential recovery function to the data were progressively worse with decreasing temperature. Accordingly, we indicated the possibility of inhomogeneous relaxation in preliminary reports.<sup>10–12</sup>

Subsequently we have chosen to perform spin-lattice relaxation-rate measurements using a similar procedure as indicated above, but in addition we modulated the static field while the comb of rf pulses was applied. In this way we irradiated the whole NMR spectrum at a fixed frequency. For single-channel relaxation, this technique yields a single-exponential recovery function, even for broad and complicated spectra. Inhomogeneous relaxation may thus be identified by observing deviations from a single-exponential recovery function. Care must be taken to irradiate the whole NMR spectrum uniformly, which normally is achieved by using a large number of rf pulses. In practice one must limit this number to avoid heating of the sample, which in our experiment has been a major concern. The finely powdered CeAl<sub>3</sub> sample was in direct contact with the liquid <sup>3</sup>He/<sup>4</sup>He mixture inside the mixing chamber of a dilution refrigerator below 4 K, and in <sup>4</sup>He gas at higher temperatures. The applied power was varied to check for heating effects at various temperatures. The previously measured low-temperature NMR spectrum of randomly oriented powder of CeAl<sub>3</sub>, has a very complicated line shape.<sup>6,7,13</sup> As we show below, the NMR spectra on partially oriented powder reveal more distinct features, in particular the presence of two components at low temperatures.

We have succeeded in performing NMR studies on partially oriented powder of this material at frequencies of 0.971, 3.964, 6.968, 7.331, and 10.651 MHz in the temperature range between 30 mK and 10 K. In Fig. 1 we show examples of our NMR spectra from *partially oriented* pow-

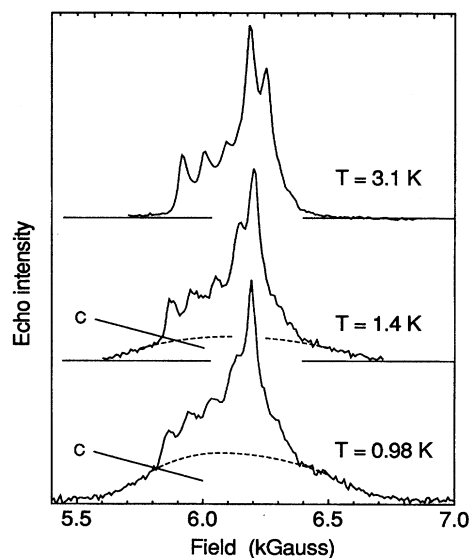


FIG. 1. NMR spectra of *partially oriented*  $\text{CeAl}_3$  at a frequency of 6.968 MHz and various temperatures. The broken lines are estimates of the contributions originating in the correlated phase (C) (see text).

der at 6.968 MHz. Here the expected five-line spectrum is distorted by the signals from randomly oriented grains, which produce the highest peak in each spectrum. Nevertheless, four of the five lines from the oriented-powder pattern are also clearly distinguishable. We also distinguish a broad structure (broken lines) whose integrated intensity increases faster than  $T^{-1}$  as the temperature decreases. As expected for a system of noninteracting nuclear magnetic moments, the integrated intensity of the total NMR spectrum has an approximate  $T^{-1}$  temperature dependence, therefore, it is clear that below 3 K, the integrated intensity of the broad structure increases progressively at the expense of the rest of the NMR spectrum. This structure cannot be caused by a temperature-dependent Knight shift since, as can be appreciated by comparing Figs. 1 and 2(a), its total width (as extrapolated to zero amplitude) is roughly field independent. We also rule out the nuclear quadrupolar interaction as the origin of this signal because we do not see any mechanism that may significantly alter the field gradients below 3 K. In fact, in this temperature regime, the quadrupolar splitting is temperature independent as judged from inspecting the signal from the oriented part of the sample.

In Fig. 2(a) we show NMR spectra of again *partially oriented* powder, with the  $c$  axis along the direction of the external field, at the frequency of 3.964 MHz. They are fully consistent with the spectra obtained at other frequencies, for example, at 6.968 MHz as shown in Fig. 1. The slight differences are well explained by the presence of an anisotropic and temperature-dependent Knight shift previously reported by other workers.<sup>13,14</sup> The broken lines again reveal the broad background whose integrated intensity clearly grows, relative to the total spectrum, with decreasing temperature. The line shape of this background signal was assumed to vary smoothly as indicated in Figs. 1 and 2(a). Below we associate this intensity with a magnetically correlated phase

