Microscopic properties of the heavy-fermion superconductor PuCoIn$_5$ explored by nuclear quadrupole resonance

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Abstract

We report $^{115}$In nuclear quadrupolar resonance (NQR) measurements on the heavy-fermion superconductor PuCoIn$_5$, in the temperature range $0.29K \leq T \leq 75K$. The NQR parameters for the two crystallographically inequivalent In sites are determined, and their temperature dependence is investigated. A linear shift of the quadrupolar frequency with lowering temperature below the critical value $T_c$ is revealed, in agreement with the prediction for composite pairing. The nuclear spin–lattice relaxation rate $T_1^{-1}(T)$ clearly signals a superconducting (SC) phase transition at $T_c \approx 2.3$ K, with strong spin fluctuations, mostly in-plane, dominating the relaxation process in the normal state near to $T_c$. Analysis of the $T_1^{-1}$ data in the SC state suggests that PuCoIn$_5$ is a strong-coupling $d$-wave superconductor.

Keywords: NQR, heavy-fermion, unconventional superconductivity, Pu-115s
1. Introduction

The character of $f$ electrons in rare earth and actinide materials, i.e. itinerant versus localized, has been the subject of considerable research effort, yet a complete description is still missing. Of particular interest is the case of plutonium, which bridges the itinerant behavior in lighter actinides where $5f$ electrons form fairly broad conduction bands and the localized, atomic-like $5f$ states in heavier actinides [1]. This somewhat dual nature of Pu’s $5f$ states is linked to the variety of unusual properties displayed by elemental Pu and its compounds, as manifested, for example, in the emergence of exotic magnetism and unconventional superconductivity. Characteristically, the Pu-based ‘115’ heavy-fermion materials exhibit a superconducting (SC) transition at critical temperature $T_c = 18.5 \text{ K}$, $8.7 \text{ K}$ for PuCoGa$_5$, PuRhGa$_5$ respectively [2, 3], an order of magnitude higher than any other Ce- or U-based superconductor. Even though the unconventional character of superconductivity in these compounds is widely accepted, the origin of the relatively high $T_c$ and, accordingly, the microscopic mechanism providing the glue for the SC condensate lack an unambiguous explanation. The most prominent relevant ideas propose antiferromagnetic (AF) spin fluctuations [4], valence fluctuations [5], or more complex mechanisms [6] as responsible for mediating superconductivity.

Recently, PuCoIn$_5$, the first In analog of the Pu ‘115’ family, was synthesized, with its physical properties classifying it as a moderately heavy-fermion compound [7]. PuCoIn$_5$ shows a SC transition at $T_c = 2.5 \text{ K}$, a much lower value than the ones measured for its Ga counterparts. The unit cell of PuCoIn$_5$ is about 30% larger than that of PuCoGa$_5$ and this volume expansion is expected to result in relatively more localized $5f$ electron states in the former, which has indeed been verified by electronic structure calculations [8, 9]. The qualitative difference of the $5f$ character in these compounds, along with the fact that PuCoGa$_5$ does not seem to be close to a magnetic instability [10], have put forward the possibility that superconductivity may not be mediated by AF fluctuations in all members of this class of materials as suggested before [11–13]. Instead, it is plausible that the high SC transition temperature of PuCoGa$_5$ is associated with the proximity to a valence instability [14], while superconductivity in PuCoIn$_5$ is mediated by antiferromagnetic spin fluctuations associated with a quantum critical point [7, 9]. An alternative theory that aspires to provide a ‘universal’ solution proposes the development of composite pairs between local moments and conduction electrons [6], and incorporates spin [15] and valence [16] fluctuations. Within this picture, both the actinide and the Ce-based heavy-fermion superconductors can be accommodated by appropriately tuning the relative strengths of the model’s parameters [15, 16].

