Evidence for spiral magnetic order in the heavy fermion material CeRhIn₅

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We report ¹¹⁵In nuclear quadrupolar resonance measurements of the heavy fermion compound CeRhIn₅ in the paramagnetic and antiferromagnetic states. The magnetic order is consistent with a model of helical modulation of the Ce moments that is incommensurate with the lattice, and the magnetic dynamics indicate possible two-dimensional behavior.

The interplay between magnetism and superconductivity in heavy fermion materials has attracted much interest since the discovery of heavy fermion superconductivity.¹ In several of the Ce based heavy fermion compounds, the behavior of the magnetic order can be understood qualitatively in terms of a simple picture, in which long-range Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions between the Ce moments compete with short-range Kondo interactions.² In this picture, both the RKKY and the Kondo interactions depend on a coupling constant J that can be tuned with pressure or chemical substitution. Since each of these interactions evolves differently with J, the nature of the ground state can change drastically with pressure or chemical substitution. Recent experimental work indicates that when the many-body Kondo effect dominates (large J), the system undergoes a zero-temperature magnetic-nonmagnetic transition. In CeIn₃ and CePd₂Si₂, both of which have antiferromagnetic ground states at ambient pressure, Tₙ decreases monotonically with pressure and superconductivity develops close to the magnetic instability where Tₙ vanishes.³ Transport measurements indicate that these systems exhibit unusual non-Fermi-liquid behavior near this point, supporting the idea that the physics of these materials is dominated by proximity to a quantum critical point, and it has been suggested that the superconductivity in these materials is mediated by spin fluctuations near this boundary.³

Recently a very interesting class of heavy fermion materials with the formula Ce₄mM₄In₃m+2n, where M is Rh or Ir, was studied.⁴ CeRhIn₅ is an antiferromagnet at ambient pressure with Tₙ=3.8 K, and becomes a superconductor with Tₙ=2.1 K above a critical pressure Pₙ~16 kbar. CeRhIn₅ differs somewhat from other Ce based heavy fermion materials in that the magnetic-nonmagnetic transition where superconductivity develops is apparently a first-order transition.⁴ It has been suggested that CeRhIn₅ exhibits two-dimensional (2D) magnetic character, thus the magnetic behavior and the origin of the superconductivity may be related to that of the cuprates. A detailed understanding of the magnetism is crucial in order to understand how the antiferromagnetism evolves into superconductivity.

Here we report ¹¹⁵In nuclear quadrupolar resonance (NQR) (I=9/2) measurements at ambient pressure in a powder sample of CeRhIn₅ in the paramagnetic and antiferromagnetic states. NQR is an ideal probe of the local magnetic fields in the unit cell as well as the dynamic behavior of the electronic system. In the paramagnetic state we find metallic behavior. Just above Tₙ, the magnetic correlations slow down, dominating the spin-lattice relaxation. Below Tₙ we observe the rapid development of an internal field that indicates that the magnetism is localized on Ce sites with a moment μCe~0.1−0.2μB. The NQR spectrum in the antiferromagnetic state indicates a spiral modulation of the Ce moments that is incommensurate with the lattice.

Crystals of CeRhIn₅ grown from an In flux were ground to a powder in order to facilitate the penetration of the rf fields necessary for NQR. Roughly speaking, CeRhIn₅ consists of alternating layers of CeIn₃ and RhIn₅ and so has two inequivalent In sites per unit cell. The In(1) site, analogous to the single In site in cubic CeIn₃, is located on the top and bottom faces of the tetragonal unit cell. There are four In(2) sites per unit cell, two on each of the lateral faces of the unit cell, equidistant above and below the Rh layer. The NQR spectrum in the paramagnetic state at 4 K reveals two sets of resonances associated with the two In sites: site A is characterized by ν₀=6.78±0.01 MHz and η=0.0, whereas site B is characterized by ν₀=16.665±0.001 MHz and η=0.445±0.001, where ν₀ and η are defined by the NQR Hamiltonian: H=ν₀/3[Q_2(Î²−Î²^2)+η(Q_1^2−Q_2^2)]. Here I is the nuclear spin, ν₀=εQV/6I(2I+1). Q is the quadrupolar moment of the nucleus, V_αα is the electric field gradient along the α direction, and η=(V_x−V_y)/V_z; this assignment is further supported by the intensity ratio. A simple point-charge calculation indicates that the electric-field-gradient (EFG) vector q (the principal axis of the EFG tensor with the largest eigenvalue) points along the crystal c axis for In(1) and points inward towards the center of the unit cell (along the crystal a or b axes) for In(2). Therefore for In(1) the z axis lies along the crystal c direction, and for In(2) the z axis lies along crystal a or b directions. Furthermore, for In(2) the x axis lies along the crystal c direction.

