RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 6 1 FEBRUARY 1993-II

Rapid Communications

Rapid Communications are intended for the accelerated publication of important new results and are therefore given priority treatment both in the editorial office and in production. A Rapid Communication in **Physical Review B** *should be no longer than four printed pages and must be accompanied by an abstract. Page proofs are sent to authors.*

Al nuclear-quadrupole-resonance studies of $CeAl_2$

J. L. Gavilano, J. Hunziker, O. Hudak,* T. Sleator,† F. Hulliger, and H. R. Ott
Laboratorium für Festkörperphysik, ETH-Hönggerberg, 8093 Zürich, Switzerland
(Received 29 May 1992; revised manuscript received 2 October 1992)

We report ^{27}Al nuclear-quadrupole-resonance (NQR) studies on $CeAl_2$ in the temperature range between 0.09 and 4.2 K. Below $T_N=3.45$ K $CeAl_2$ orders antiferromagnetically. The spin-lattice relaxation rate (T_1^{-1}) shows a sharp peak at T_N, and the NQR linewidth increases from 27±3 kHz in the paramagnetic state to 270±15 kHz at 2 K. Below 1.5 K, in the low-temperature regime of the magnetically ordered state, the temperature dependence of the spin-lattice relaxation rate follows a Korringa law with $(T_1T)^{-1}=7.9\pm0.8$ (K sec)$^{-1}$. This relaxation rate is much larger than those found in normal metals. Above 1.5 K deviations from the Korringa law are observed. These deviations are consistent with a relaxation produced by magnonlike excitations with an energy gap of 11±3 K, in agreement with results of previous neutron scattering and T_1 measurements in the temperature range above 1.5 K.

$CeAl_2$ is an intermetallic compound that has been intensively studied since the early 1970s, however, many of its low-temperature properties are still not well understood. $CeAl_2$ orders antiferromagnetically with reported Néel temperatures, T_N, ranging between 3.4 and 3.9 K and with a sinusoidally modulated magnetic structure incommensurate with the crystalline structure as determined by neutron scattering experiments.[1-3] In this compound, crystal-field splitting, Kondo effect, and magnetic ordering maintain a delicate balance at low temperatures.[4] A remarkable feature of $CeAl_2$ is the presence of a large linear coefficient (γ) of the temperature dependence of the specific heat $C_p(T)$ in the ordered state.[4] The origin of the large γ value may be attributed to low-energy excitations in the $4f$ electron system which, at low temperatures, should also result in a large spin-lattice relaxation rate varying linearly with temperature. We report here the observation of a Korringa-type law in the temperature dependence of the spin-lattice relaxation rate in the magnetically ordered state of $CeAl_2$, at temperatures between 0.09 and 1.5 K.

$CeAl_2$ crystallizes in the cubic Laves phase of $MgCu_2$ type, where each Ce atom site is tetrahedrally surrounded by 4 Ce atoms at a distance of 3.4 Å. In the magnetically ordered state the cerium magnetic moments are directed along the [111] direction, with their magnitudes modulated by the wave vector $\mathbf{Q}=(2\pi/a)(\frac{1}{2}+\tau,\frac{1}{2}-\tau,\frac{1}{2})$,[1,3] where a is the lattice constant and $\tau=0.112$. The modulation of the magnetic structure by $\mathbf{Q}$ corresponds to an antiferromagnetic coupling between the cerium moments in neighboring (111) planes and a modulation of this structure along the $[1\bar{1}0]$ direction with a magnetic period of 8.93 unit cells, incommensurate with the crystal structure.