Nuclear quadrupolar resonance (NQR) experiments constitute an ideal tool for the study of PuCoIn$_5$, since they provide a microscopic probe sensitive to both magnetic and charge degrees of freedom. In this report, we present a detailed $^{115}$In NQR investigation of PuCoIn$_5$ for a wide range of temperature values ($0.29\text{K} \leq T \leq 75\text{K}$). From the identified spectral lines, we deduce the quadrupolar parameters for the two inequivalent In sites, which are found to be qualitatively similar to those for other Ce- and Pu-115s. The quadrupolar frequency $\nu_0$ varies with temperature in the normal state as per the empirical formula for conventional metals. As superconductivity develops, however, $\nu_0$ exhibits a sharp, albeit small shift, which is a key prediction of the theory of composite SC pairing [15, 16]. Moreover, the temperature variation of the nuclear spin–lattice relaxation rate $T_1^{-1}$ delineates distinctive regimes of dynamic...
behavior. An excess of strong in-plane AF spin fluctuations is observed in the vicinity of \( T_c \approx 2.3 \) K, which are believed to be important for the formation of the SC condensate in this material. Our data below \( T_c \) suggest that PuCoIn\(_5\) is a strong-coupling superconductor with anisotropic gap symmetry.

2. Sample and experimental details

Our sample consisted of about 100 mg of PuCoIn\(_5\) single crystals grown from In flux [7], which were ground to powder and placed in a cylindrical coil of 3 mm diameter and 7 mm length. Prior to sample insertion, in order to prevent any radioactive contamination, the coil was encapsulated in a Stycast 1266 epoxy cast of dimensions \( \sim 20 \) mm \( \times \) 20 mm \( \times \) 20 mm, which was drilled along the coil’s axis. Upon sample insertion, the cast’s ends were sealed by titanium frits with 2 \( \mu \)m diameter pores, allowing for thermal contact with the respective cooling fluid. For \( T \geq 1.45 \) K, temperature was regulated in a standard gas-flow \( ^4\)He cryostat with variations limited to \( \delta T/T < 1\% \), while, for \( T < 1.3 \) K, the coil was mounted into the mixing chamber of a \( ^3\)He/\( ^4\)He dilution refrigerator. Due to the sample’s inherent radiation heating, the lowest achieved sample temperature was limited to \( T \sim 290 \) mK. The sample temperature was verified by \textit{in situ} measurements of the \(^{63}\)Cu NMR \( T_1 \) on the coil’s copper nuclei, which should satisfy the relation \( T_1T = 1.26 \) sK [17].

The reported NQR spectra were recorded using a conventional pulsed NMR spectrometer. They were obtained by summing the Fourier transforms of standard Hahn spin-echo transients from the \(^{115}\)In nuclear spins \( (I = 9/2) \), recorded at constant frequency intervals. \( T_1 \) was measured using the \textit{inversion recovery} method: the values were determined by fitting the appropriate function to the magnetization recovery profile after an inversion pulse, depending on the probed nuclear transition.

3. NQR parameters and discussion

For nuclei carrying spin \( I > 1/2 \), the nuclear quadrupolar moment \( Q \) couples to the local electric field gradient (EFG) created by their surrounding charge distribution. This interaction is described by the Hamiltonian

\[
\mathcal{H}_Q = \frac{h\nu_Q}{6} \left[ 3\hat{J}_z^2 - \hat{J}^2 + \frac{1}{2}\eta \left( \hat{J}_+^2 + \hat{J}_-^2 \right) \right],
\]

where the characteristic frequency \( \nu_Q \) is defined as \( \nu_Q \equiv 3eQV_{ZZ}/(h2I(2I-1)) \), \( \eta \equiv |V_{XX} - V_{YY}|/|V_{ZZ}| \) is the asymmetry parameter, and \( h \) is Planck’s constant. Here, \( V_{ij} = \partial^2V/\partial x_i\partial x_j \) are the components of the EFG tensor with the axes labeled according to the convention \( |V_{ZZ}| \geq |V_{XX}| \geq |V_{YY}| \), and \( e \) is the electron charge. Thus, \( \mathcal{H}_Q \) can be fully characterized by \( I, \nu_Q, \eta, \) and the unit vector \( \hat{n} \) defining the direction of \( V_{ZZ} \), the EFG tensor principal axis with the largest eigenvalue.