In order to measure the internal field in the antiferromagnetic state, we consider the splitting of the In(1) spectrum by

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an internal field. In the absence of such a field, the In(1) spectrum consists of four transitions given by $v = n v_Q$, where $n = 1, 2, 3, or 4$. The $2v_Q$ ($3/2 \rightarrow 5/2$) transition is shown as a function of temperature in the inset to Fig. 1. In the presence of a nonzero internal field the nuclear Hamiltonian must include the Zeeman term $\mathcal{H}_Z = g_\text{nuc} \mathbf{I} \cdot \mathbf{H}_{\text{int}}$. Here $g_\text{nuc}$ is the gyromagnetic ratio and $\mathbf{H}_{\text{int}}$ is the internal field at the In site. For $g \mathbf{H}_{\text{int}} < v_Q$, the NQR resonance lines are split by the internal field. We find that the $3v_Q$ and $4v_Q$ transitions are unaffected by $H_{\text{int}}$, but the $2v_Q$ transition is split into two resonances that are asymmetric with respect to the original transition (Fig. 1 inset). If there were a component of the internal field along the $c$ axis then all of the transitions would be split equally by $gH_c$; there is no such splitting. Thus $\mathbf{H}_{\text{int}}$ lies in the $ab$ plane.

We diagonalize the full Hamiltonian $\mathcal{H}_{\text{full}} = \mathcal{H}_Q + \mathcal{H}_Z$ and determine $\mathbf{H}_{\text{int}}$ as a function of temperature from the resonance positions shown in the inset to Fig. 1; the results are shown in Fig. 1. The internal field of 1.7 kG at the In(1) site can be compared with an internal field of 5.0 kG at the equivalent In site in CeIn$_3$, where neutron-scattering measurements indicate a Ce moment of $0.4 \mu_B$. Assuming a similar hyperfine coupling, the Ce moment in CeRhIn$_5$ is $\sim 0.1 – 0.2 \mu_B$. The direction of the Ce moments within the $ab$ plane cannot be determined because the field gradient at the In(1) site is axially symmetric about the $c$ axis, thus the splitting of the NQR transition is sensitive only to the magnitude of the internal field. Note, however, that the sharp lines in the antiferromagnetic state (see the inset of Fig. 1) indicate that there exists a single value of the magnitude of the internal field.

The growth of the sublattice magnetization below $T_N$ is quite rapid: a fit to $H_{\text{int}}$ versus $(1 - T/T_N)\beta$ gives $\beta = 0.25 \pm 0.03$, much faster than mean field ($\beta = 0.5$). It is interesting to compare this result with a similar result found in the cuprate antiferromagnet La$_2$CuO$_4$, in which the transition to the antiferromagnetic state is almost first-order-like, with critical exponent $\beta \sim 0.1$.\textsuperscript{8} Note that the reduced critical exponent in La$_2$CuO$_4$ is related to the two-dimensional magnetism in this material; the reduced exponent in CeRhIn$_5$ may also indicate 2D magnetic behavior.

