Pressure-induced variation of the ground state of $CeAl_3$

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Pressure-induced variations of ^{27}Al NMR spectra of $CeAl_3$ indicate significant changes in the ground-state characteristics of this prototypical heavy-electron compound. Previously reported magnetic and electronic inhomogeneities at ambient pressure and very low temperatures are removed with external pressures exceeding 1.2 kbars. The spectra and results of corresponding measurements of the NMR spin-lattice relaxation rates indicate a pressure-induced emergence of a simple paramagnetic state involving electrons with moderately enhanced masses and no magnetic order above 65 mK.

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At low temperatures, the specific heat of $CeAl_3$ is dominated by a contribution that varies linearly with temperature. Likewise, a large Pauli-type magnetic susceptibility, $\chi(T\rightarrow 0)=0.036$ emu mol^{-1}, indicates a much enhanced density of electron states at the Fermi energy $D(E_F)$, a feature that is typical for heavy-electron compounds.[1] The ground state of $CeAl_3$ has been investigated with a large number of experimental techniques. An early indication for inhomogeneities of this ground state was provided by muon spin resonance experiments[2,3] and this conjecture was later confirmed by ^{27}Al NMR results.[4] Subsequently, based on NMR results, Nakamura *et al.*[5] claimed a magnetically ordered ground state for $CeAl_3$, while Wong and Clark,[6] again employing NMR, found no evidence for magnetic ordering. The early results suggesting an inhomogeneous ground state revealed two phases: one of them exhibiting quasistatic magnetic correlations, leading to a distribution of local magnetic fields at the Al sites, and a second, paramagnetic phase. The corresponding NMR experiments were made on a powder sample, and the role of strain effects due to the powdering of the sample material and, thus, introducing inhomogeneities that mimic an inhomogeneous ground state remained unclear. NMR experiments under pressure as those presented here aimed at resolving this issue. Experimental data at pressures up to 15 kbars probing the specific heat and the electrical resistivity are available in the literature.[7,8] To our knowledge, no experimental investigation probing microscopic aspects of binary $CeAl_3$ under pressure has been reported so far. Our results reveal that the ground state of $CeAl_3$ is very sensitive to pressure-induced volume changes. In particular, we note that the two mentioned phases collapse into one at surprisingly moderate pressures.

The ^{27}Al NMR experiments on $CeAl_3$ at low temperatures and under pressure were made in a top-loading dilution refrigerator. The $CeAl_3$ powder sample was the same as that investigated in the previous NMR study.[4] A possible deterioration of the sample was checked by repeating the measurement of the NMR spectrum at low temperatures and ambient pressure. No detectable changes of the spectra were observed. For the experiments under pressure, a BeCu piston cylinder type pressure cell with 14 (3.8) mm outer (inner) diameter was used. In the pressure cell, the $CeAl_3$ sample was embedded in paraffin and surrounded by a small NMR rf coil with a volume of ~ 1 mm^3. The pressure was determined by the ^{63}Cu nuclear quadrupole resonance frequency of Cu_2O at $T=1$ K.[9] The powdered Cu_2O, also embedded in paraffin, was placed in a second rf coil. The NMR resonant circuit consisted of the inductance in the pressure cell containing the sample and of two capacitors placed outside the pressure cell. The NMR signal was monitored with the standard spin echo method by using a home-built heterodyne, phase sensitive NMR spectrometer. The ^{27}Al NMR spectra were recorded at a fixed frequency and with varying magnetic field. The magnetic field was calibrated by using the ^{1}H NMR resonance from the protons which are present in the pressure medium[10] and in the paraffin. This approach assures that possible magnetic field changes due to paramagnetic impurities in the pressure cell material can be taken into account. Monitoring the width of the ^{63}Cu signal gave evidence that the applied pressure was, indeed, hydrostatic. The spectral weight (spin echo intensity) was obtained by integrating the detected spin echo signal in the time domain. The spin-lattice relaxation rate (SLRR) T_1^{-1} was measured on the central NMR line with a pulse sequence made up of a comb of ten pulses (8 μs rf pulses, 35 μs time lag), a variable delay, and a spin echo sequence. The main experimental difficulty was to cope with the low measuring frequency of about 1 MHz, resulting in very small signals. This and the long spin-lattice relaxation times at low temperatures provoked measuring times of several days for a single NMR spectrum or a magnetization recovery curve. In order to minimize the undesired effects of external magnetic fields on the ground state of $CeAl_3$, also at elevated pressures, and possible heating effects, we restricted our measurements to Larmor frequencies of the order of 1 MHz.

