Anisotropic Spin Fluctuations and Superconductivity in "115" Heavy Fermion Compounds: ^{59}Co NMR Study in PuCoGa$_5$

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(Received 6 May 2010; revised manuscript received 3 October 2010; published 19 November 2010)

We report results of ^{59}Co nuclear magnetic resonance measurements on a single crystal of superconducting PuCoGa$_5$ in its normal state. The nuclear spin-lattice relaxation rates and the Knight shifts as a function of temperature reveal an anisotropy of spin fluctuations with finite wave vector q. By comparison with the isostructural members, we conclude that antiferromagnetic XY-type anisotropy of spin fluctuations plays an important role in mediating superconductivity in these heavy fermion materials.

DOI: 10.1103/PhysRevLett.105.217002 PACS numbers: 74.70.Tx, 76.60.−k

The observation of unconventional superconductivity in the heavy fermion (HF) compounds (e.g., CePd$_2$Si$_2$ [1] and CeRhIn$_5$ [2]) in proximity to a magnetic instability initiated the now well-accepted belief that spin fluctuations (SF) mediate Cooper pairing in these materials. Recently discovered transuranic HF compounds PuCoGa$_5$ [3], PuRhGa$_5$ [4], and NpPd$_5$Al$_2$ [5] develop superconductivity at temperatures nearly an order of magnitude higher ($T_c = 18.5$ K in PuCoGa$_5$) than in the previously known Ce-, U-, and Yb-based HF materials. Nuclear quadrupole resonance (NQR) studies [6] confirm that superconductivity in PuCoGa$_5$ is mediated by spin fluctuations, also providing an important bridge linking the physics between HF and high T_c cuprate superconductors. More importantly, the actinide based superconductors enable the possibility to investigate the microscopic factors which influence superconductivity within a single structural family of "115" HF superconductors.

In the SF-mediated superconductors, the anisotropy of local SF appears to be relevant to the symmetry of superconducting pairs. In general, while the spin-triplet (p-wave) superconductivity favors Ising-type coupling since only longitudinal fluctuations can induce an attractive force [7], the spin-singlet (d-wave) superconductivity prefers rather isotropic coupling since both longitudinal and transverse fluctuations can mediate Cooper pairing. In cuprates, the local SF is indeed isotropic in the normal state [8]. We show in this Letter, via the ^{59}Co NMR, that the XY-type anisotropy of antiferromagnetic (AFM) SF scales with T_c in the 115 HF superconductors, in striking contrast to the case of cuprates. Possible origins for this unexpected correlation are discussed.

NMR is an ideal local probe since the spin-lattice relaxation rate (T_1^{-1}) is quite sensitive to these spin fluctuations. Generally, T_1^{-1} is expressed [9] in terms of the dynamical susceptibility $\chi(\mathbf{q}, \omega_n)$ and hyperfine coupling A whose components are perpendicular to the quantization axis:

$$(T_1T)_{\parallel}^{-1} \propto \sum_{\mathbf{q}} [\gamma_n A_{\perp}(\mathbf{q})]^2 \chi''_{\perp}(\mathbf{q}, \omega_n)/\omega_n, \qquad (1)$$

