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Antiferromagnetic spin fluctuations in CeRhSn probed by ^{119}Sn NMR

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We have carried out ^{119}Sn nuclear magnetic resonance (NMR) measurements on the quasi-Kagomé compound CeRhSn. We found that ^{119}Sn Knight shift (^{119}K) is highly anisotropic and shows Curie-Weiss type temperature (T) dependence above 25 K. In this T range, the NMR relaxation rate shows $^{119}(1/T_1) \propto \sqrt{T}$ and is enhanced by magnetic fluctuations. At low T's, ^{119}K stays constant and the enhanced Korringa relation of $^{119}(T_1TK^2)$=const is observed, differently from the non-Fermi-liquid behavior observed for bulk measurements. The present NMR results suggest that antiferromagnetic spin fluctuations exist in CeRhSn.

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Certain heavy-fermion metals have attracted a great deal of attention because of anomalous low temperature (T) thermodynamics and transport properties such as the so-called "non-Fermi-liquid (NFL)" phenomena.[1] In these materials, the Landau Fermi-liquid (LFL) state no longer holds on at low T's and the T dependence of physical quantities obey as follows: the electronic specific-heat coefficient $C/T \propto -\ln T$; the magnetic susceptibility $\chi \propto 1-aT^{1/2}$, $\propto -\ln T$, or $\propto T^{-1+\lambda}$; the electrical resistivity $\rho \propto T^n (1<n<2)$. During the past decades, extensive experimental and theoretical attempts to understand these NFL behaviors made it roughly classified into three categories, i.e., (1) the unconventional multichannel Kondo effect models,[2–4] (2) quantum critical point (QCP) models,[5–8] and (3) disorder-induced NFL models.[9–11] All of these scenarios have had partial success in explaining some of the experimental results.[1]

In particular, NMR studies have brought about crucial clues to understanding NFL behaviors. Bernal and coworkers reported that the NFL behaviors observed in $UCu_{5-x}Pd_x$ are explained in terms of the distribution of T_K due to the atomic disorder.[9,12] Such a disorder-driven model gives good account of NFL behaviors in other doped systems, such as $CeRhRuSi_2$,[13] and $U_{1-x}Th_xPd_2Al_3$.[14] On the other hand, Kambe *et al.* adopted the self-consistent renormalized (SCR) spin-fluctuation theory[7] for the $Ce_{1-x}La_xRu_2Si_2$ system, and they succeeded in explaining the NFL anomalies observed in the NMR relaxation rate $1/T_1$ as well as macroscopic physical quantities.[15] Ishida *et al.* pointed out that the NFL behavior in $YbRh_2Si_2$ is ascribed to the competition between antiferromagnetic (AFM) spin fluctuations and ferromagnetic (FM) spin fluctuations at the QCP from the ^{29}Si-NMR experiments.[16]

Recently, NFL behaviors of ρ, C/T, and χ were reported for CeRhSn having a quasi-Kagomé lattice.[17,18] Ślebarski and co-workers proposed that the NFL anomalies can be interpreted in terms of a Griffith's singularity close to a QCP from the systematic studies of impurity-doped polycrystalline $Ce_{1-x}La_xRhSn$.[17] Kim *et al.* found that single-crystalline samples of CeRhSn also exhibit NFL-like anomalies at low T's, at least down to 0.4 K.[18] A relatively large residual resistivity of $\sim 50\ \mu\Omega$ cm in a single crystal suggested that the NFL behaviors are ascribed to the Sn-Rh atomic disorder,[18] i.e., the replacement of Sn atoms into the regular Rh site, proposed by Ślebarski *et al.*[17] It is, however, still unclear to what extent the Sn-Rh atomic disorder gives rise to the NFL behaviors. In this paper, we report the results of ^{119}Sn NMR experiments for the polycrystalline CeRhSn.