In Fig. 1, ^{27}Al NMR spectra recorded at $T\approx 65$ mK and at different pressures are displayed. The ambient pressure results coincide with the data obtained in the quoted former work[4] on the same sample. A drastic narrowing of the ^{27}Al NMR spectrum is observed for p exceeding 1.25 kbars. The spectrum then consists of a narrow central line and a broader wing pattern. The spectra recorded at 1.25 and 2.17 kbars are very similar in shape, but still much broader than those obtained at 5.60 or 9.15 kbars. The central line and the wings are both affected by the Knight-shift and electric-field gradient. Hence, the precise identification of the relevant param-

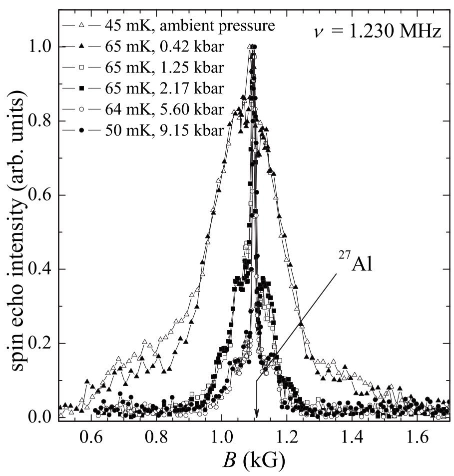

FIG. 1. ^{27}Al NMR spectra of $CeAl_3$ for different pressures at very low temperatures.

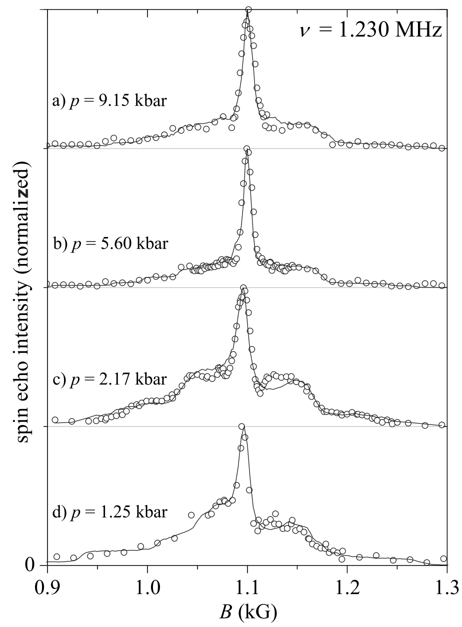

FIG. 3. Simulated ^{27}Al NMR spectra (solid lines) of $CeAl_3$ for different pressures. Empty circles represent the same experimental data as in Fig. 1.

eters directly from the spectra is difficult; the employed procedure is explained below. The crystal structure of $CeAl_3$ has important implications on the ^{27}Al NMR features. The Al sites are on positions with a point symmetry *mm* in the hexagonal lattice. The low point symmetry dictates axially nonsymmetric tensors and three Al sites must be distinguished. In Fig. 2, the three different sites are designated as Al^1, Al^2, and Al^3, respectively. The relevant NMR parameters are captured in the tensors for the Knight-shift K and the electric-field gradient (EFG), respectively. For all three Al sites, the tensors are equal, but rotated by 120° around the c axis (Fig. 2). In external magnetic fields with arbitrary orientations, the three Al sites are inequivalent.

In a powder sample, all orientations of the crystalline axes with respect to the magnetic field are equally distributed. The calculation of ^{27}Al NMR powder spectra can thus be performed assuming only one Al site, as long as no magnetic order or any other symmetry breaking is present. These calculations may be based on an effective static nuclear Hamiltonian

$$\mathcal{H} = \mathcal{H}_Z(B_0, K_{iso}, K_{ani}, \epsilon) + \mathcal{H}_Q(V_{zz}, \eta), \qquad (1)$$

i.e., the sum of a Zeeman term $\mathcal{H}_Z$, including an anisotropic Knight shift $\overleftrightarrow{K}$, and a nuclear quadrupolar term $\mathcal{H}_Q$.[11] The eigenvalues of $\mathcal{H}$ depend on the orientation of the external magnetic field. The largest components of the Knight-shift tensor $K_Z = K_{iso} + K_{ani}$ and of the electric-field gradient, V_{zz}, were previously found to be parallel to the c axis.[4] Thus, the spatial relation between the Knight shift and the EFG tensors is known, except for the relative orientation in the x-y plane, which is restricted by symmetry to two cases with either $V_{xx} \| K_X$ or $V_{xx} \| K_Y$. It is assumed that these symmetry relations are not altered by the application of moderate hydrostatic pressures. With these considerations, the powder spectra could fairly well be reproduced by simulation calculations, varying the free parameters given in Eq. (1) (see Fig. 3). The nonperturbative calculation was based on a full diagonalization of the static nuclear Hamiltonian, and the powder spectrum was simulated with 10 000 arbitrary crystalline orientations. The parameters, which were found to reproduce the spectra, are summarized in Table I.[12] Our extensive simulations, involving a wide range of parameters, allowed the estimate of statistical uncertainties shown in Table I. These uncertainties represent the change of the parameters that would increase chi-squared by 50%. The change in K_{iso} is thus significant, because it varies by a factor of 2 over the covered pressure range.

