Anisotropy of Spin Fluctuations in a Tetragonal Heavy Fermion Antiferromagnet CeRhAl$_4$Si$_2$

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Abstract. An antiferromagnetic (AFM) Kondo lattice compound CeRhAl$_4$Si$_2$, which exhibits successive AFM transitions at $T_{N1}=14$ K and $T_{N2}=9$ K in zero external field, has been microscopically investigated by means of $^{27}$Al nuclear magnetic resonance (NMR) technique. In the high temperature range, magnetic excitations of 4$f$ electrons can be well explained by isotropic localized spin fluctuations. Below $\sim 50$ K, it begins to show a characteristic anisotropy of spin fluctuations, which suggests a competition between spin fluctuations and nesting instability in this system.

1. Introduction

The tetragonal compound CeRhAl$_4$Si$_2$, which is one of the series Ce$^T$Al$_{2n+2}$Si$_2$ ($T=$Rh, Ir, Pt), has been reported as a new antiferromagnetic (AFM) Kondo lattice with successive AFM transitions of $T_{N1}=14$ K and $T_{N2}=9$ K at zero external field. [1, 2] These Ce$^T$Al$_4$Si$_2$ ($T=$Rh, Ir, Pt) materials crystallize in the tetragonal KCu$_4$S$_3$-type structure with space group $P4/mmm$, as displayed in Fig. 1 for CeRhAl$_4$Si$_2$. In this quaternary compound, the square lattices of Ce-Ce with $a=4.22$ Å are well separated from each other along the $c$-axis of 8.01 Å. Due to the layered crystal structure, a quasi-two-dimensional electronic structure might be expected. Indeed, density functional theory (DFT) calculations using the generalized gradient approximation (GGA) predict a quasi-two-dimensional character of the Fermi surface with a propensity for nesting in the $ab$ plane as well as along the $c$-axis. [1] From magnetization measurements on CeRhAl$_4$Si$_2$, the effective moment in the paramagnetic (PM) state above about 200 K is close to the free ion value 2.54 $\mu_B$ of Ce$^{3+}$, indicating localized 4$f$ electrons. The estimated entropy via specific heat measurements suggests that the Kondo energy scale is comparable to the RKKY interaction scale ($T_K \sim T_N$), where the $f$ electrons strongly hybridize with conduction electrons. Recent magnetization and specific heat experiments on CeRhAl$_4$Si$_2$ have clarified the complex phase diagram of external field ($H_0$) vs temperature, and proposed that the $J = 5/2$ manifold is split into three doublets by the crystalline electric field (CEF), i.e., the ground state would be a $\Gamma_7^{(1)}$ doublet, the first excited $\Gamma_6$ doublet would lie at $E_1 = 136$ K, and the second

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excited $\Gamma_7^{(2)}$ doublet is estimated to be 342 K from the ground state. Indeed, this CEF level scheme has been used to explain the Ising-anisotropy of magnetic susceptibility along the c-axis. Two AFM transitions at $T_{N1}$ and $T_{N2}$ are observed in specific heat, confirming long-range antiferromagnetism [1, 2]. Powder neutron diffraction experiments [3] provide evidence for a simple AFM structure below $T_{N2}$ with a propagation vector $Q_2 = (0, 0, 1/2)$, where the Ce moments of $\sim 1$ $\mu_B$ align ferromagnetically in the $c$ plane and stack antiferromagnetically along the $c$-axis. Recently, the intermediate AFM structure has been determined by neutron diffraction on single crystals [4] to have an incommensurate wavevector of $Q = (\delta, \delta, 1/2)$, with a temperature dependent propagation and “locks in” to the commensurate AFM at $T_{N1}$. To account for their data, the authors propose a model of spin-density wave order with the Ce moments modulated along the $a$-axis due to Fermi surface nesting. [4]

In general, nuclear magnetic resonance (NMR) is a particularly useful tool for the microscopic investigation of the magnetism of materials, providing information about magnetic ordering that is complementary to other microscopic probes. Indeed, our spectral study of $^{27}$Al NMR has confirmed the incommensurability between $T_{N1}$ and $T_{N2}$ and the commensurability below $T_{N1}$, which will be published elsewhere. In this proceedings, we will discuss anisotropy of spin fluctuations in the PM state of CeRhAl$_4$Si$_2$, studied through nuclear relaxation measurements.