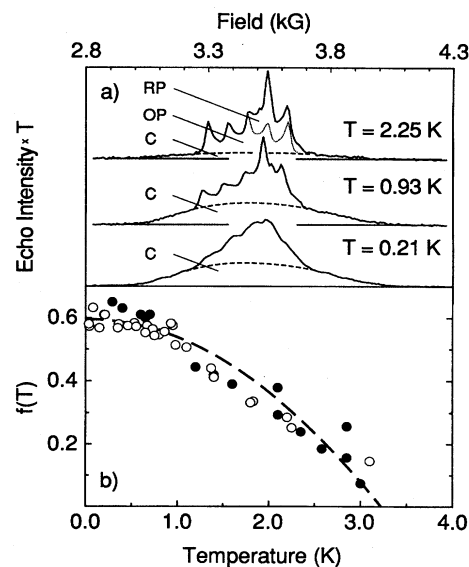


FIG. 2. (a) NMR spectra of *partially oriented*  $\text{CeAl}_3$  at a frequency of 3.964 MHz and various temperatures. The broken lines are estimates of the contributions originating in the correlated phase (C). For  $T=2.25$  K, the dotted line indicates the high-field part of the spectrum for the paramagnetic phase in *oriented* grains (OP) while the solid line gives the entire spectrum including contributions from the paramagnetic phase in *randomly oriented* grains (RP). (b) Integrated intensity of the correlated phase expressed as a fraction  $f(T)$  of the total spectrum obtained from the NMR spectra (empty circles) and magnetic relaxation data (full circles) (see text).

gradually developing in  $\text{CeAl}_3$  at low temperatures. For  $T=2.25$  K, the dotted line indicates an estimate of the high-field part of the spectrum from the paramagnetic phase of the oriented grains. We also note a sharp maximum and additional intensity, representing the powder pattern from the randomly oriented paramagnetic phase of the sample which is dominated by crystallites with the  $c$  axis perpendicular to the applied field. The oriented fraction of about 60%, was estimated by comparing the corresponding integrated intensities. The same fraction was obtained in several runs, attempts to enhance it failed. Fits to the spectra with no broad background, i.e., above 3 K, but containing also the contribution from randomly oriented powder, yielded good agreement with the results obtained by previous workers.<sup>14</sup> Differences in observation and interpretation occur at low temperatures.

In Fig. 2(b) two independent estimates of the integrated intensity of the broad structure,  $f(T)$ , expressed as a fraction of the integrated intensity of the total spectrum are given as a function of temperature. The broken line represents

$$f(T) = 0.6[1 - (T/3.2)^2]. \quad (1)$$

In one case the integrated intensity is derived from fits to the wings of the NMR spectra (empty circles) and a second possibility, to be discussed below, uses fits to magnetic relaxation data (full circles).

We emphasize, that we have no indication of a cooperative phase transition to a magnetically ordered state near 3 K.

The two components in the NMR spectra indicate two different regions of the sample. We postulate that the broad structure is due to regions with correlated magnetic moments. The rest of the spectrum we ascribe to a normal paramagnetic phase. In the correlated phase a distribution of internal static fields at the Al sites with an amplitude of the order of 0.5 kG corresponds to Ce moments of less than  $0.05 \mu_B$ . We note that this value does not vary much with temperature. This observation is compatible with previous  $\mu$ SR results. With decreasing temperature, an increase of the width of the individual lines in the paramagnetic phase is observed [see Fig. 2(a)]. An intrinsic broadening of the spectrum representing this phase is not expected because both the relaxation rate and the susceptibility are nearly temperature independent. One may then speculate that an increasing and significant fraction of Al sites are near the boundary with the correlated phase, implying that the correlated phase may appear in rather small regions whose number increases as the temperature lowers. In this sense, the phenomenon has some similarities with first-order phase transitions occurring in disordered magnetic systems but here, we are dealing with an unusually broad region of coexistence of correlated and paramagnetic regions.

The results of the relaxation-rate measurements performed at various fields near the line center corroborate the picture of two coexisting phases for  $\text{CeAl}_3$  at low temperatures. By modulating the static field during application of the comb of rf pulses we obtained a single-exponential recovery of the magnetization at temperatures above 3 K, as expected for homogeneous materials whose relaxation is characterized by a single  $T_1$ . At lower temperatures a strong alteration was observed. The magnetization recovery data  $m(t, T)$  as a function of time  $t$  and temperature  $T$  could not be satisfactorily fitted with one- or two-exponential functions. Our data, however, could be fitted very well to a function of the form

$$\frac{m(t, T)}{m(\infty, T)} = 1 - \left\{ [1 - f(T)] \exp\left(-\frac{t}{T_1(T)}\right) + f(T) \exp\left[-\left(\frac{t}{\tau(T)}\right)^{1/2}\right] \right\}, \quad (2)$$