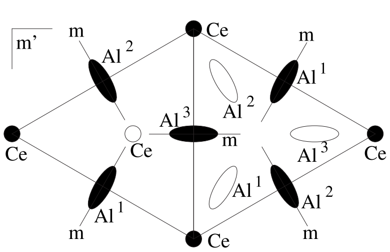

FIG. 2. Symmetry considerations for ^{27}Al NMR in $CeAl_3$. The black circles and ellipses denote ion positions, which lie in the same plane perpendicular to the c axis, i.e., the mirror plane m' at $z=1/4$. The open circles and ellipses are sites at $z=3/4$.

In the experiments probing the SLRR at nonzero pressure, we irradiated only the narrow central line in a field range of approximately ±30 G around the maximum.[13] Therefore, the recovery of the nuclear magnetization cannot be described by a single exponential and the data need to be fitted to the relevant multiexponential function[15]

$$1 - \frac{m(t)}{m(\infty)} = \frac{9}{35}e^{-t/T_1} + \frac{4}{15}e^{-6t/T_1} + \frac{10}{21}e^{-15t/T_1}. \qquad (2)$$

As explained in Ref. 4 the spin-lattice relaxation is rather complicated at ambient pressure (and also at 0.4 kbar). Here,

TABLE I. Summary of the parameters used for the calculated ^{27}Al NMR spectra. K_{iso}, K_{ani}, and ϵ represent the anisotropic Knight shift, and V_{zz} and η characterize the electric-field gradient. The parameter LW reflects the broadening of the calculated discrete resonance fields. The last row cites data from Ref. 14 evaluated at 35 mK, for comparison. The numbers in parentheses are error estimates of the respective parameters.

p (kbar)	K_{iso} (%)	K_{ani} (%)	ϵ 1	V_{zz} (a.u.)	η 1	LW (kHz)
1.25	2.1(2)	3.5(9)	0	0.026(3)	0.40(10)	4
2.17	2.1(2)	3.2(8)	0	0.026(3)	0.15(4)	6
5.60	1.0(1)	1.0(3)	0	0.018(2)	0.50(13)	2
9.15	0.9(1)	0.8(2)	0	0.021(2)	0.45(11)	3
Ambient	2.1(1)	0.8(1)	0	0.019	0.2	

we restrict ourselves to pressures at and above 1.25 kbar, where the "correlated phase" is suppressed (see Fig. 1). The fraction of powder grains, where the quadrupolar signal is within the irradiation window, is less than 15%. This leads to a correction of the above recovery function and to the values of T_1, in the form of a reduction of maximally 20%. In Fig. 4, the low temperature relaxation rates T_1^{-1} divided by the temperature T are plotted versus T for various pressures.

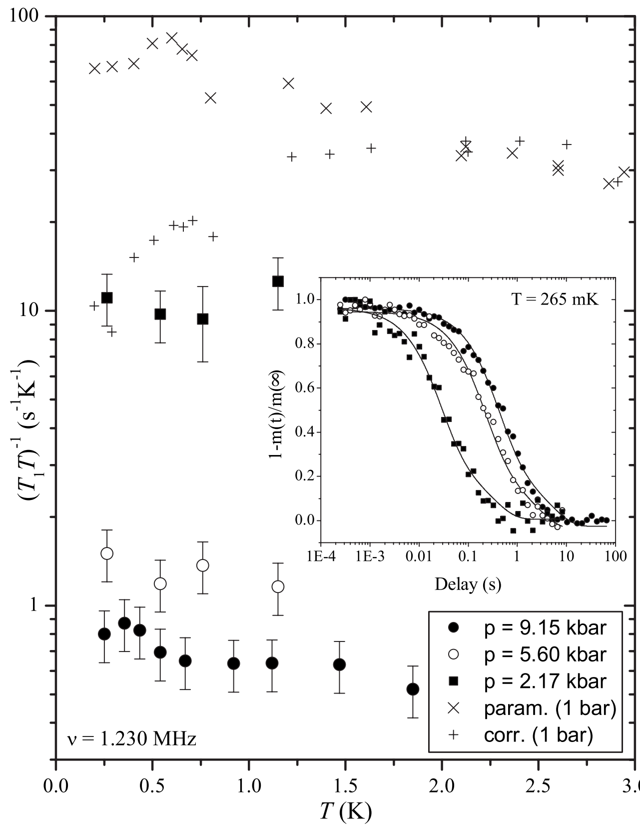

FIG. 4. ^{27}Al SLRR of $CeAl_3$ for different pressures and temperatures. We also measured T_1 at 1.25 kbars at the lowest temperature. The corresponding value is very close to that measured at 2.17 kbars. Ambient pressure data are taken from Ref. 4. For $LaAl_3$, the T-independent value for $(T_1T)^{-1}$=0.037 (s K)$^{-1}$ (Ref. 16).