For \( I = 9/2 \), the eigenstates of equation (1) result in four distinct spectral lines. If the nuclear site possesses uniaxial symmetry, i.e. \( \eta = 0 \), the resonance frequencies are given by
integer multiples of $\nu_Q (\nu = n\nu_Q, \text{with } n = 1 - 4)$. In case of lower symmetry, $\eta$ is non-zero and the spectral lines are not equally spaced.

PuCoIn$_5$ crystallizes in a tetragonal HoCoGa$_5$-like structure with space group P4/mmm (inset of figure 2), featuring two crystallographically inequivalent In sites: the high symmetry In(1) site sits in the middle of the basal plane, which corresponds to $\eta = 0$ and $\hat{n}||\hat{c}$, hence four equidistant NQR lines should be observed. On the other hand, the lower symmetry In(2) site has orthorhombic symmetry with $\hat{n}$ pointing perpendicular to the face of the unit cell (i.e. $\hat{n}||\hat{a}$ or $\hat{b}$) and $\eta \neq 0$, leading to four not equally separated quadrupolar transitions.

The $^{115}$In NQR signal in PuCoIn$_5$ was searched between 20 MHz and 90 MHz at temperature $T = 3.95$ K. The detected resonance frequencies are listed in table 1. The quadrupolar parameters $\nu_Q$ and $\eta$ for both $^{115}$In sites were deduced from a $\chi^2$ minimization of the difference between the observed resonance frequencies and the eigenvalues of $\mathcal{H}_Q$, taken from the full diagonalization of equation (1). The derived values are $\nu_Q = 9.434$ MHz and $\eta = 0$ for In(1), and $\nu_Q = 15.716$ MHz and $\eta = 0.366$ for In(2). These values are in reasonable agreement with those calculated using the full potential linear-augmented-plane-wave method within a local density approximation $\nu_Q = 11.50$ MHz, $\eta = 0$, and $\nu_Q = 15.97$ MHz, $\eta = 0.27$ for In(1), and In(2) respectively [18], further attesting to the correct assignment of the spectral lines.

It is important to note that additional spectral lines were detected in the aforementioned frequency range. Upon careful inspection of their temperature dependence, these lines were associated with the quadrupolar transitions of the uniaxially symmetric $^{115}$In nuclear site in a secondary, impurity PuIn$_3$ phase present in our sample ($\sim 17\%$ of sample’s mass), with $\nu_Q = 10.56$ MHz and $\eta = 0$. This was verified by independent measurements on a pure PuIn$_3$ single crystal, which reveal a phase transition to an antiferromagnetically ordered state at $T_N \approx 14$ K [19]. In fact, this impurity phase of PuIn$_3$ in the PuCoIn$_5$ sample is responsible for the apparent anomaly at $T \sim 14$ K in the latter’s specific heat [7].

The evolution of the quadrupolar frequency as a function of temperature for both $^{115}$In sites, In(1) and In(2), is depicted in figures 1(a) and (b), respectively, for $T > T_c$. For In(1), $\nu_Q$ is derived from the position of the $\nu_i \equiv 4\nu_Q$ line, while, for In(2), $\nu_Q$ and $\eta$ at each temperature were deduced using a fit of the measured frequencies $\nu_1, \nu_2, \nu_3$ to the eigenvalues of equation (1), as described above. The quadrupolar frequency increases with decreasing temperature for both nuclear sites, while $\eta$ is only very weakly affected. In general, in conventional non-cubic metals, the temperature dependence of $\nu_Q$ due to the lattice contraction can be described by the empirical relation