The spin lattice relaxation rate ($1/T_1$) of the In(1) (Fig. 1) was measured as a function of $T$ by fitting the recovery of the magnetization at the $4v_Q$ transition to equilibrium after an inversion pulse. This transition exhibits no splitting due to the internal field in the antiferromagnet state. The time dependence of the recovery was well fit to the expected multi-exponential recovery for a spin 9/2 nucleus\textsuperscript{9} using a single $T_1$ at all temperatures. $T_1^{-1}$ exhibits critical fluctuations within $\sim 1 – 2 K$ of $T_N$; this behavior contrasts with that of CeIn$_3$, which shows no critical slowing down through $T_N$ ($= 10$ K).\textsuperscript{6} The dotted line through the data in Fig. 1 is fit to the Moriya et al. theory for self-consistent renormalized (SCR) spin fluctuations for weak itinerant antiferromagnets:10

$$
\frac{1}{T_1} = \begin{cases} aT + bT/\sqrt{T - T_N} & \text{for } T > T_N \\
cT/M(T) & \text{for } T < T_N, \end{cases}
$$

where $a = 133$ s K$^{-1}$, $b = 41.1$ s$^{-1}$ K$^{-1/2}$, and $c/M_0 = 12.5$ s K$^{-1}$ are fitting parameters, and $M(T) = M_0 (1 - T/T_N)^{0.25}$ is the antiferromagnetic order parameter. The SCR expression for $T_1^{-1}$ has been used successfully to fit the $T_1^{-1}$ in other heavy fermion materials which exhibit magnetic order,\textsuperscript{11} however, it fails to capture all of the behavior below $T_N$ in CeRhIn$_5$, perhaps reflecting enhanced fluctuations associated with the 2D character. The first term in the expression allows for a Korringa-type relaxation expected in a metal. Above $10$ K CeRhIn$_5$ is metallic, and $\rho \approx 10$ $\mu\Omega$ cm. Below $T_N$, spin-lattice relaxation due to quasiparticles at the Fermi surface is suppressed as magnetism develops.

Figure 2 shows the NQR spectrum of the In(2) site in the paramagnetic and antiferromagnetic states. Since this site is not axially symmetric, the transition frequencies do not pos-
assess a simple relationship as do those of the In(1) site. In the paramagnetic state the spectrum consists of four sharp transitions; however, as the internal field develops below \( T_N \) the low-frequency lines broaden (by several MHz) and exhibit a pattern which indicates a distribution of internal fields. The electric field gradient at the In(1) site is axially symmetric; in contrast, the spectrum of the In(2) site is sensitive not only to the azimuthal angle between \( \mathbf{H}_\text{int} \) and the EFG (along \( a \) or \( b \) for this site), but to the polar angle as well. The fact that the transitions at 48 and 65 MHz are affected less than the low frequency transition demonstrates that \( H_\text{int} \) has no component parallel to the EFG, for if it did then each transition would experience an equal splitting \( \gamma H_\text{int} \). We find good agreement between the measured spectrum and a simulation assuming the internal field varies along the agreement between the measured spectrum and a simulation.

In the antiferromagnetic state of CeRhIn\(_5\) neighboring In nuclei if they possess multiple nuclear transitions at different frequencies, whereas in this case we conduct SEDOR between nuclei of the same species. One can perform SEDOR between two like nuclei if the two transitions are neighboring transitions, the SEDOR pulse will create a higher-order coherence, which is undesired.

To demonstrate the viability of such an experiment we measured the SEDOR reduction between different nuclear transitions of the In(2) in the paramagnetic state. We employed the double-resonance probe design of Haase et al., which allows one to tune to close frequencies. The inset of Fig. 3 shows the SEDOR reduction as a function of the pulse spacing. Here the 48 MHz transition is observed with a standard echo sequence, and a \( \pi \) pulse is applied to the 34 MHz transition (see inset, Fig. 2). The echo reduction with increasing pulse spacing clearly indicates a strong coupling between In(2) neighbors.

Figure 3 presents the SEDOR data in the antiferromagnetic state. Here the SEDOR irradiation (IRR) pulse is applied slightly below the 37 MHz horn (see Fig. 2), and the observed frequency is swept from 45 to 50 MHz. The irradiation frequency corresponds to an internal field \( H_0 = 2.29 \) kG; if the coupled nucleus experienced the same internal field one would expect a correlation at 46.3 MHz at the higher nuclear transition. Instead, there is a clear decrease in the echo integral at 45.95 MHz while SEDOR pulses were applied at 34.2 MHz. Plotted is the echo integral obtained with the SEDOR pulse normalized to the echo integral obtained without.