The material for our samples was prepared by induction heating of rare-earth metal and aluminum of nominal purity 99.9% and 99.999%, respectively. X-ray patterns showed that the material was homogeneous and well crystallized with the $MgCu_2$ structure. Comparing low-temperature experimental results for various properties characterizing $CeAl_2$ has been difficult in the past, because they were found to be sensitive to sample preparation techniques. The reported measurements, however, cluster into two distinct set of values that seem to correspond to two different types of $CeAl_2$ materials with nominally the same composition, similar physical properties in the paramagnetic state and the following Néel temperatures: (i) $T_N=3.9$ K (see, for example, Ref. 4 and references therein), and (ii) $T_N=3.4$ K (this work, Ref. 5 and references therein). The linear coefficient of the low-temperature specific heat differs by a factor of 2 in these two materials and particularly for this reason we have performed specific heat $C_p(T)$ and nuclear-quadrupole-resonance (NQR) measurements on samples prepared from the same piece of material. Specific-heat and ac magnetic-susceptibility measurements of our $CeAl_2$ sample above 1.5 K were found to be consistent with those reported by Walker *et al.*[5] For the NQR measurements the sample was ground to powder with grain sizes less than 50 μm. NQR was probed by using the spin-echo technique.

We studied the Al$\pm5/2\leftrightarrow\pm3/2$ NQR transition corresponding to a frequency of 1.458 MHz. The NQR or zero-field NMR technique[6,7] was preferred to high-field NMR to avoid disturbing the delicate antiferromagnetic ordering of $CeAl_2$. The NQR spectrum was obtained by measuring the spin echo at various frequencies. The bandwidth of the spectrometer was kept very wide (about

300 kHz), however, the NQR spectrum of $CeAl_2$ in the ordered state was found to be very wide and some distortion of the line shape was observed. Nevertheless, multiplying the integrated intensity of the zero-field spectrum with the corresponding temperature resulted in approximately the same value at 4 K and below 2 K. Although uncertainties of the order of 30% could not be ruled out in this estimate, the linewidth is likely a reliable indicator of the hyperfine-field distribution[7] which we assume to have the same temperature dependence as the sublattice magnetization. The spin-lattice relaxation rate was measured using the "saturation-comb" technique. The recovery to equilibrium was fitted to a two-exponential expression:[8]

$$S(t)-S(\infty)=A_1\exp(-3t/T_1)+A_2\exp(-10t/T_1)\ , \tag{1}$$

suitable to describe the relaxation of Al NQR. Magnetization-recovery data were taken over several time decades, typically from $0.02T_1$ to $200T_1$. The quality of the fits to Eq. (1) worsened with decreasing temperature. This may be expected because the magnetic ordering modifies inhomogeneously the splittings of the energy levels of the Al nuclei through the sample. Although the relaxation measurements may be consistent with a distribution of T_1's, a single spin-lattice relaxation time describes reasonably well our data in the temperature range of the work reported here. In view of this, all the quoted errors correspond to statistical uncertainties only.

The linewidth [half width at half maximum (HWHM)] of the spectrum as a function of temperature is shown in Fig. 1. In the magnetically ordered state a distinct increase of the linewidth occurs, from 27±3 kHz in the paramagnetic state to a saturation value of 270±15 kHz. The temperature dependence of the linewidth $W(T)$ is compatible with that of the sublattice magnetization of an anisotropic antiferromagnet in the long-wavelength approximation,[9] shown as the solid line in Fig. 1,

$$W(T)=a_1[1-a_2T^{3/2}\exp(-T_G/T)]\ , \tag{2}$$

with an energy gap in the magnon excitation spectrum corresponding approximately to $T_G=11\pm3$ K, in agreement with results from previous neutron measurements.[3,4] The low-temperature specific heat $C_p(T)$ of our sample was measured between 0.05 and 6 K. Below 1 K the data are reproduced very well by