where  $T_1(T)$  is the spin-lattice relaxation time of the normal phase of  $\text{CeAl}_3$ ,  $\tau(T)$  is a parameter characterizing the relaxation in the correlated phase, and  $f(T)$  is the fraction of the integrated intensity due to the correlated phase obtained from the spectra. This parameter  $f(T)$  resulting from fittings with Eq. (2) is expected to be somewhat smaller than  $f(T)$  derived from analyzing the spectra. Nevertheless, we observe that these two quantities show the same temperature dependence, suggesting a common origin; namely the gradual development of a new phase below 3 K. Although the choice of a stretched exponential function was guided by the “best fit” criterion, such a recovery is expected to occur in systems where the relaxation is either due to nonrandom fluctuations or characterized by several  $T_1$ 's.<sup>15</sup> Both scenarios are plausible for a phase that is gradually developing and where correlations among Ce moments are thought to be present.<sup>14,15</sup> We emphasize that our  $T_1$  measuring technique has been designed to avoid extraneous factors that may lead to deviations from the expected single-exponential recovery func-

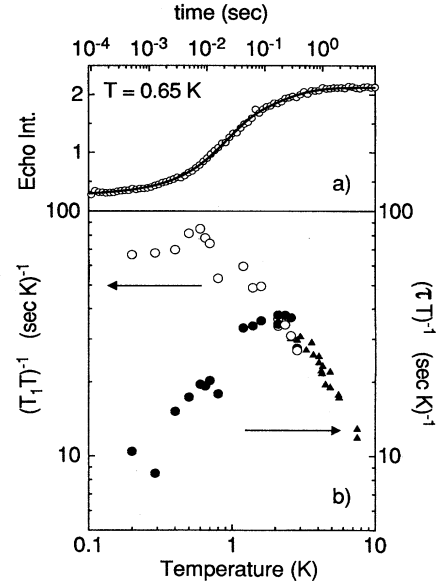


FIG. 3. (a) Magnetization recovery curve measured at a frequency of 7.331 MHz and a temperature of 0.65 K. The solid line is a fit using Eq. (2) given in the text; (b) Spin-lattice relaxation rates measured at a frequency of 7.331 MHz as a function of temperature. Data above 3 K (full triangles) were obtained from fits to single-exponential magnetization recoveries. Below 3 K, two terms were considered. The full circles correspond to parameter  $\tau$  of the stretched exponential (see text). The empty circles denote  $T_1$ .

tion. Among other things, we believe that neither spin diffusion nor incomplete saturation of the magnetization play a major role in our experiments. Testing our assumptions would include  $T_1$  measurements at very low temperatures and far from the center of the spectra, where only the correlated phase contributes to the signal. Several technical difficulties render such tests impractical for the time being.

An example of a fit and the resulting values of  $T_1$  and  $\tau$  obtained from these fits as a function of temperature are shown in Fig. 3. The relaxation rate  $T_1^{-1}(T)$  associated with the normal phase joins the behavior smoothly above 3 K and agrees well with previous results.<sup>6,7,13</sup> The Korringa-type variation for  $T_1$  below 0.6 K, is expected from thermodynamic and transport measurements, but the relaxation rate  $\tau^{-1}$  is less easy to interpret. In analogy to cases of ordering of small moments in some heavy-electron metals,<sup>17</sup> the considerable decrease of  $\tau^{-1}$  with decreasing temperature may be interpreted as a growing degree of correlation among fluctuating Ce moments. As opposed to magnetic ordering, where a Korringa type of  $T_1^{-1}(T)$  is reestablished at low temperatures,<sup>16,17</sup> no such trend is observed for the correlated phase of  $\text{CeAl}_3$ . It remains a puzzle, how these correlations affect the thermodynamic and transport properties. At the moment we have no full description and we only note that because thermodynamic properties usually probe  $k \rightarrow 0$ , a large part of the correlated-phase properties may effectively be averaged out.

Finally we discuss whether the effects that we associate with a correlated phase could be due to other factors not intrinsic to  $\text{CeAl}_3$ . While we cannot completely rule out this

possibility, we believe that the phenomena we describe are also present in various degrees in previously published work on  $\text{CeAl}_3$ , although different conclusions have been reached by various authors. The low-field NMR spectra presented by Nakamura and co-workers<sup>6</sup> have similar features as our NMR spectra, including the broad structure, and Wong and Clark reported small deviations from a single-exponential recovery at low temperatures.<sup>7,14</sup> The main suspects to cause a broadening of NMR spectra at low temperatures are magnetic impurities. Fortunately there has been related work to practically rule out this possibility (see Refs. 14 and 18). In NMR measurements at temperatures above 1 K, 2% of Gd impurities in  $\text{CeAl}_3$  cause an extra broadening of the NMR spectra of the order of 20 G. Similarly the effect on the spin-lattice relaxation rate is within the experimental uncertainty. This implies that the effects that we encounter in our NMR measurements, which are an order of magnitude larger than those produced by 2% of Gd impurities, are not due to magnetic impurities. Nevertheless, we keep in mind that paramagnetic impurities do cause a relaxation rate of the form of a stretched exponential as shown by Tse and Hartmann<sup>19</sup> but only under conditions where spin diffusion is

strongly inhibited. Magnetic impurities in  $\text{CeAl}_3$  are most likely in another regime, the diffusion-limited relaxation.<sup>18</sup>