where χ'' is the imaginary part of $\chi(\mathbf{q}, \omega_n)$, ω_n is the nuclear Larmor frequency, and the symbols $\parallel$ and $\perp$ denote the direction with respect to the quantization axis. The $\mathbf{q}$-dependent $A(\mathbf{q})$ can be approximated as $A(0)f(\mathbf{q})$, because the hyperfine coupling is local near the nucleus. In this relation, $A(0)$ is the hyperfine coupling constant and $f(\mathbf{q})$ is the hyperfine form factor determined by the geometrical configuration of nuclear sites. Because the hyperfine coupling constant $A(0)$ is determined from a linearity between the NMR shifts ($\mathcal{K}$) and the static susceptibility $\chi(0, 0) \equiv \chi$ for each direction of the applied field H, exact alignment of the sample with respect to H is required. To prevent possible radioactive contamination during these experiments, the single crystal of ^{239}PuCoGa$_5$ must be encapsulated, making it very difficult to confirm the alignment of the sample after the encapsulation. Here we take advantage of the quadrupole perturbed spectrum of ^{59}Co ($I = 7/2$) which is very sensitive to the angle between the applied field and the nuclear principal axis. For the axial symmetry, we expect seven spectral lines for $I = 7/2$, which, in first order perturbation, should be equally separated by $\Delta\nu(\theta) = \nu_Q(3\cos^2\theta - 1)/2$, where θ is the angle between the principal c axis of the electric field gradient (EFG) at the ^{59}Co and the external field H, and ν_Q is the nuclear quadrupole frequency. By examining the ^{59}Co spectra for $H \parallel c$ and $H \perp c$ shown in Figs. 1(a) and 1(b), misalignment of the sample for each direction, if any, is within 3°. We also determine the nuclear quadrupole frequency $\nu_Q = 1.02$ MHz, which is comparable to ν_Q found in other 115 compounds [10,11].

For measurements of $\mathcal{K}$, the central transition ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) is tracked as a function of temperature, shown in Fig. 1(c). Both $\mathcal{K}_c$ and $\mathcal{K}_a$ show similar temperature dependencies in the normal state: $\mathcal{K}_{a,c}$ decreases slightly with decreasing T, but becomes T independent below ~40 K. At T_c both shifts drop sharply, indicating spin-singlet pairing. From the extrapolated zero-temperature values, $\mathcal{K}(T \to 0)$, we can estimate the orbital shift $\mathcal{K}_0$: $\mathcal{K}_{0a} = 0.5\%$ and $\mathcal{K}_{0c} = 1.1\%$. The difference

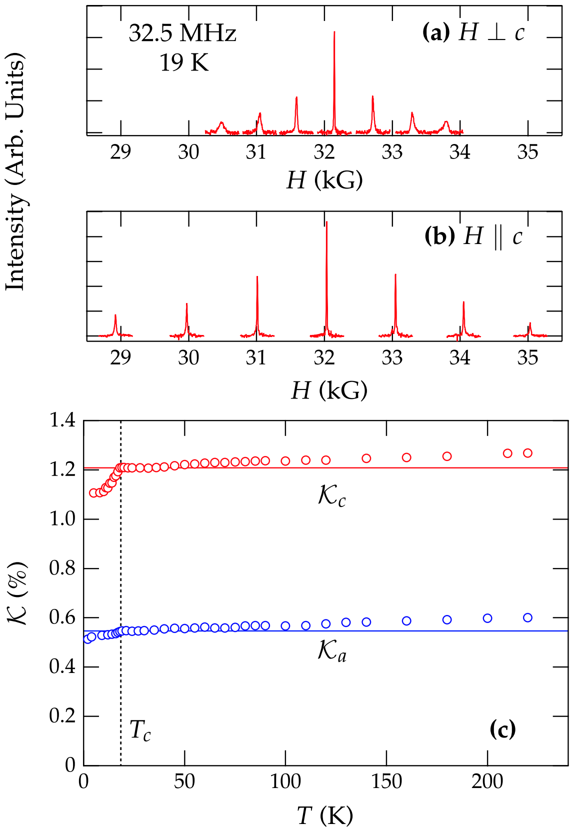

FIG. 1 (color online). (a) and (b) ^{59}Co NMR spectra at 19 K obtained by sweeping the external field H at a fixed frequency 32.5 MHz. (c) Knight shifts of the central transition for $H \parallel c$ and $H \perp c$. For $H \perp c$, a second order quadrupole correction was made, which is given by $\Delta\nu = (15/16)(\nu_Q^2/\nu_0) \sim 0.03$ MHz, or $\sim$0.09%, where ν_0 is the resonance frequency.