The details of sample preparation and characterization were reported elsewhere.[18] X-ray diffraction data clearly show a single phase, although the possibility of the Sn-Rh atomic disorder cannot be ruled out because of the closeness of the atomic numbers for Rh and Sn. The polycrystal ingots were crushed into powder with a smaller grain size than the skin depth for NMR measurements. ^{119}Sn ($I=1/2$, $\gamma_n/2\pi = 15.867$ MHz/T) NMR measurements were carried out on field-aligned powder samples by using a conventional pulsed spectrometer at fixed frequencies of $f=22.806$, 34.24, and 75.153 MHz, respectively. The ^{119}Sn NMR spectrum was obtained by tracing the spin-echo intensity as a function of the magnetic field (H). The nuclear spin-lattice relaxation rate ($1/T_1$) of ^{119}Sn was measured using the saturation recovery method.

Figure 1 shows the T dependence of (a) the Knight shifts ^{119}K and (b) the linewidths $^{119}\delta H$ of the ^{119}Sn-NMR spectrum. The inset shows a typical ^{119}Sn NMR spectrum observed at $T=100$ K and $f=75.153$ MHz for an aligned-powder CeRhSn. Since χ is strongly anisotropic at low T's, where the c-axis susceptibility $\chi_\parallel (H \parallel c)$ is much larger than the c-plane one $\chi_\perp (H \perp c)$, the c axis of each grain tends to align along the external magnetic field. Note that $^{119}\delta H$ is quite narrow, $^{119}\delta H_\parallel \sim 14$ Oe at $f=75.153$ MHz (~ 9 Oe at 34.240 MHz) and $T=100$ K, which is about one-half of that in the Kondo semiconductor CeNiSn,[19] assuring the sufficiently good quality of the present sample on a microscopic level. We examined signals in the field range of 3–7 T at $f=75.153$ MHz to check the existence of Sn atoms replaced from the regular site.[18] No signals were observed, however, which is different from the case for the impurity-doped NFL system, such as $UCu_{5-x}Pd_x$,[9,12] $CeRuRhSi_2$,[13] and $U_{1-x}Th_xPd_2Al_3$,[14] in which the additional NMR satellites as well as the spectral broadening were observed. Therefore, a large amount of the atomic disorder is excluded in CeRhSn.

Above 25 K, the overall T dependence of $^{119}K_\perp$ and $^{119}K_\parallel$ is similar to that of the susceptibility. Below 25 K, however, ^{119}K stays constant for both field directions, though the bulk susceptibility reveals the NFL anomalies as $\chi \sim T^{-n}$ with n

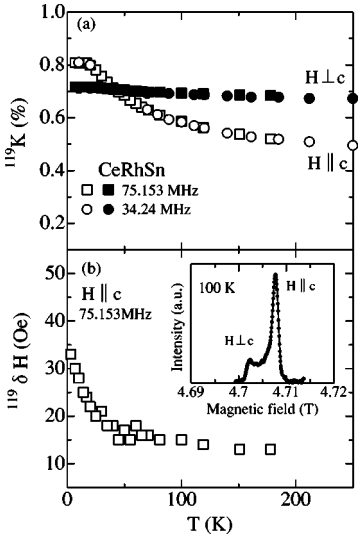

FIG. 1. (a) Temperature dependence of the ^{119}Sn Knight shift of CeRhSn for $H \perp c$ and $H \| c$ at various magnetic fields. (b) T dependence of linewidth, measured at $f \sim 75.153$ MHz. The inset in (b) shows typical ^{119}Sn-NMR spectra at $f \sim 75.153$ MHz and $T = 100$ K for aligned powder CeRhSn.

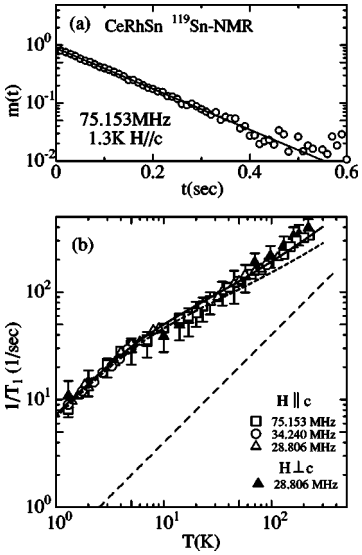

FIG. 3. (a) ^{119}Sn NMR relaxation curve at $T = 1.3$ K and 75.153 MHz for $H \| c$. (b) Temperature dependence of $^{119}(1/T_1)$ in CeRhSn. The solid line is the result calculated by the SCR model (short-dashed line) for a three-dimensional system incorporated with the Sn 5p orbital relaxation (long-dashed line).