In conclusion, the results of our NMR measurements cast serious doubts on a simple Fermi-liquid description of the electronic ground state of  $\text{CeAl}_3$ . Below 3 K, gradually a new phase develops in  $\text{CeAl}_3$  thought to arise from correlations among Ce  $4f$  electron moments, and confirming results of  $\mu\text{SR}$  experiments performed on a sample prepared from the same piece of material. The relative volume of the correlated phase increases as the temperature decreases, reaching about 60% of the total sample below 0.5 K. Its spin-lattice relaxation rate is strongly and progressively suppressed with respect to the relaxation in the normal paramagnetic phase, which follows a Korringa-type variation below 0.6 K. All this indicates that the low-temperature state of  $\text{CeAl}_3$  is characterized by the coexistence of two magnetically very different phases.

We gratefully acknowledge S. Büchi and P. Vonlanthen for their help with the data acquisition at some stages of the project. This work was supported by the Schweizerische Nationalfonds zur Förderung der Wissenschaftlichen Forschung.

- 
- <sup>1</sup>K. Andres, J. E. Graebner, and H. R. Ott, *Phys. Rev. Lett.* **35**, 1779 (1975).
- <sup>2</sup>H. R. Ott, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North Holland, Amsterdam, 1987), Vol. XI, and references therein.
- <sup>3</sup>O. Avenel, J. S. Xia, B. Andraka, C. S. Jee, M-F. Xu, Y. J. Qian, T. Lang, P. L. Moyland, W. Ni, P. J. C. Signore, E. D. Adams, G. G. Ihas, M. W. Meisel, G. R. Stewart, N. S. Sullivan, and Y. Takano, *Phys. Rev. B* **45**, 5695 (1992).
- <sup>4</sup>S. Barth, H. R. Ott, F. N. Gyax, B. Hitti, E. Lippelt, A. Schenck, C. Baines, B. van den Brandt, T. Konter, and S. Mango, *Phys. Rev. Lett.* **59**, 2991 (1987).
- <sup>5</sup>A. Schenck, in *Frontiers in Solid State Sciences*, edited by L. C. Gupta and M. S. Multani (World Scientific, Singapore, 1993), Vol. 2, p. 269.
- <sup>6</sup>H. Nakamura, Y. Kitaoka, K. Asayama, and J. Flouquet, *J. Phys. Soc. Jpn.* **57**, 2644 (1988).
- <sup>7</sup>W. H. Wong and W. G. Clark, *J. Magn. Magn. Mater.* **108**, 175 (1992).
- <sup>8</sup>H. R. Ott, O. Marti, and F. Hulliger, *Solid State Commun.* **49**, 1129 (1984).
- <sup>9</sup>A. P. Murani, K. Knorr, and K. H. J. Buschow, in *Crystal Field Effects in Metals and Alloys*, edited by A. Furrer (Plenum, New York, 1977), p. 268.
- <sup>10</sup>J. L. Gavilano, J. Hunziker, and H. R. Ott, *Physica B* **194-196**, 195 (1994).
- <sup>11</sup>J. L. Gavilano, J. Hunziker, P. Vonlanthen, and H. R. Ott, *Physica B* **199-200**, 593 (1994).
- <sup>12</sup>J. Hunziker, J. L. Gavilano, S. Büchi, and H. R. Ott, *Physica B* **194-196**, 273 (1994).
- <sup>13</sup>M. J. Lysak and D. E. MacLaughlin, *Phys. Rev. B* **31**, 6963 (1985).
- <sup>14</sup>W. H. Wong, Ph.D. thesis, University of California, Los Angeles, 1991.
- <sup>15</sup>P. Beckmann, *Phys. Rep.* **171**, 85 (1988).
- <sup>16</sup>J. L. Gavilano, J. Hunziker, O. Hudak, T. Sleator, F. Hulliger, and H. R. Ott, *Phys. Rev. B* **47**, 3438 (1993).
- <sup>17</sup>J. L. Gavilano, P. Vonlanthen, B. Ambrosini, J. Hunziker, F. Hulliger, and H. R. Ott, *Europhys. Lett.* (to be published).
- <sup>18</sup>J. M. Moore, W. G. Clark, J. Sanny, W. H. Wong, W. A. Hines, D. P. Yang, and M. Schlott, *Physica B* **163**, 522 (1990).
- <sup>19</sup>D. Tse and S. R. Hartmann, *Phys. Rev. Lett.* **21**, 511 (1968).