$\{\mathcal{K} - \mathcal{K}_0\}_{a,c}$ corresponds to the temperature-dependent spin part of $\mathcal{K}_{a,c}(T)$. These $\mathcal{K}_{a,c} - T$ behaviors seem to be inconsistent with earlier results [6]. Although the origin of this discrepancy is not clear, recent polarized-neutron diffraction measurements on ^{242}PuCoGa$_5$ [12] indicate a small, weakly temperature-dependent static susceptibility, which suggests itinerancy of $5f$ electrons in PuCoGa$_5$. Unlike the anisotropy found in $\mathcal{K}_{a,c}$, static susceptibility measurements on the same sample used in this work do not show anisotropy, which also is the case with PuRhGa$_5$ and UCoGa$_5$ [13,14]. We note, however, that reliable measurements of the uniform χ were complicated due to (i) encapsulation of the sample, (ii) Co impurities, and (iii) radioactive damage from the decay process of Pu (^{239}Pu $\longrightarrow$ ^{235}U + α). To check its order of magnitude, we roughly estimate $A_{a,c} = \mathcal{K}_{a,c}/\chi_{a,c}$ using the reported uniform χ [12]. This estimate gives $A_{a,c}$ in the range 5 to 10 kOe$/\mu_B$, which is close to values found in UCoGa$_5$ [11] and NpCoGa$_5$ [10].

The T dependence of the nuclear spin-lattice relaxation rate divided by T, $(T_1T)^{-1}$, is plotted in Fig. 2 for $H \parallel c$ and $H \perp c$. Though both $(T_1T)_\parallel^{-1}$ and $(T_1T)_\perp^{-1}$ become T independent with a small anisotropy at high temperatures, both increase with decreasing T and are accompanied by an increasing anisotropy $(T_1T)_\parallel^{-1}/(T_1T)_\perp^{-1}$ that reaches a maximum just above T_c. In contrast, $^{59}(T_1T)^{-1}$ for LuCoGa$_5$ with its filled f shell shows a very small and nearly isotropic $(T_1T)^{-1}$, as shown in Fig. 2. Thus, the T-independent $(T_1T)^{-1}$ in PuCoGa$_5$ at high temperatures should originate from itinerancy of Pu's $5f$ electrons and not from conduction electrons. On the other hand, the enhancement of $(T_1T)^{-1}$ below 100 K implies the partially localized nature of the $5f$ electrons. These observations may suggest evidence for a dual nature of $5f$ electrons in PuCoGa$_5$, which was previously implied from photoemission experiments [15]. It is noteworthy that, among the 115 HF superconductors, a T-independent $(T_1T)^{-1}$ at high temperatures has been observed *only* in the Rh analog PuRhGa$_5$ [16], suggesting a unique feature of Pu-based materials.

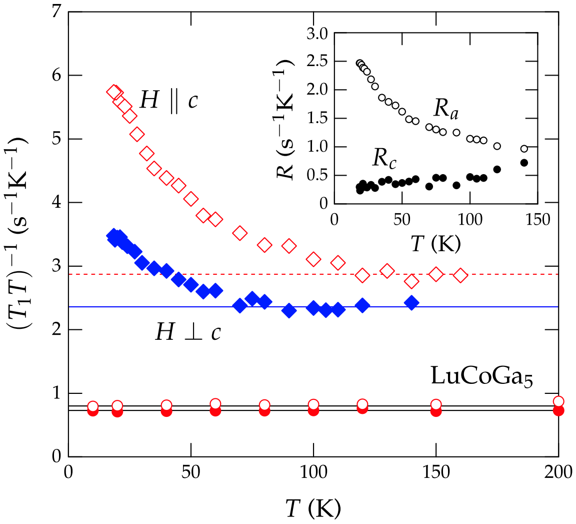

FIG. 2 (color online). Nuclear spin-lattice relaxation rate divided by T, $(T_1T)^{-1}$, as a function of T. For comparison, ^{59}Co NMR of the nonmagnetic metal LuCoGa$_5$ is presented (filled circle: $H \perp c$; empty circle: $H \parallel c$). Inset: A plot of the in-plane component of fluctuations (R_a), which increases rapidly with decreasing T, and the out-of-plane component (R_c), which is almost independent of T.