2. Experimental

Single crystals of CeRhAl$_4$Si$_2$ were grown from Al/Si flux. The chemical composition and homogeneity of single crystals were confirmed using a scanning electron microscope (SEM) with an energy dispersive x-ray spectrometer (EDS). A single crystal with dimensions $2 \times 2 \times 0.16$ mm$^3$ was inserted into an rf excitation coil of copper, and mounted on a two-axes goniometer installed in the NMR probe. NMR measurements were carried out using a phase-coherent, pulsed spectrometer. External magnetic fields were applied using a homogeneous superconducting magnet specified for NMR. The nuclear spin-lattice relaxation time $T_1$ was measured using the inversion-recovery method with a $\pi$-pulse. Values of $T_1$ were obtained from fits to an appropriate relaxation function. The magnetization recovery ($\{M(\infty) - M(t)/M(\infty)\}$) for the central and second satellite NMR transitions of the $^{27}$Al ($I = 5/2$) nuclei gave satisfactory fits to the single-$T_1$ functions: $\frac{1}{35} \exp(-t/T_1) + \frac{8}{35} \exp(-6t/T_1) + \frac{26}{35} \exp(-15t/T_1)$ for the central transition, and $\frac{1}{35} \exp(-t/T_1) + \frac{3}{11} \exp(-3t/T_1) + \frac{6}{11} \exp(-6t/T_1) + \frac{2}{11} \exp(-10t/T_1) + \frac{1}{11} \exp(-15t/T_1)$ for the second satellite transition, respectively.

![Figure 1. (Color Online) Unit cell of CeRhAl$_4$Si$_2$. The local principal axes of electrical field gradient on the Al sites are also shown. Although all the Al sites are crystallographically equivalent, if the external field ($H_0$) is applied along the a axis, two Al sites which are denoted as Al(a) and Al(b) sites are distinguished by local field directions, i.e., $H_0 \parallel V_{ZZ}$ and $H_0 \perp V_{ZZ}$, respectively.](image-url)
3. Results and discussions

From the $^{27}$Al NMR spectral study, it has been identified that the principal electrical field gradient (EFG) axis ($V_{ZZ}$) is perpendicular to the $ac$-plane and that the $V_{XX}$ is parallel to the $c$-axis, as shown in Fig. 1, reflecting the local orthorhombic symmetry ($2mm$) of the Al sites. The EFG parameters are obtained at 50 K as $\nu_Q = \frac{3\hbar Q}{2(2I-1)} = 1.607$ MHz, with an asymmetry EFG parameter $\eta = \frac{|V_{\chi 2} - V_{\chi 1}|}{V_{ZZ}} = 0.856$. If the external field ($H_0$) is applied along the $a$-axis, as illustrated in Fig. 1, the Al sites split into two magnetically distinguished sites, i.e., $H_0$ is parallel to $V_{ZZ}$ on half of the Al sites, which are defined as Al($a$) sites, but $H_0$ is perpendicular to $V_{ZZ}$ on the other half of Al sites, defined as Al($b$) sites. Here, the $b$ axis is defined as a local axis (in-plane) along $V_{YY}$.

In this proceedings, our concern is to consider the anisotropy of spin fluctuations in the PM state. In general, $1/T_1$ on the ligand sites can be written [5] as

$$\frac{1}{T_1} = 2(\gamma_N A_{\perp}/\gamma_e)^2 T \sum q f_\perp^2(q) \frac{\text{Im} X_{\perp}(q,\omega_0)}{\omega_0},$$

in units of $k_B = \hbar = 1$, and where $\gamma_e$ is the electronic gyromagnetic ratio, $A_{\perp}$ is the transferred hyperfine coupling constant, $f_\perp(q)$ is the hyperfine form factor (taken as unity for simplicity in the following analysis), $\text{Im} X_{\perp}(q,\omega_0)$ is the imaginary part of the dynamical susceptibility by $\text{f}$ electrons, $\omega_0$ is the nuclear Larmor frequency and $\perp$ refers to the component perpendicular to the quantization axis. Thus, the nuclear spin-lattice relaxation rate $1/T_1$ is driven by low-energy spin-fluctuation spectra, and $1/T_1$ is sensitive to the perpendicular fluctuations in an applied external field. In order to decompose in-plane and out-of-plane components of spin fluctuations, a new spin-lattice relaxation rate can be defined as $R_i = (\gamma_N A_i/\gamma_e)^2 \sum q |\text{Im} X_{\perp}(q,\omega_0)|$ ($i = a, b, c$). Using these new $R_i$, the experimental $1/T_1 T$ along $a$, $b$, and $c$ can be written as

$$\left(\frac{1}{T_1 T}\right)_{H_0||a} = R_b + R_c; \quad \left(\frac{1}{T_1 T}\right)_{H_0||b} = R_c + R_a; \quad \left(\frac{1}{T_1 T}\right)_{H_0||c} = R_a + R_b$$

