NMR evidence for f-electron excitations in the multipolar ground state of NpO$_2$

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An analysis is presented of the ^{237}Np-^{17}O cross-relaxation (CR) process at temperatures below $T = 10$ K that was reported [Tokunaga *et al.*, Phys. Rev. B **74**, 064421 (2006)] in ^{17}O NMR studies of NpO$_2$. The CR evidently results from ^{237}Np spin fluctuations driven by indirect spin-spin interactions analogous to the Suhl-Nakamura [Nakamura, Prog. Theor. Phys. **20**, 542 (1958)] effect in conventional magnets. Here, however, there is a body of evidence that the interacting Np^{4+} ions are in a magnetic, rank-5 dotriakontadipolar ground state [Santini *et al.*, Phys. Rev. Lett. **97**, 207203 (2006); Magnani *et al.*, Phys. Rev. B **78**, 104425 (2008)]. Owing to the observed exponential form of the fluctuation spectrum, it is possible to evaluate explicitly the CR bandwidth in terms of any specified ^{237}Np-^{237}Np (spin-spin) coupling Hamiltonian. We model the latter as an enhanced dipolar coupling. The enhancement is concluded to be compound, with the "enlarged nuclear moment" mechanism identified in the paramagnetic state [Tokunaga *et al.*, Phys. Rev. B **74**, 064421 (2006)] responsible for a factor $\sim$22, while the indirect ^{237}Np-^{237}Np coupling effect is found to be $\sim$240 times the amplitude of the classical dipolar interaction. We suggest that these results are consistent with the identification of a magnetic rank 5 multipolar ground state [Magnani *et al.*, Phys. Rev. B **78**, 104425 (2008)] for NpO$_2$.

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I. INTRODUCTION

After many years of uncertainty, combined data from resonant x-ray scattering [1], muon spin rotation [2], and ^{17}O NMR studies [3,4] led to identification of the ground state of the $5f$ electrons in NpO$_2$ as one of combined octupolar and quadrupolar character. Further examination of these data led to a further suggestion that the magnetic octupolar character was actually a magnetic, rank-5 triakontadipolar orbital [5,6]. In view of the residual uncertainty, here we shall refer to the ground state as multipolar, having definite magnetic character [7]. While multipolar states are difficult to probe directly, characteristic ^{17}O NMR shift effects in NpO$_2$ based on induced octupolar moments [8] have been identified and measured [4].

Further interest in NMR studies of NpO$_2$ was sparked by the identification of a substantial cross relaxation (CR) process between the 100% abundant ^{237}Np nuclei and the observed ^{17}O NMR [9]. In the CR processes studied, ^{237}Np T_1 fluctuations in the paramagnetic state were found to drive a greatly enhanced coupling between the ^{237}Np (I) and the ^{17}O (S) nuclear spins to give a field- and temperature-dependent CR process. The evident indirect I-S coupling was modeled in a straightforward way to be proportional to the f-electron susceptibility and the ^{237}Np hyperfine (HF) interaction. Consequently, the CR process in NpO$_2$ was found to scale quite accurately with the square of the bulk susceptibility [9].

For NpO$_2$ a T-independent (^{17}O) CR process was also noted to occur at the low end of the experimental temperature scale at $T \sim 6$ K [9]. There, of course, the relaxation effect from fluctuating f-electron dipoles above $T \sim 30$ K will have

vanished with the collapse of the dipoles themselves, amid multipolar ordering [1]. Thus, prospects for the CR process at low T were uncertain. Nonetheless, magnetic fluctuations with a spectral width of a few MHz and with a fluctuation density asymptotically independent of T were clearly present at the ^{17}O sites. In view of the puzzling character of these low-T results, however, the problem was set aside at the time.