$= 0.35$ and 1.1 for $H \perp c$ and $H \| c$, respectively.[18] Since χ and ^{119}K were measured under different magnetic fields, we suspect such a disagreement at low T's is due to the nonlinearity of the magnetization curve. However, the nonlinear effect of the magnetization is too small to explain the present results. As seen in Fig. 1(b), $^{119}\delta H_{\|}$ does not show any saturation below 25 K down to $T = 1.3$ K, though the T dependence $^{119}\delta H_{\|}$ is not so strong compared with that of the bulk susceptibility (see the $^{119}\delta H_{\|}$ vs χ plot in Fig. 2). This might be due to a small amount of the atomic disorder.

In Fig. 2, ^{119}K and $^{119}\delta H$ are plotted against χ with T as an implicit parameter. The ^{119}K vs χ plot shows a linear relation above 25 K. The hyperfine coupling constants are estimated to be $A_{hf}^{\|} = 7.83$ kOe/μ_B, and $A_{hf}^{\perp} = 5.16$ kOe/μ_B. As will be discussed later, the small anisotropy in the NMR relaxation rate $^{119}(1/T_1)$ supports small anisotropy of hyperfine coupling constants. The anisotropy of the hyperfine coupling constant, $A_{hf}^{\|} - A_{hf}^{\perp}$, is obtained to be ~ 2.7 kOe/μ_B, which is much larger than the classical dipolar contribution, $H_{dip}^{\|} - H_{dip}^{\perp} \sim 0.7$ kOe/μ_B. This suggests that the transferred hyperfine coupling due to the hybridization of Ce 4f electrons with Sn 5p ones is important to discuss the anisotropy of ^{119}K.

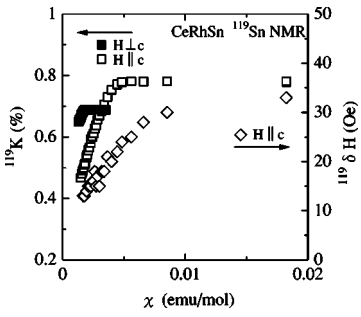

FIG. 2. ^{119}Sn-Knight shift and linewidth versus the susceptibility plots with temperature as an implicit parameter.

The extrapolation of ^{119}K to $\chi = 0$ intersects the vertical axis at $\sim 0.26\%$ and $\sim 0.53\%$ for $H \| c$ and $H \perp c$, respectively, which may be ascribed to the Van Vleck contributions. If a localized Ce^{3+} picture with the hexagonal crystal electric field (CEF) is applied to the present system, the anisotropy of ^{119}K is qualitatively explained by assuming the ground state of $|\pm 3/2\rangle$, the first excited state of $|\pm 1/2\rangle$ at 100–300 K, and the second excited state of $|\pm 5/2\rangle$ at 500–800 K. Although this model is oversimplified for the present system as already pointed out by Kim *et al.*[18] the anisotropy of both ^{119}K and χ might be ascribed to the CEF effect.

Below 25 K, both the ^{119}K and $^{119}\delta H_{\|}$ vs χ plots deviate from a linear relation and tend to saturate at low T's. These are different from the case for the impurity-doped NFL systems,[9,13,14] suggesting that the atomic disorder is not attributed to the NFL behaviors in CeRhSn.

In order to gain further insights into low-energy excitations in CeRhSn, ^{119}Sn NMR relaxation measurements were performed at various frequencies of 22.806, 34.24, and 75.153 MHz. Figure 3 shows the T dependence of the $^{119}(1/T_1)$ for $H \| c$ and $H \perp c$. The NMR relaxation curves, $m(t) = [M(\infty) - M(t)]/M(\infty)$, where $M(t)$ is the nuclear magnetization at time t after saturation pulses, can be fitted by a single exponential function as expected for $I = 1/2$ in the whole observed T range [see Fig. 3(a)]. That is, a large amount of atomic disorder is unlikely for CeRhSn. This is because the distribution of the NMR relaxation is expected when the atomic disorder exists, as reported in $CePd_2Al_3$.[20] Weak NMR signals for the $H \perp c$ axis cause large experimental errors for $^{119}(1/T_1)_{\perp}$. Within the experimental errors, $^{119}(1/T_1)$ is almost isotropic, which reflects the nearly isotropic hyperfine coupling constants. As is shown in Fig. 3(b), $^{119}(1/T_1)$ is not saturated up to 250 K, but is proportional to