### Table 1.

| site  | $\nu_Q$(MHz) | $\eta$ | $\nu_1$(MHz) | $\nu_2$(MHz) | $\nu_3$(MHz) | $\nu_4$(MHz) |
|-------|--------------|-------|--------------|--------------|--------------|--------------|
| In(1) | 9.434        | 0     | 28.301       | 28.301       | 29.116       | 45.901       |
| In(2) | 15.716       | 0.366 | 28.358       | 29.116       | 45.901       | 62.180       |

The quadrupolar parameters for PuCoIn$_5$ at $T = 3.95$ K. The frequencies $\nu_i$ denote the measured spectral lines arising from transitions between the energy levels of Hamiltonian (1) with $|\Delta E| = 1$, so that $\nu_i$: $\left\{ \frac{1}{2} + i \iff \frac{1}{2} + i - 1 \right\}$. The values of $\nu_Q$ and $\eta$ were derived from a $\chi^2$ fit to the data.
where there exists a correlation between the magnitude of $\nu_0^Q$ and the strength of the EFG's temperature variation, quantified by the coefficient $A$ \cite{20}. Specifically, a larger value of $\nu_0^Q$, arising from a stronger coupling of the surrounding non-spherical charge clouds, results in a smaller value of $A$. A least-squares fit of our data to equation (2) yields the following values: $\nu_0^Q(0) = 9.435 \text{ MHz}$, $A = 4.44 \cdot 10^{-6} \text{ K}^{-3/2}$ for In(1), and $\nu_0^Q(0) = 15.718 \text{ MHz}$, $A = 3.01 \cdot 10^{-6} \text{ K}^{-3/2}$ for In(2). Based on this result, the fractional change of $\nu_0^Q$ as a function of temperature is plotted in figure 2. It is evident that a $T^{3/2}$ behavior describes well the data for both sites. Moreover, the value of $A$ is indeed lower for In(2), the site with the higher $\nu_0^Q(0)$, as
indicated by the slope of the fit curves in figure 2. Thus, the effect of temperature on the $^{115}$In quadrupolar parameters in PuCoIn$_5$ in the normal state seems to conform to the phenomenological description set out by equation (2).

The transition line $\nu_3$ for the In(2) site was carefully traced as a function of temperature in the vicinity of $T_c$, and representative spectra are shown in figure 3(a). The resonance frequency deduced from the spectrum’s first moment, and the line’s full-width-at-half-maximum (FWHM) are plotted in figure 3(b). Even though the position change is small relative to the linewidth, a sharp positive frequency shift is evident in the SC state, beginning precisely at $T_c$. In particular, a linear fit to the data (red solid line in figure 3(b)) gives an increase of $9.4$ kHz K$^{-1}$ for $\nu_3$ below $T_c$, which corresponds to a change of $\sim 3$ kHz K$^{-1}$ for $\nu_Q$. This observation indicates that the Pu 5f-electron charge degrees of freedom are readily affected by the emergence of the SC condensate, leading to an altered EFG and hence a shift in $\nu_Q$. This change in $\nu_Q$ upon entering

\[ \frac{T}{T_c} = 
\]

\[ 0.58, 0.68, 0.72, 0.83, 0.91, 1.02, 1.19 \]

\[ 45.70, 45.80, 45.90, 46.00, 46.10 \]

\[ \text{Frequency (MHz)} \]

\[ \text{Normalized Intensity (arb. units)} \]

\[ a) \]

\[ \text{b) First moment (left) and full-width-at-half-maximum (right) of the spectrum described in (a) as a function of temperature near } T_c. \]

\[ \text{The red solid line depicts a linear fit to the data in the SC state.} \]

\[ \text{The exact value of } T_c \text{ was verified by in situ ac-susceptibility and } T_1 \text{ measurements.} \]

\[ 3 \]
the SC state is not expected within models of unconventional superconductivity mediated by AF spin fluctuations [4] or valence fluctuations [5, 14], which predicts a smooth variation of the valence in the SC state (see figure 6 in [14]). However, such a shift of \( \nu_Q \) is predicted to occur within the theoretical framework of composite pairing [15, 16]. Specifically, the composite pair condensate is electrostatically active, as its formation results in the redistribution of the f-electron charge and thus the change of the EFG around the nucleus, which in turn gives rise to a shift in \( \nu_Q \), contrary to the case of conventional superconductivity. Although the details of the effect’s manifestation strongly depend on the symmetry of the model’s two distinct scattering channels in the particular material, and their relative strengths [15, 16], our present finding in PuCoIn\(_5\) provides evidence for possible composite pair mediated superconductivity.