![Figure 3](image_url)

**FIG. 3.** The SEDOR reduction across the spectrum in the antiferromagnetic state: single resonance spectrum (○); the SEDOR reduction as a function of frequency (●), where the SEDOR pulse is applied at 37.2 MHz (see Fig. 2), and \( \tau = 70 \) \( \mu \)sec. The solid line is a Gaussian fit to the data with center frequency 45.95 MHz and FWHM 0.31 MHz. Inset: The SEDOR reduction as a function of \( \tau \) in the paramagnetic state at 4 K. Spin echoes were acquired at 48 MHz while SEDOR pulses were applied at 34.2 MHz.
neighbor of the irradiated nucleus (separated along the $c$ axis by a distance $0.38c$ where $c = 6.782$ Å is the lattice spacing) implies a wavelength $\lambda = 4.6c \pm 0.8c$ assuming that the internal field varies as $\cos(2\pi z/\lambda)$. Note that there is a component of the SEDOR fraction that is independent of frequency, i.e., the signal is reduced by approximately 10%. The origin of this offset is not understood, but may be related to higher-order coherences generated by the SEDOR $\pi$ pulse on the observed nuclei. We are currently investigating this effect in greater depth.

A well-known class of helical antiferromagnets includes the rare-earth metals Ho, Dy, and Tb, where the magnetic coupling is given by the RKKY interaction. A model Hamiltonian that can give rise to the magnetic structure seen in these materials as well as in CeRhIn$_5$ is one in which the couplings between all nearest-neighbor pairs, $J_1$, is antiferromagnetic and along one particular direction the couplings between next-nearest-neighbor pairs, $J_2$, is ferromagnetic. The frustration between the two competing interactions gives rise to the spiral along the $c$ direction when $|J_2/J_1|$ exceeds a critical value. It is not unreasonable to expect that such interactions may be present in CeRhIn$_5$.

Spiral magnetic order along the $c$ axis can also explain the unusual anisotropy of the bulk magnetic susceptibility $\chi(T)$. In the paramagnetic state $\chi^{-1} \propto T$ for $T > 100$ K, with Curie-Weiss constant $\theta_c = -79$ K for $H$ along the $c$ axis, and $\theta_{ab} = +16$ K for $H$ in the $ab$ plane. Although anisotropic crystal-field effects cannot be excluded, such a result could arise if the average coupling along the $c$ direction were ferromagnetic, and the average coupling in the plane were antiferromagnetic. Furthermore, $\chi_c(T) \sim 2\chi_{ab}(T)$, suggesting that the easy axis is along the spiral direction. This picture is further supported by de Haas–van Alphen and magnetization measurements, which reveal a magnetic transition in fields on the order of 2 T along the $c$ axis. The behavior of this transition is consistent with an anisotropic antiferromagnetic spin-density wave or helical magnetic order. Finally, recent elastic neutron-scattering results indicate an incommensurate spin modulation along the $c$ direction with period $3.3c$.

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1 F. Steglich et al., Phys. Rev. Lett. 43, 1892 (1979).
2 S. Doniach, in Valence Instabilities and Related Band Phenomena, edited by R. D. Parks (Plenum, New York, 1977), p. 169.
3 N. D. Mathur et al., Nature (London) 394, 39 (1998).
4 H. Hegger et al., Phys. Rev. Lett. 84, 4986 (2000).
5 C. P. Slichter, Principles of Magnetic Resonance, 3rd ed. (Springer-Verlag, New York, 1990).
6 Y. Kohori et al., Physica B 259-261, 103 (1999).
7 J. M. Lawrence et al., Phys. Rev. B 22, 4379 (1980).
8 D. E. MacLaughlin et al., Phys. Rev. Lett. 72, 760 (1994).
9 A. Narath, Phys. Rev. 162, 320 (1967).
10 T. Moriya et al., Solid State Commun. 15, 169 (1974).
11 M. Kyogaku et al., J. Phys. Soc. Jpn. 62, 4016 (1993).
12 J. Haase et al., J. Magn. Reson. 135, 273 (1998).
13 J. L. Sarrao (private communication).
14 H. Kawamura, J. Phys.: Condens. Matter 10, 4707 (1998).
15 A. L. Cornelius et al. (unpublished).
16 W. Bao (private communication).