Given T_1^{-1} and $\mathcal{K}$, it is possible to estimate the magnetic nature of the spin fluctuations through the Korringa ratio defined as $R_K \equiv S/(T_1T)\mathcal{K}^2$, where $S = \mu_B^2/(\pi\hbar\gamma_n^2k_B)$. In a simple metal or noninteracting Fermi gas, $R_K \sim 1$, but this ratio deviates from unity when electron-electron correlations are present [9,17]. For AFM fluctuations (i.e., magnetic fluctuation at finite $\mathbf{Q}$), R_K becomes larger than 1, but it tends to be smaller than 1 when dominated by ferromagnetic fluctuations. From $\mathcal{K}(T)$ and the $5f$-derived contribution $(T_1T)_f^{-1}$ obtained by subtracting $(T_1T)^{-1}$ of LuCoGa$_5$, we find that R_K ranges from 5 to 16, indicating the presence of strong AFM fluctuations in PuCoGa$_5$.

To discuss in more detail the anisotropic nature of the AFM SF in PuCoGa$_5$, it is convenient to define new spin-lattice relaxation rates that *probe* SF along the quantization axis. In the tetragonal structure ($a = b \neq c$) of PuCoGa$_5$, these rates are defined by $R_\alpha \equiv [\gamma_n A(0)]^2 \sum_{\mathbf{q}} \chi''_\alpha(\mathbf{q}, \omega_n)/\omega_n$, where $\alpha = a, c$. Here the form factor $f(\mathbf{q}) = 1$ is assumed for simplicity, as it is irrelevant to our discussion [18]. Then, from Eq. (1) $(T_1T)^{-1}_{H\parallel c} = 2R_a$ and $(T_1T)^{-1}_{H\perp c} = R_a + R_c$. As shown in the inset of Fig. 2, the in-plane component R_a, which is always larger than the out-of-plane R_c, becomes prominent with decreasing T, while R_c slightly decreases. In the case of AFM fluctuations, we may take the main weight of $\chi''(\mathbf{q}, \omega_n)$ around a finite $\mathbf{Q}$ as $\langle \chi''(\mathbf{q}, \omega_n) \rangle$, where $\langle \ldots \rangle$ denotes the q average. In the limit of strong correlations, the approximation $\chi''(\mathbf{Q}, \omega_n)/\omega_n = 2\pi\chi^2(\mathbf{Q}) = 1/2\pi\Gamma^2(\mathbf{Q})$ holds [19]. Thus, the spin fluctuation energy becomes [20]

$$\Gamma_\alpha = \frac{\gamma_n A_\alpha(0)}{\sqrt{2\pi R_\alpha}}, \tag{2}$$

where $\Gamma_\alpha = \sqrt{\langle \Gamma_\alpha^2(q) \rangle}$. Using $A(0) \sim$ 5–10 kOe$/\mu_B$ estimated above, we find the average of $\Gamma_{a,c}$ to be 4–8 meV, which is much larger than 0.5–1 meV in CeCoIn$_5$ ($T_c = 2.3$ K) [21] but lies in the range of the values found in many actinide 115 compounds [20]. Inelastic neutron scattering measurements are necessary to confirm Γ and $\mathbf{Q}$.