the square root of temperature ($\sim\sqrt{T}$). These features are contrasted with the typical relaxation behavior of the heavy Fermion system, where $1/T_1$ undergoes a moderate crossover from the $1/T_1=$const behavior at higher T's than a characteristic temperature, $T^* \sim T_K$, to the $T_1T=$const behavior at low T's. This is understood as the crossover from localized state of f electrons into delocalized ones with lowering T.

The fact that $^{119}(1/T_1)$ in CeRhSn is already varying with T at 250 K indicates that $T^* \sim T_K$ is an order of $\sim 10^2$ K. This is consistent with the fact that the Curie-Weiss law of χ due to the localized spin is not observed below 250 K where the effective magnetic moments for both directions are much reduced from the localized moment for the Ce^{3+} ion. Actually, T_K is estimated to be rather high, as $T_K \sim 140$ K from ρ,[17] or $\sim$240 K from C/T.[18] At low T's below 10 K, a Korringa relation of $^{119}(1/T_1TK^2)=$const was observed, indicating that a LFL state is established. This behavior is inconsistent with the NFL anomalies found in the bulk quantities.[17,18] Note that our NMR measurements were performed at relatively high magnetic fields above 1.5 T, whereas χ was measured at low fields below 0.1 T. This inconsistency is possibly explained by the field-induced LFL state as reported in $YbRh_2Si_2$.[16] Anyway, the overall behavior of $^{119}(1/T_1)$ suggests that the $4f$ electrons are itinerant rather than localized in this T range.

We now compare the present NMR results with theoretical predictions: The quantum phase transition model[5] predicts $1/T_1 \propto T^{1/3}$; the $T=0$ spin-glass transition model[6] does $1/T_1 \propto T^{1/4}$; the disordered Griffiths-phase model[11] does $1/T_1 \propto \omega^{-1+\lambda}$, where ω is the NMR frequency and $0<\lambda<1$. These models do not agree with the present NMR results.

In general, the Korringa relation gives $1/S \equiv 1/T_1TK^2 = \pi\hbar\gamma_n^2 k_B/\mu_B^2$ for the noninteracting electron system.[16] Including the electronic correlation, the Korringa relation is modified as $1/T_1TK^2 = \mathcal{K}(\alpha)/S$, where $\mathcal{K}(\alpha)$ is a measure of the electronic correlation, i.e., $\mathcal{K}(\alpha)>1$ indicates the existence of the AFM correlations while $0<\mathcal{K}(\alpha)<1$ does the FM ones among the quasiparticles. A simple estimate for the correlation parameter $\mathcal{K}(\alpha)$ for CeRhSn yields $\mathcal{K}(\alpha) \sim 5$ below 10 K, suggesting the existence of the AFM correlations.

Together with the $1/T_1 \propto \sqrt{T}$ behvaior at high T's in CeRhSn, $^{119}(1/T_1)$ is tentatively fitted with the SCR expressions as[7,8]

$$\frac{1}{T_1} = aT + \frac{\hbar\gamma_n^2 A_{hf}^2}{2\pi T_A} 3\frac{T}{T_0}\int_0^{x_c} dx \frac{x}{(y+x^2)^2}, \tag{1}$$

where the first term is due to the Sn $5p$ orbital relaxation process obeying the $T_1T=$const law. The second one is due to the relaxation channel open to f-electron spin fluctuations through the transferred hyperfine interactions from the Ce f-electron spin. This term was derived from the SCR theory of spin fluctuations originating from the Curie-Weiss-type behavior of the staggered susceptibility at an AFM wave vector $q=Q$. T_A and T_0 are the characteristic energy scales which specify the spin-fluctuation energies in the q and ω space, respectively. The parameter y relates to the self-consistent reduced inverse staggard susceptibility as