It is worth noting that a variation in the electronic density of states arising from the thermal expansion below the SC transition results in an EFG change too small to account for the observed \( \nu_Q \) shift. However, changes in \( \nu_Q \) in the SC state have been previously observed in some conventional superconductors such as In [21] and Ga [22], as well as in the high-\( T_c \) \( \text{Ba}_2\text{YCu}_3\text{O}_7\) [23], warranting caution in the phenomenon’s interpretation. Hence, further studies and verification of this small, but discernible shift in \( \nu_Q \) below \( T_c \) in other members of the PuMX\(_5\) family and/or in Ce-115s are necessary to validate the role of composite pairing in heavy-fermion superconductivity.

4. \( T_1 \) measurements and discussion

The nuclear spin–lattice relaxation rate \( T_1^{-1} \) characterizes the time scale in which the nuclear ensemble reaches thermal equilibrium. This mechanism originates in the coupling of the nuclei to the fluctuations of the local field created by their surrounding lattice. \( T_1^{-1} \) is directly related to the dynamical spin susceptibility \( \chi''(\mathbf{q}, \omega_0) \) as [24]:

\[
\left( \frac{1}{T_1} \right)_{\|} \propto \sum_{\mathbf{q}} \left[ \gamma_n A_{\perp}(\mathbf{q}) \right]^2 \frac{\chi''(\mathbf{q}, \omega_0)}{\omega_0},
\]

where \( \gamma_n \) is the nucleus’ gyromagnetic ratio, \( A(\mathbf{q}) \) is the \( \mathbf{q} \)-dependent hyperfine coupling constant, \( \omega_0 \) is the Larmor frequency, and || (\( \perp \)) denotes the direction parallel (perpendicular) to the quantization axis of the nuclear spins. Hence, \( T_1 \) measurements provide an excellent probe of the system’s spin dynamics.

Figure 4 shows the NQR relaxation rate \( T_1^{-1} \) as a function of temperature for \( T = 0.29 \text{ K–75 K} \). The measurements were performed on the \( \nu_3 \) line, \( \langle \pm 7/2 \leftrightarrow \pm 5/2 \rangle \), of the In(2) site (see table 1). Above \( T \sim 60 \text{ K} \), \( T_1^{-1} \) is nearly temperature independent, indicating that, in this temperature range, the Pu 5\( f \) electronic spins act like localized moments, uncorrelated with the conduction electrons. The In nuclei see the fluctuating local field from these exchange-coupled 5\( f \)-electrons via a transferred hyperfine interaction, giving rise to the temperature independent relaxation. The absence of Kondo coherence in this temperature region is corroborated by the electrical resistivity behavior, which displays a weak temperature dependence above \( T \sim 70 \text{ K} \) [7].
As the Pu 5f-electrons hybridize with the itinerant electrons and the Kondo lattice develops, the electrical resistivity decreases rapidly with lowering $T$ \cite{7}, a hallmark of the emergence of the heavy-fermion state \cite{25}. In this regime, the low-lying magnetic excitations are expected to be heavy quasiparticles due to electron-hole pair excitations across the Fermi surface, and this should translate into a Korringa-type relaxation, i.e. constant $\kappa T_1$ \cite{17}. Indeed, for $T \approx T_{c}$, it is evident that $\kappa T_1^{-1}$ is proportional to $T$, attesting that the system’s electronic properties reflect the coherent heavy Fermi-liquid state of the Kondo lattice in this temperature range.