$$C_p=\alpha T^{-2}+\gamma T+\beta T^3\ , \tag{3}$$

where the first term represents the contribution due to the Al nuclear specific heat, the linear in T term is, without further analysis, expected to to be due to low-energy excitations with constant densities of states (as, e.g., conduction-electron excitations). The spin-wave excitations of the magnetically ordered state, with a large energy gap, are expected to have a negligible contribution to C_p in this temperature range, and they should not be associated with the cubic term in Eq. (3). From fitting the data we obtain $\alpha=(8.3\pm0.8)\times10^{-3}$ mJ K/mole, $\gamma=(274\pm2)$ mJ/K^2 mole, and $\beta=(197\pm5)$ mJ/K^4 mole. Our value of α is about 1 order of magnitude larger than the one reported by Steglich *et al.*,[4] and used by MacLaughlin, Pena, and Lysak[7] in the analysis of their NQR data above 1 K. It is important to notice that our $CeAl_2$ samples and those used by MacLaughlin, Pena, and Lysak also have very different linear and cubic specific-heat coefficients, and as noted previously, they seem to belong to different types of material. The prefactor α scales with the square of the average hyperfine field at the Al sites. We note that an order of magnitude enhancement of α corresponds to an increase of a factor of about 3.3 in the linewidth of the $CeAl_2$ NQR, in the ordered state. This is in agreement with the ratio between our value (270 kHz) and that reported in Ref. 7 (90 kHz).

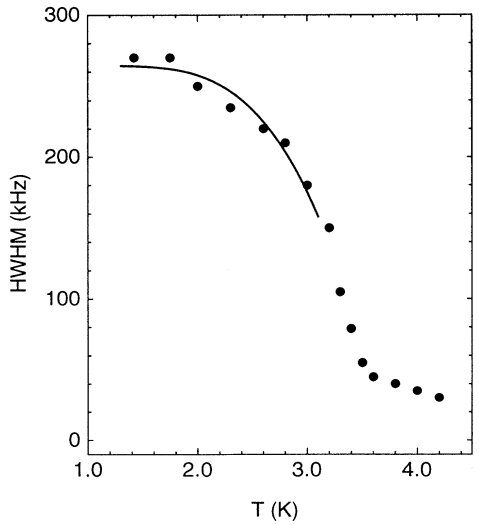

FIG. 1. Linewidth (HWHM) of the NQR spectrum of $CeAl_2$, as a function of temperature. The solid line represents a fit to the temperature dependence of the magnetization of an antiferromagnet in the long-wavelength approximation.

For an estimate of the hyperfine fields at the various Al sites we first recall that the Ce ions form a diamond structure and the Al ions occupy the vertices of small tetrahedra at the interstices of the diamond lattice, with symmetry axes along the [111] directions. In the absence of modulation, three Al sites on each tetrahedron are at zero-field due to cancellations of the contributions from different neighbors, and one Al site is in a "strong" field, where all the contributions add up. In the presence of a single-q modulation, the following field distribution is anticipated: (i) One site experiences a "strong" field $H=(2.1\pm0.1)\cos(\varphi)$ tesla, (ii) one site is at zero field, and (iii) two sites are in a "weak" field $H=(1.3\pm0.1)10^{-1}\cos(\varphi)$ tesla. The phase φ takes all possible values from 0 to 2π. The numerical values of the field amplitudes have been calculated from the nuclear specific-heat contribution. At the sites of "weak" fields the angle between the axes of symmetry of the Zeeman and quadrupolar interaction, respectively, is $2\pi/3$. Although the Al nuclei on "strong"-field sites dominate the nuclear specific heat, they contribute very little to the NQR signal, because their signal is distributed over a very broad range of frequencies. Considering the remain-

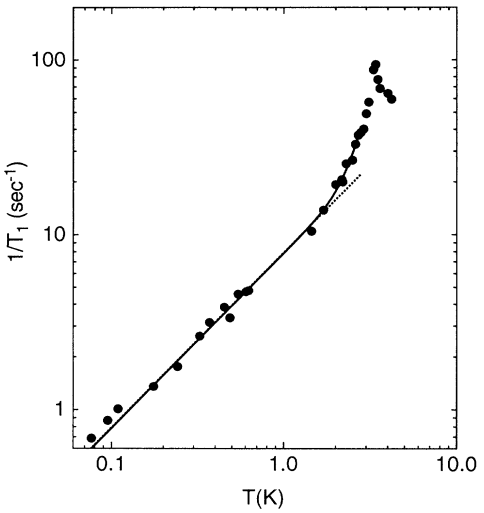

FIG. 2. Temperature dependence of the spin-lattice relaxation rate T_1^{-1} as a function of temperature. The solid line represents a fit to a function that includes a Korringa term and a contribution due to magnon-driven relaxation and the dotted line represents a Korringa law.