![Figure 2](image_url)

**Figure 2.** (Color online) (a) Directionally decomposed spin-lattice relaxation rates divided by temperature along the $a$-, $b$-, and $c$-axes. (b) Normalized $R_i/|A_i|^2$ ($i = a, b, c$) for $^{27}$Al NMR in CeRhAl$_4$Si$_2$ under an external field of $H_0=40.002$ kOe.
For temperature above \( \sim 100 \, \text{K} \), the values and temperature dependence of \( 1/T_1 \) can be well reproduced by the computed local spin fluctuations, assuming that the f electrons are fully localized. Namely, using the proposed CEF scheme, this contribution may be calculated from the following formula \([6, 7, 8, 9]\),

\[
\left( \frac{1}{T_1} \right)_{\text{CEF}} = \frac{2\gamma^2 N |(A/z')^2|}{\omega_{\text{ex}}} \sum_j |\langle J_z \rangle_j|^2 \exp(-E_j/k_BT) / Z,
\]

with a characteristic exchange frequency \( \omega_{\text{ex}} \), where \( z' \) and \( z \) are the number of nearest neighboring Ce ions from the ligand sites and Ce sites, respectively, and \( \langle J_z \rangle_j \) is the expectation value of \( J_z \) for the \( j \)-th CEF eigenstate and \( Z \) is the single-ion partition function. \( \omega_{\text{ex}} \) may be expressed as \( (\sqrt{2z}/\sqrt{3h})J_{\text{ex}}p_{\text{eff}} \) with an exchange interaction \( J_{\text{ex}} \) and an effective moment \( p_{\text{eff}} \) of Ce ions. \([10]\) The \( 1/T_1 \) data can be reproduced by the sum of \( (1/T_1)_{\text{CEF}} + rT \) with \( p_{\text{eff}} = 2.54 \, \mu_B, \) \( J_{\text{ex}} \sim 14 \, \text{K} \) and a small Korringa rate \( r \) of 0.07 \( \text{sec} \, \text{K}^{-1} \) due to conduction electrons (not shown). To determine the spin-fluctuation contribution of \( f \) electrons to \( T_1 \), a small contribution \( r \) of Korringa term is subtracted before the decomposition of \( 1/T_1T \). Below \( \sim 50 \, \text{K} \), the deviation of \( 1/T_1 \) from the calculated curve is seen (not shown), which may suggest development of hybridization between \( f \) and conduction electrons.

Figure 2(a) shows the temperature dependence of the derived \( R_i \) (\( i = a, b, c \)) from Eq. 2 below \( \sim 50 \, \text{K} \) in the PM state of CeRhAl\(_4\)Si\(_2\). Although the \( R_i \) are rather isotropic around \( 50 \, \text{K} \), \( R_a \) and \( R_b \) increase toward \( T_{\text{N1}} \) and \( R_a \) is nearly temperature independent. In order to compare the \( R_i \) quantitatively, as shown in Fig. 2(b), each \( R_i \) are divided by the square of the transferred hyperfine coupling constant \( A_i \), which is determined as \( A_a = -0.60 \, \text{kOe}/\mu_B, \) \( A_b = -0.73 \, \text{kOe}/\mu_B, \) and \( A_c = 1.35 \, \text{kOe}/\mu_B \), respectively, from the Knight shift measurements. Interestingly, spin fluctuations along the \( b \)-axis become the largest and those along the \( c \)-axis also increase after the \( b \)-component with decreasing temperature. On the other hand, the \( a \)-component is less enhanced and becomes much smaller near \( T_{\text{N1}} \).