Below $T \approx 10$ K, the relaxation rate deviates markedly from the $T$-linear Korringa behavior down to $T_c \approx 2.3$ K \cite{4}, as highlighted by the shaded area in figure 4. This trend becomes more evident when plotting $(T_1 T)^{-1}$ versus $T$, shown in the inset of figure 4, and it is qualitatively similar to the observations for PuCoGa$_5$ \cite{11, 26}. The apparent enhancement of $(T_1 T)^{-1}$ hints at the presence of strong AF spin fluctuations near to $T_c$ \cite{27}, which may be important for stabilizing the unconventional SC condensate.

$^4$ The sample used for the reported $T_1$ measurements was about three months old, hence the suppression of the deduced $T_c$ compared to the measured by electrical resistivity and specific heat value of $T_c = 2.5$ K. The sample’s $T_c$ at the time of our experiments was verified by in situ ac-susceptibility measurements, performed using the NQR tank circuit.
The temperature evolution of $T^{-1}_1$ below $T_c$ demonstrates the non-conventional pairing symmetry in this system: the onset of superconductivity is clearly discerned by the sharp drop of $T^{-1}_1$ below $T_c \approx 2.3$ K. Nevertheless, a coherence peak is not detected in the vicinity of $T_c$, and $T^{-1}_1$ follows a $T^3$ power-law as $T$ decreases just below $T_c$. Both these observations contradict the expectations for an isotropic SC gap with conventional $s$-wave symmetry. In contrast, the observed $T^{-1}_1$ behavior can be replicated successfully assuming an anisotropic line-nodal gap, as illustrated by the solid black line in figure 4. Specifically, the temperature dependence of the relaxation rate in the SC state is given by the following equation:

$$\frac{1}{T^{1\text{SC}}_1(T)} = \frac{2}{k_B T} \int \left\langle \frac{N^2_0(E)}{N^2_0} \right\rangle f(E) \left[ 1 - f(E) \right] dE. \quad (4)$$

Here, $f(E)$ is the Fermi–Dirac distribution function, $N_0$ is the normal state density of states (DOS), $N_0(E) = N_0 E / \sqrt{E^2 - \Delta^2(\theta, \phi)}$ is the DOS in the SC state, and $\langle \cdots \rangle$ denotes an average over the Fermi surface. The anisotropic line-nodal gap is taken to be $\Delta(\theta, \phi) \equiv \Delta_0(T) \cos \theta$, where $\theta$ and $\phi$ define the Fermi surface angular parameters and $\Delta_0(T)$ is the BCS gap function. Typically, at low temperature and well below $T_c$, $T^{-1}_1$ in the $d$-wave SC state deviates from the $T^3$ behavior due to impurities which contribute a residual DOS $N_{res}$ at the Fermi level, leading to a $T$-linear temperature dependence. Nevertheless, in our case, this behavior of $T^{-1}_1$ is further masked by the large impurity scattering associated with crystal defects caused by the radioactive decay of Pu and secondary phases. Consequently, we take into consideration an impurity relaxation term in order to account for our data. Accordingly, the total low-temperature relaxation rate in the SC state is calculated as

$$1/T^{1\text{imp}}_i(T) \equiv 1/T^{1\text{imp}}_i + \left[ 1/T^{1\text{SC}}_i(T) - 1/T^{1\text{imp}}_i \right] \cdot 1/T^{1\text{SC}}_i(T), \quad (5)$$

where $1/T^{1\text{imp}}_i$ is the impurity contribution and $1/T^{1\text{SC}}_i$ is given by equation (4).