ing three sites we estimate a broadening of the NQR linewidth of 660±60 kHz due to the field distribution. Although the observed linewidth in the magnetically ordered state of $CeAl_2$ is only 40% of this estimated value, we believe that the essential origin of the NQR linewidth is recognized in this crude estimate that is used to evaluate the leading contribution to the hyperfine fields at the Al sites. The inclusion of the contribution to the hyperfine fields due to other Ce ions in addition to the nearest neighbors is expected to modify the above picture, however, the main conclusion remains. One Al site is in a "strong" field and dominates the nuclear specific heat, and the other three Al sites are in "weak" fields, thus determining the NMR results.

In Fig. 2 we display the spin-lattice relaxation rate T_1^{-1}

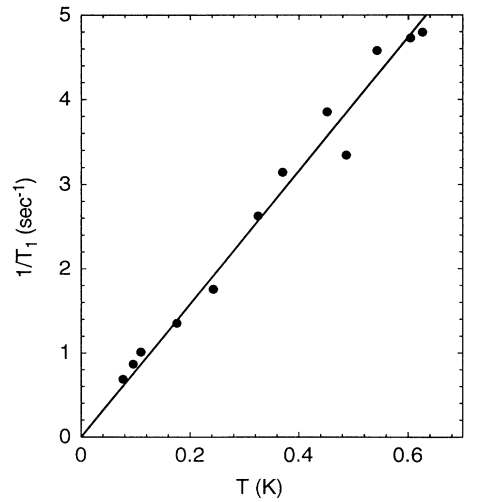

FIG. 3. Temperature dependence of the spin-lattice relaxation rate T_1^{-1} below 1 K. The solid line represents a fit to a Korringa-type law.

as a function of temperature. A sharp peak at $T_N=3.45$ K signals the onset of magnetic ordering. A critical region above T_N, not observed in previous NQR measurements,[7] is also clearly seen. One observes a rapid decrease of T_1^{-1} below T_N, as expected for antiferromagnetic materials where the spin-wave excitations provide the main relaxation mechanism. Since these excitations are thermally activated over an energy gap one anticipates that the temperature dependence of a magnon-dominated relaxation ought to be characterized by an exponential temperature dependence.[9] Below 1.5 K, however, we find a different regime where the magnon-driven relaxation is negligible. Instead a Korringa-type law $T_1T=0.13$ ±0.01 Ksec characterizes the temperature dependence of the spin-lattice relaxation, as can be seen in Fig. 3. A fit to the temperature dependence of T_1^{-1} including both terms linear and exponential in T,

$$1/T_1=7.91T+cT^2\exp(-T_G/T)\ , \tag{4}$$

yields an energy gap corresponding to $T_G=11\pm3$ K in agreement with the results from our measurements of the NQR spectra and again, with the results from previous neutron scattering measurements.[3,4] With the exponential term in Eq. (4) we implicitly assume that the spin-wave description of the excitations in $CeAl_2$ is valid for temperatures up to about $0.8T_N$, and that two-magnon Raman scattering is the dominant process of the spin-lattice relaxation even at temperatures near $0.8T_N$. This assumption may be justified because the spin-wave description of magnetically ordered systems can be extended to high temperatures, in the neighborhood of the ordering temperature, by including the weak magnon-magnon interactions. Magnon mean free paths are expected to be very large compared to the lattice constant even at T_N (or T_C), and the corresponding renormalizations of the magnon energy and the magnetization due to magnon-magnon interactions are small.[10]

We note that the measured relaxation rates, at low temperatures, are much larger than those found in normal metals, where one expects that $(TT_1)^{-1}\propto[\rho(E_F)]^2 \propto\gamma_{\rm el}^2$; with $\rho(E_F)$ as the electronic density of states at the Fermi surface, and $\gamma_{\rm el}=(\pi^2/3)k_B^2\rho(E_F)$. A similar relation $(TT_1)^{-1}\propto\gamma^2$ where γ is the linear coefficient of the specific heat, is expected from the theory of dilute Kondo impurities.[11] Comparing the results of our measurements in $CeAl_2$ with those reported[12,13] for $LaAl_2$ we observe that $(TT_1)^{-1}$ rather seems to scale linearly with the total linear in T contribution to C_p.