In general, anisotropy of \( R_i/|A_i^2| \) in PM state near the ordering temperature closely reflects the direction of the ordered moments, because \( 1/T_1 \) on the ligand sites senses the local fluctuations from the neighboring magnetic sites. In such cases, the spectrum of dynamical susceptibility can be approximated by Lorentzian (or Gaussian in some cases) form with spectral width \( \Gamma \) from the neighboring magnetic sites. In such cases, the spectrum of dynamical susceptibility can be expressed as \( (\sqrt{2z}/\sqrt{3h})J_{\text{ex}}p_{\text{eff}} \) with an exchange interaction \( J_{\text{ex}} \) and an effective moment \( p_{\text{eff}} \) of Ce ions. \([10]\) The \( 1/T_1 \) data can be reproduced by the sum of \( (1/T_1)_{\text{CEF}} + rT \) with \( p_{\text{eff}} = 2.54 \, \mu_B, \) \( J_{\text{ex}} \sim 14 \, \text{K} \) and a small Korringa rate \( r \) of 0.07 \( \text{sec} \, \text{K}^{-1} \) due to conduction electrons (not shown). To determine the spin-fluctuation contribution of \( f \) electrons to \( T_1 \), a small contribution \( r \) of Korringa term is subtracted before the decomposition of \( 1/T_1T \). Below \( \sim 50 \, \text{K} \), the deviation of \( 1/T_1 \) from the calculated curve is seen (not shown), which may suggest development of hybridization between \( f \) and conduction electrons.

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In general, anisotropy of \( R_i/|A_i^2| \) in PM state near the ordering temperature closely reflects the direction of the ordered moments, because \( 1/T_1 \) on the ligand sites senses the local fluctuations from the neighboring magnetic sites. In such cases, the spectrum of dynamical susceptibility can be approximated by Lorentzian (or Gaussian in some cases) form with spectral width \( \Gamma \) at a specific \( q \), which corresponds to an ordering propagation vector. Indeed, the anisotropy of \( 1/T_1T \) can tell the preferred orientation of ordered moments in many cases: for example, in the heavy fermion ferromagnet CeRu\(_2\)Ga\(_2\)B \([11]\), and heavy fermion antiferromagnets CePd\(_5\)Al\(_2\) \([12]\), UPtGa\(_5\) \([13]\) NpFeGa\(_5\) \([13]\), and NpCoGa\(_5\) \([14]\). In CeRhAl\(_4\)Si\(_2\), from Fig. 2(b), one might expect moments in the ordered state to lie along the \( b \)-axis. Below \( T_{\text{N1}} \), however, the ordered moment is identified to be along the \( c \)-axis, while an incommensurate spin density modulation \( Q^* = (\delta, \delta, 1/2) \) of the ordered moments is also identified between \( T_{\text{N1}} \) and \( T_{\text{N2}} \) by NMR and neutron diffraction measurements \([4]\). It is noted that such a moment modulation vanishes below \( T_{\text{N2}} \) and that the AFM propagation is locked to \( Q = (0, 0, 1/2) \) below \( T_{\text{N2}} \). \([3, 4]\) Thus, in the case of CeRhAl\(_4\)Si\(_2\), the anisotropy of \( R_i/|A_i^2| \) cannot predict the orientation of ordered moments correctly.

In principle, in-plane anisotropy of \( R_i/|A_i^2| \) between \( a \)- and \( b \)- directions under zero-field is not expected because the electronic \( \text{Im} \chi(q, \omega) \) should have tetragonal symmetry. Therefore, there should be a directional dependence of the in-plane fluctuation spectrum induced by external fields, which may be due to a strong nesting instability, at \( Q_{\text{nest}} = (\delta, \delta, q_z) \) with arbitrary \( q_z \), coming from the quasi-two dimensional electronic state \([1]\). On the other hand, the anisotropy between \( c \) and \( a \)- directions reflect anisotropy of AFM fluctuations at \( Q \). The first order transition at \( T_{\text{N2}} \) from incommensurate to commensurate AFM orderings \([1, 2, 4]\) may come from such a band effect (nesting instability) which was previously discussed theoretically \([15, 16]\).
4. Summary
We have performed $T_1$ measurements for $^{27}$Al NMR in the Kondo lattice compound CeRhAl$_4$Si$_2$. At high temperatures, the rather isotropic $1/T_1$ can be interpreted as fully localized $f$ electrons. Below $\sim$50 K, the $f$ electrons hybridize with conduction electrons to acquire itinerant character. Then, $1/T_1$ begins to show an anisotropy reflecting anisotropic spin fluctuations and a nesting instability in this compound. Further Fermi surfaces investigations using quantum oscillations or angle-resolved photoemission spectroscopy in CeRhAl$_4$Si$_2$ should be particularly promising.

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