A calculation of $T^{-1}_1$ per equation (5), for a SC gap $2\Delta_0(0)/k_B T_c = 8$ with a residual DOS $N_{res}/N_0 \approx 0.32$ and $1/T^{1\text{imp}}_i = 6.5$ s$^{-1}$, is illustrated by the solid black line in figure 4. The amplitude of the gap is very similar to that of PuCoGa$_5$, $2\Delta_0/k_B T_c = 6.4 - 8$ [11, 28], larger than that of PuRhGa$_5$, $2\Delta_0/k_B T_c \approx 5$ [29], and also much larger that the value of 4.28 predicted for a weak electron–boson coupling $d$-wave superconductor. In principle, it is not possible to distinguish with certainty between spin-singlet and -triplet pairing nodal superconductivity solely from the $T^{-1}_1$ temperature dependence and without measurements of the NMR shift. Nevertheless, such measurements in the isostructural PuCoGa$_5$ [11, 26] and PuRhGa$_5$ [30] have provided clear evidence for singlet-pairing, rendering the possibility of $p$-wave triplet pairing in PuCoIn$_5$ highly unlikely. Thus, in light of our NQR $T^{-1}_1$ results, PuCoIn$_5$ can be classified as an unconventional, strong-coupling $d$-wave superconductor.

In order to further investigate the character of the strong spin fluctuations in the normal state, we examined separately the relaxation rates that are sensitive to fluctuations along different directions, according to equation (3). To this end, the rates $R_\alpha \equiv \left( \gamma_s A^j \right)^2 \sum_\xi \chi^{s*}_\alpha \left( \mathbf{q}, \omega_0 \right) / \omega_0$ are defined, where $\alpha = a, b, c$ [31]. Due to the system’s
tetragonal symmetry, these are reduced to the in- and out-of-plane components \( R_a \) and \( R_c \), respectively. Then, it follows from equation (3) that 
\[
R_a = 1/2 (T T)^{-1}_{\parallel c}
\]
and 
\[
R_c = (T T)^{-1}_{\perp c} - 1/2 (T T)^{-1}_{\parallel c}.
\]
As discussed above, the principal axis of the EFG for the In(1) site is \( \hat{n} \parallel \hat{c} \), while for In(2) it is \( \hat{n} \perp \hat{c} \). That is to say, the quantization axis of the NQR Hamiltonian equation (1) is \( \parallel \) for In(1), In(2), respectively, and thus it is 
\[
(T T)^{-1}_{\parallel c} \equiv (T T)^{-1}_{\ell c}.
\]
and 
\[
(T T)^{-1}_{\perp c} \equiv (T T)^{-1}_{\ell c} (\text{assuming } A(1) \sim A(2)).
\]

Figure 5 plots the temperature evolution of the relaxation rates \( R_{\alpha} \) in the normal state, as calculated from the \( T_1^{-1} \) values of the two distinct In sites (see inset). The in-plane component \( R_a \) is larger than its out-of-plane counterpart \( R_c \) throughout the examined temperature range, and increases rapidly below \( T \sim 10 \text{ K} \) on approaching \( T_c \). In contrast, \( R_c \) remains nearly unchanged with temperature. This observation suggests that the excess of spin fluctuations reflected in the system’s \( (T T)^{-1} \) behavior for \( T_c \leq T \leq 10 \text{ K} \) stems predominantly from the in-plane component.

5. Conclusion

Our \(^{115}\text{In}\) NQR measurements provide a comprehensive picture for the quadrupolar parameters and the dynamical spin susceptibility, via the nuclear spin–lattice relaxation probe, in PuCoIn\(_5\), both in the normal and SC states. While the quadrupolar frequency temperature variation is typical of a conventional metal above \( T_c \), the observation of a sharp frequency shift emerging precisely with the development of superconductivity confirms a major prediction of the composite pairing theory. The \( T_1^{-1} \) results reveal the deviation from Fermi-liquid behavior below \( T \sim 4T_c \) and approaching the SC transition, characterized by the appearance of strong in-plane spin fluctuations. Furthermore, below \( T_c \), the data are accurately reproduced by a line-nodal order parameter calculation with strong coupling. Thus, we conclude that PuCoIn\(_5\) is an
anisotropic $d$-wave superconductor, likely near a magnetic instability, where spin fluctuations appear to be playing a central role in promoting superconductivity.

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