MacLaughlin, Pena, and Lysak[7] have estimated the contribution to T_1^{-1} due to Ce spin fluctuations, using a single Kondo-impurity model. They found $(T_1T)^{-1}=300$ (K sec)$^{-1}$ for the paramagnetic state of $CeAl_2$, an irrelevant value for $T>T_N$, since $T_N\approx T_K$. From this estimate one can, however, infer the corresponding relaxation in the magnetically ordered state of $CeAl_2$, using a simple two-fluid model developed by Gan, Coleman, and Andrei[14] for under-screened Kondo-impurity systems with spin greater than $\frac{1}{2}$. In this model the relevant magnetic and Fermi-liquid properties are completely decoupled. In the case of $CeAl_2$ the magnetic

excitations (spin waves) are frozen out below 1 K and only the spin-fluctuations of the Kondo-screened fraction of the $4f$ electron magnetic moments [approximately 11% (Ref. 4)] are responsible for the spin-lattice relaxation. This implies a strong reduction in the spin-lattice relaxation rate which scales as $T_1^{-1} \propto (M_{Ce})^2$ where M_{Ce} is the fluctuating magnetic moment of the Ce $4f$ electron. With this correction to the estimated value of MacLaughlin, Pena, and Lysak, one obtains $(T_1T)^{-1}=3.8$ $(\mathrm{K\,sec})^{-1}$, roughly half of our measured value.

Hudak, Gavilano, and Ott[15] argue that low-energy excitations in $CeAl_2$ that may account for a large fraction of both the temperature dependence of T_1^{-1} at low temperatures and a large linear term in the specific heat can be found in the spectra of magnetic excitations of incommensurably modulated magnets. The model employs a simple pseudospin Hamiltonian for the localized $4f$ system leading to the description of the modulated structure and which has the form[16,17]

$$H=-\int_{BZ} d^3q\left[\tfrac{1}{2}J(\mathbf{q})(S_{\mathbf{q}}^{+}S_{\mathbf{q}}^{-}+S_{\mathbf{q}}^{-}S_{\mathbf{q}}^{+})+K(\mathbf{q})S_{\mathbf{q}}^{z}S_{\mathbf{q}}^{z}\right] \tag{5}$$

where

$$J(\mathbf{q})=J_1\cos(\mathbf{q}\cdot\mathbf{e}_1)+J_2\cos(2\mathbf{q}\cdot\mathbf{e}_1)$$
$$+J_0[\cos(\mathbf{q}\cdot\mathbf{e}_2)+\cos(\mathbf{q}\cdot\mathbf{e}_3)]\ ,$$

$K(\mathbf{q})=J(\mathbf{q})+D$, and the integral is over the first Brillouin zone. In this Hamiltonian ferromagnetic and antiferromagnetic exchange interactions along the $[1\bar{1}0]$ direction ($\mathbf{e}_1$) with energies J_1 and J_2 between nearest and next-nearest neighbors, respectively, are included. An exchange interaction with energy J_0 in the plane perpendicular to $\mathbf{e}_1$ (directions $\mathbf{e}_2$ and $\mathbf{e}_3$) and a strong uniaxial anisotropy energy $D>0$, favoring alignment of the spins along the [111] direction corresponding to the z axis ($\mathbf{e}_3$), are also considered. The calculated $(\mathbf{q},\omega)$ dependence of the imaginary part of the dynamical susceptibility, χ, in this model, shows a number of sharply defined excitations at high energies.[15] These excitations are a somewhat broadened version of the magnon excitations appearing in antiferromagnetic materials. At very low energies a broad structure, almost dispersionless and linear in ω in the limit of small ω was found, corresponding to low-energy spin excitations. This latter part of $\chi(\mathbf{q},\omega)$ completely vanishes in commensurate magnetic structures.