TABLE II. Pressure dependence of relaxation-related NMR parameters for the paramagnetic phase at low temperatures.

p (kbar)	$(T_1T)^{-1}$ (s^{-1} K^{-1})	$T_1TK_{iso}^2$ (10^{-6} s K)	R 1
0	68		
2.17	10 ± 2	44 ± 10	0.088 ± 0.021
5.6	1.2 ± 0.24	83 ± 20	0.046 ± 0.011
9.15	0.7 ± 0.014	115 ± 28	0.033 ± 0.008

Shown for comparison are the ambient pressure data that were reported in Ref. 4. The "×" symbols are relaxation rates from the spectral part between 0.9 and 1.3 kG, reflecting the paramagnetic phase, and the "+" symbols represent data points obtained from the broadest part of the ambient pressure spectrum (see Fig. 4).

Most obvious is the significant reduction of $(T_1T)^{-1}$ with increasing pressure by almost 2 orders of magnitude in the covered pressure range. This signals a diminishing density of electronic states at the Fermi energy and is in qualitative agreement with the pressure-induced reduction of the Knight-shift components that results from the analysis of the ^{27}Al NMR spectra. The temperature variation of $(T_1T)^{-1}(T)$ is fairly small for nonzero pressures. By considering the spectra in Fig. 1 and the T_1^{-1} data in Fig. 4, it may be noted that the pressure-induced single phase does not order magnetically above 50 mK. This and the reduction of $D(E_F)$ are both consistent with previously published specific-heat data obtained at high pressures.[7] In Table II, we list approximate values of $(T_1T)^{-1}$, $T_1TK_{iso}^2$, and the parameter R which appears in the well known relation[17]

$$T_1TK^2R = \frac{\hbar}{4\pi k_B}\left(\frac{\gamma_e}{\gamma_N}\right)^2. \quad (3)$$

The parameter R reflects the ratio between the effective magnetic susceptibility χ and density of electronic states $D(E_F)$. The decrease of R must therefore be traced back to a strong reduction of $\chi(q)$. A previously published neutron scattering study on La-doped $CeAl_3$ (Ref. 18) also indicated that pressure diminishes the tendency to a magnetic instability in that material at low temperatures. We emphasize that our main claims do not depend on the results of the details of the analysis. They are evident from the raw data. Nevertheless, also the quoted pressure-induced variations of the relevant parameters resulting from our quantitative analysis are significant.

We conclude that in $CeAl_3$, the inhomogeneous ground state is quenched by the application of moderate pressures. The so-called correlated phase, reflected in the broad part of the low-pressure Al NMR spectra, vanishes upon increasing external pressure between 0.42 and 1.25 kbars. The remaining phase is modified in the sense that we observe a clear drop in $D(E_F)$ with increasing pressure, reflected in the SLRR and in the Knight shift, which has also been suggested on the basis of macroscopic quantities such as the specific heat or the electrical resistivity.[7,8] The observations imply that the inhomogeneous ground state at ambient pressure is, indeed, an intrinsic property of $CeAl_3$ and that the broad line, previously attributed to the correlated phase, is not simply an artifact. A more detailed account of this work will be published elsewhere.

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[10] As pressure medium, a Balzers silicone oil for vacuum pumps was used.

[11] See, e.g., G. C. Carter, L. H. Bennett, and D. J. Kahan, *Metallic Shifts in NMR: A Review of the Theory and Comprehensive Critical Data Compilation of Metallic Materials*, Progress in Materials Science (Pergamon, New York, 1977).

[12] The anisotropy ϵ of the Knight shift is not restricted to zero. However, the agreement between the simulations and experiment was found to be worse for $\epsilon > 0$.

[13] The pulse sequence used for SLRR measurements consisted of 10 comb pulses of 8 μs length and 35 μs delay, followed by the variable delay. The subsequent spin echo consisted of a 4 μs pulse, a delay $\tau = 50$ μs, and a second pulse of 8 μs duration. Avoiding heating effects was a major concern in this experiment. For instance, by using other intermetallic compounds in the same pressure cell, we measured T_1 by employing longer rf combs with much higher rf-pulse amplitudes and frequencies and, otherwise, the same conditions. We found that heating effects could be observed only below 0.5 K. By reducing the rf-pulse energies and frequencies and by decreasing the number of pulses in the rf comb to levels still higher than those used here, we found that the useful temperature range without noticeable heating effects could be extended down to 0.25 K.

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