Now we turn to the in-plane anisotropy of AFM SF in PuCoGa$_5$. From Eq. (2) we define the anisotropy of Γ,

$$\frac{\Gamma_c}{\Gamma_a} = \frac{A_c}{A_a}\sqrt{\frac{R_a}{R_c}} = \frac{\mathcal{K}_c(T)}{\mathcal{K}_a(T)}\sqrt{\frac{R_a}{R_c}\frac{\chi_a}{\chi_c}}. \tag{3}$$

The ratio $\rho \equiv \Gamma_c/\Gamma_a$ is displayed in Fig. 3 as a function of T. We interpret this ratio as the anisotropy of SF which are peaked at $\mathbf{Q}$. Heisenberg systems such as the cuprates have $\rho \approx 1$ [22,23], while values less than 1 reflect Ising-like anisotropy, as is exemplified in the p-wave superconductor Sr$_2$RuO$_4$ [24]. In contrast, the d-wave superconducting 115 systems all have values of $\rho > 1$ which indicate XY-like anisotropy. As noted above, $A_{a,c}$ cannot be determined accurately for PuCoGa$_5$; therefore, we express $A_{a,c}$ in terms of $\chi_{a,c}$ and $\mathcal{K}_{a,c}(T)$. $\chi(T)$ appears to be nearly isotropic, i.e., $\chi_a/\chi_c \sim 1$, and thus anisotropy in the spin fluctuation energy is dominated by $R_{a,c}$ and $\mathcal{K}_{a,c}(T)$. ρ is a maximum just above $T_c = 18.5$ K and shows an abrupt change at $T^* \sim 60$ K, which corresponds to the hybridization gap observed in the photon-induced relaxation measurement [25]. As shown in Fig. 3, this behavior is somewhat similar to $\rho(T)$ observed in CeCoIn$_5$ [21] but different from that of PuRhGa$_5$. Clearly, ρ just above T_c for PuCoGa$_5$ is unprecedentedly large, much beyond the value in PuRhGa$_5$ that had been the largest ρ among 115 compounds.

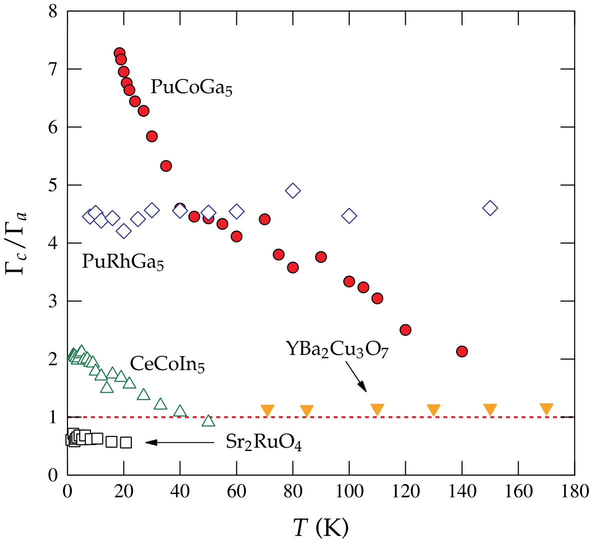

FIG. 3 (color online). Ratio of spin fluctuation energy $\rho \equiv \Gamma_c/\Gamma_a$ as a function of temperature in the normal state. Shown for comparison are results from ^{69}Ga NMR in PuRhGa$_5$, ^{59}Co NMR in CeCoIn$_5$ [21], ^{101}Ru NMR in Sr$_2$RuO$_4$ [24], and ^{63}Cu(2) NMR in YBa$_2$Cu$_3$O$_7$ [22,23].