Using appropriate parameters for $CeAl_2$, the model predicts at low temperatures a Korringa-type law with T_1T of the order of 10^{-1} K sec, and a contribution to the specific heat varying linearly in T as $\gamma_{\mathrm{spin}}T$ with $\gamma_{\mathrm{spin}}=154\pm70$ mJ/K^2 mole. The γ_{spin} value is very large compared to electronic contributions in normal metals, but only about half the observed total $(C_p/T)_{T\to0}$ ratio. This indicates that still a substantial contribution from itinerant electron excitations of heavy-mass quasiparticles has to be considered. The calculated relaxation rate is comparable with the experimental value.

In conclusion we have performed NQR studies of the magnetically ordered state of $CeAl_2$. Our measurements of the spin-lattice relaxation time and the linewidth above 1.5 K are consistent with the presence of thermally activated magnonlike excitations with an energy gap of the order of 11 ± 3 K. This value is in good agreement with results of previous NQR and neutron-scattering experiments. The large increase of the NQR linewidth below T_N is only 40% of the estimated value for a sinusoidally modulated magnetic structure, incommensurate with the lattice and with a corresponding field distribution deduced from the nuclear specific-heat data. The main result is the observation of a Korringa law in the magnetically ordered state of $CeAl_2$, below 1.5 K, corresponding to a relaxation much larger than those found in normal metals indicating relaxation mechanisms involving low-energy excitations with a large effective density of states. Our results can be qualitatively described by a phenomenological model of incommensurably modulated magnets.

We are grateful to E. Felder for carrying out specific-heat measurements and to K. Ueda and S. Takagi for useful discussions. This work was supported by the Schweizerische Nationalfonds zur Fördenrung der Wissenschaftlichen Forschung.

---

*Permanent address: Institute of Physics, Czechoslovakia Academy of Science, Na Slovance 2, Praha 8-liben, Czechoslovakia.

†Permanent address: Department of Physics, New York University, New York, NY 10003.

[1]B. Barbara, J. X. Boucherle, J. L. Buevoz, M. F. Rossignol, and J. Schweizer, Solid State Commun. **24**, 481 (1977).

[2]S. M. Shapiro, E. Gurewitz, R. D. Parks, and L. C. Kupferberg, Phys. Rev. Lett. **43**, 1748 (1979).

[3]R. Osborn, M. Loewenhaupt, B. D. Rainford, and W. G. Stirling, J. Magn. Magn. Mater. **63-64**, 70 (1987).

[4]F. Steglich, C. D. Bredl, M. Loewenhaupt, and K. D. Schotte, J. Phys. (Paris) **40**, C5-301 (1979), and references therein.

[5]E. Walker, H.-G. Purwins, M. Landolt, and F. Hulliger, J. Less-Common Met. **33**, 203 (1973), and references therein.

[6]In the ordered state of $CeAl_2$ one measures both NQR and zero-field NMR, however, we refer to them simply by NQR.

[7]D. E. MacLaughlin, O. Pena, and M. Lysak, Phys. Rev. B **23**, 1039 (1981).

[8]D. E. MacLaughlin, J. D. Williamson, and J. Butterworth, Phys. Rev. B **4**, 60 (1971); **5**, 241(E) (1972).

[9]V. Jaccarino, in *Magnetism II,* edited by G. Rado and H. Suhl (Academic, New York, 1965), p. 307, and references therein.

[10]M. Bloch, Phys. Rev. Lett. **9**, 286 (1962).

[11]A. Narath, in *Magnetism V,* edited by G. Rado and H. Suhl (Academic, New York, 1973), p. 149.

[12]F. Steglich, Z. Phys. B **23**, 331 (1976).

[13]M. J. Lysak and D. E. MacLaughlin, Phys. Rev. B **31**, 6963 (1985).

[14]J. Gan, P. Coleman, and N. Andrei, Phys. Rev. Lett. **68**, 3476 (1992).

[15]O. Hudak, J. L. Gavilano, and H. R. Ott (unpublished).

[16]R. J. Elliot, Phys. Rev. **124**, 346 (1961).

[17]T. Ziman and P.-A. Lindgard, Phys. Rev. B **33**, 1976 (1986).