$$y = y_0 + \frac{3}{2}y_1\int_0^{x_c} dx x^2 \left\{ \ln\left(\frac{x(y+x^2)T}{T_0}\right) - \frac{T}{2x(y+x^2)T_0} - \Psi\left(\frac{x(y+x^2)T_0}{T}\right)\right\}, \tag{2}$$

where $y_0=1/[2T_A\chi_Q(T=0)]$, and $y_1=2J_Q/(T_A\pi^2)$ with the exchange energy J_Q [roughly comparable to the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction]. x_c is the cut-off vector in units of the magnetic zone boundary vector.

The best fit is obtained for parameters $a=0.396$ $(\text{sec K})^{-1}$, $y_0=0.01$, $y_1=4$, and $T_A=270$ K, assuming $T_K \sim T_0=150$ K and $x_c=1$. In the SCR theory, T_0 is taken so as to be comparable to T_K,[7] which is estimated to be 140 K (Ref. 17) to 240 K.[18] The value of $T_A=270$ K is consistent in order with the value of $T_A=200-450$ K calculated by using the relation $T_A \sim 0.75/\chi$,[7] with $\chi=0.17-0.36 \times 10^{-2}$ (emu/mole).[18] Thus, the nice fit of the SCR model to $^{119}(1/T_1)$ strongly suggests that the spin fluctuations are essential for low-energy excitations in CeRhSn, where the spin fluctuations are strongly peaked around the AFM wave vector $q=Q$ at low energy. If the low-energy excitations are dominated by the spin fluctuations, other experimental quantities, e.g., C/T, ρ should be scaled with the value T_0.[7,15] Unfortunately, it is difficult to extract such low-energy excitations from the macroscopic measurements because of rather high $T_K>100$ K.

As for the validity of the above analysis, to our knowledge, we should note that the SCR theory does not include the effects of any kind of microscopic disorder, which might exist in this system as suggested from macroscopic measurements.[17,18] Furthermore, it is not obvious how the CEF splitting, which might cause anisotropic magnetic excitations through an anisotropic c-f mixing, does affect the nature of the spin fluctuations. Although the interplay of both the atomic disorder and CEF splitting with the spin fluctuations still remains as the open question, the present results strongly suggests that CeRhSn is placed in the vicinity of the magnetic instability.

We now turn our attention to the fact that CeRhSn has a quasi-Kagomé structure. Then the present results can be compared with the geometrically frustrated metal compounds such as LiV_2O_4, (Ref. 21) and $Y_{1-x}Sc_xMn_2$.[22] In $Y_{1-x}Sc_xMn_2$, large spin fluctuations arising from geometrical frustration of magnetic interactions play a vital role in quantum critical behavior at low T's, and the NFL-like behavior was also observed in doped $Y_{0.97}Sc_{0.03}Mn_2$.[22] The NFL behavior was reported in LiV_2O_4, although its mechanism has been still controversial.[23–25] In fact, anomalous field-dependent $1/T_1$ at low T's observed in LiV_2O_4,[25] which were explained by the slowing down of spin fluctuations, may be another possible origin for the discrepancy between the bulk and NMR results observed in the present system.

In summary, the ^{119}Sn NMR shift and relaxation rate were measured for the polycrystalline CeRhSn. The present NMR studies displayed the LFL behavior at low T's below 10 K, whereas the macroscopic measurements detected the NFL

anomalies. This is probably ascribed to the difference of the field strengths, where $H > 1.5$ T for NMR is much higher than $H < 0.1$ T for bulk measurements. Therefore, this discrepancy may be reconciled by such a context that NFL anomalies are suppressed by applied fields and the field-induced LFL state is stabilized under high magnetic fields. The T dependence of $^{119}(1/T_1)$ was analyzed in terms of the SCR model for AFM spin fluctuations, and the results strongly suggests that CeRhSn is placed in the vicinity of the AFM instability. In order to clarify the anomalous low-energy excitations in CeRhSn, further precise NMR measurements under lower fields are needed, and NMR studies for a single- crystal CeRhSn are now in progress.

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