The primary result is presented in Fig. 4, which shows the relationship between T_c and ρ just above T_c for PuCoGa$_5$, PuRhGa$_5$ [26], CeCoIn$_5$ [21], CeIrIn$_5$ [27], and NpPd$_5$Al$_2$ [28]. The error bar for ρ of PuCoGa$_5$ is due to the estimate $\chi_a/\chi_c = 1 \pm 0.2$, which should also include possible errors for $\mathcal{K}_c/\mathcal{K}_a$ in Eq. (3). The correlation between T_c and ρ shown in Fig. 4, in conjunction with the fact that $\rho \sim 1$ in nonsuperconducting 115 compounds [11], indicates that an increase of T_c is associated with more in-plane SF [29]. This result contradicts the expectation that Heisenberg systems should be more

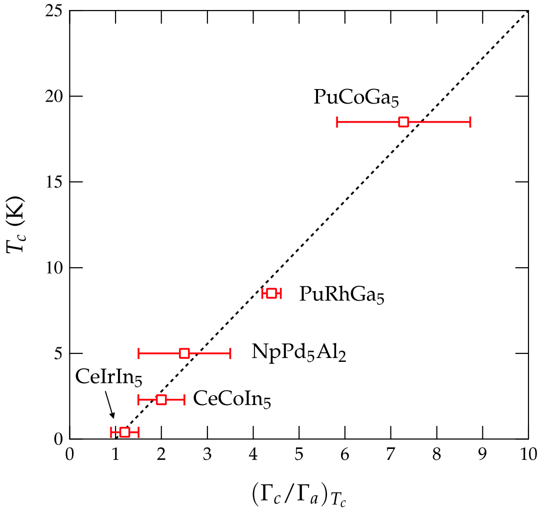

FIG. 4 (color online). T_c versus Γ_c/Γ_a just above T_c for 115 HF superconductors. Data for CeIrIn$_5$ and NpPd$_5$Al$_2$ are taken from Refs. [27,28], respectively. The dotted line is a guide to the eye, and the error bar for PuCoGa$_5$ is estimated assuming anisotropy of the static susceptibility is unity ±20%.

favorable for superconductivity due to the increased number of modes available to mediate pairing [7]. A likely explanation is tied to the fact that spin-orbit coupling and crystal electric fields restrict the spin anisotropy in the 115 system. Consequently, the correlations found in Fig. 4 reflect the ability of the 115 compounds to optimize the spin anisotropy within the constraints of spin-orbit and crystal field interactions.

We believe the most important parameter for setting the scale of T_c is still the spin fluctuation energy scale $T_{\rm SF}$, which explains why the superconducting transition temperature increases from Ce-based 115's to Pu-based 115's to pnictides to cuprates [6]. In addition to $T_{\rm SF}$, the reduced dimensionality of electronic correlations could also enhance T_c. However, within 115 materials where $T_{\rm SF}$, the correlation length (ξ) and its anisotropy (ξ_c/ξ_a) are the same order of magnitude, the degree of XY anisotropy represented by Γ_c/Γ_a is shown here to be a good parameter for determining T_c. It is surprising that both Ce-based 115's and Pu-based 115's lie on the same curve in Fig. 4. This may reflect the fact that due to spin-orbit coupling, spin anisotropy is naturally tied to the c-f hybridization strength, which is a key parameter in setting the spin fluctuation energy scale. This gives a natural explanation for the observed temperature dependence of ρ as well.

In conclusion, ^{59}Co NMR measurements in the normal state of $\mathrm{PuCoGa_5}$ have uncovered the role of spin fluctuations in promoting d-wave superconductivity in the isostructural 115 heavy fermion compounds. Both the Knight shift $\mathcal{K}$ and the spin-lattice relaxation rate T_1^{-1} show strongly anisotropic behavior. An analysis of the normal-state data finds an enhancement of SF at finite $\mathbf{Q}$ and strong in-plane (XY-type) anisotropy. We suggest that the ratio Γ_c/Γ_a, a measure of the anisotropic spin fluctuations, is a characteristic quantity closely connected to the unconventional superconductivity in the 115 heavy fermion family.

We thank N. J. Curro, S. Kambe, S. E. Brown, H. Ikeda, and T. Takimoto for useful suggestions and discussions. H. S. acknowledges the hospitality of Los Alamos National Laboratory. Work at Los Alamos National Laboratory was performed under the auspices of the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, and supported in part by the Los Alamos Laboratory Directed Research and Development program.

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