On re-examination, it was noted recently that the functional form of the low-T fluctuation spectrum is exponential, which is highly unusual. It is reminiscent of a rotating frame double resonance experiment from many years ago, in which an exponential dipolar fluctuation spectrum came to light [10]. Such a circumstance allowed a detailed analysis of the fluctuations to be performed, yielding quantitative agreement with the experimental results. Here we have employed the same procedure, yielding interesting, if not fully quantitative, results. Some uncertainty stems from a lack of detailed knowledge of the *precise form of the spin-spin coupling* in the multipolar ground state of NpO$_2$. Nonetheless, adopting here an enhanced dipolar form for the ^{237}Np nuclear spin-spin couplings, we are able to draw important conclusions about the state of spin-spin interactions and, thus, of magnetic multipolar excitations in the ground state of NpO$_2$.

This paper is organized as follows. In Sec. II A we review the analysis of CR results for ^{17}O in the paramagnetic state of NpO$_2$. In the process of describing the features of the paramagnetic state CR data, we will establish the basic procedures of our analysis of the CR effect and introduce two important changes in the parametrization. First, we correct an inappropriate choice made for the dipolar Hamiltonian term that couples the ^{17}O (S) and ^{237}Np (I) nuclear spins [9]. Second, we suggest a different choice for the magnitude of the ^{237}Np nuclear moment. There is apparently no directly measured value for this moment. There is an indirectly

inferred value that is listed in more than one compilation of the properties of atomic nuclei [11]. We adopt this value for the current work, noting that some conclusions may depend on the value of the ^{237}Np moment. We also emphasize that an indirect I-S coupling is critical to the successful observation of the CR effect in NpO$_2$ [9], as well as in NpPd$_5$Al$_2$, a heavy fermion superconductor for which CR effects have also been investigated [12].

In Sec. II B we return to the low-T results for NpO$_2$ to discuss the CR process and the remarkably strong fluctuations exhibited by the ^{237}Np spins in the multipolar ground state of this compound. There, the central feature is analysis of the broad, exponential fluctuation spectrum exhibited by these low-T results.

In Sec. III we summarize our results and briefly discuss the striking contrast between like spin and unlike—spin indirect couplings and the implications for the magnetic properties of the multipolar ground state of NpO$_2$.

II. COMPARATIVE ANALYSIS OF CROSS RELAXATION EFFECTS IN NpO$_2$

A. Review of the paramagnetic state CR effect

In the original report of CR effects in f-electron compounds [9], these effects were characterized by field-dependent ^{17}O T_1 data in the paramagnetic state of NpO$_2$. These data appear in the right-hand portion of Fig. 1. When the CR data were analyzed, an enhanced value emerged for the I-S unlike spin coupling. This was easily traced to the very large values for the HF coupling and susceptibility of the Np^{4+} ions, so that the ^{237}Np nuclear moment induces an even larger moment on the ion itself [9]. By this mechanism, dipolar interactions with neighboring nuclear spins are correspondingly enhanced.

Here we give a brief review of the CR effect analysis [9], based on the data shown in Fig. 1. There, relaxation rates are plotted vs temperature T, measured at the series shown of ^{17}O NMR frequencies $f_{17} = \omega_0/2\pi = \gamma_S H_0/2\pi$, corresponding to the applied fields H_0 given in parentheses. We also wish to highlight two small changes that we suggest would be appropriate. These are, first, that the unlike-spin coupling that drives the CR should be the $I_{zi}S_\pm$ dipolar term [13]. (For simplicity we assume just a single S spin, noting that the density matrix treatment of relaxation implies an ensemble.) The previous analyses were done with the $I_{zi}S_\pm$ term, but the strength of the I-S spin-spin coupling was incorrectly evaluated using the unlike-spin term of the second moment of the ^{17}O NMR line. The resulting differences in numerical values are minor.

The second change is to revise the value adopted for the ^{237}Np nuclear moment. In contrast to our earlier choice of γ_{237}(old)$/2\pi = 478$ Hz/Oe, we find that several compilations [11] quote $\mu_{237} = 3.14\mu_N$, from which we find $\gamma_{237}/2\pi = 957.4$ Hz/Oe, which we now adopt. This choice will reduce the magnitude of the paramagnetic I-S coupling enhancement factor ξ_{SP} by a factor ~ 2. ξ_{SP} will nonetheless be large compared with unity.

For the updated analysis in this paper we employ for the CR process a well-known result from the density-matrix formulation of nuclear relaxation processes [10,13], namely
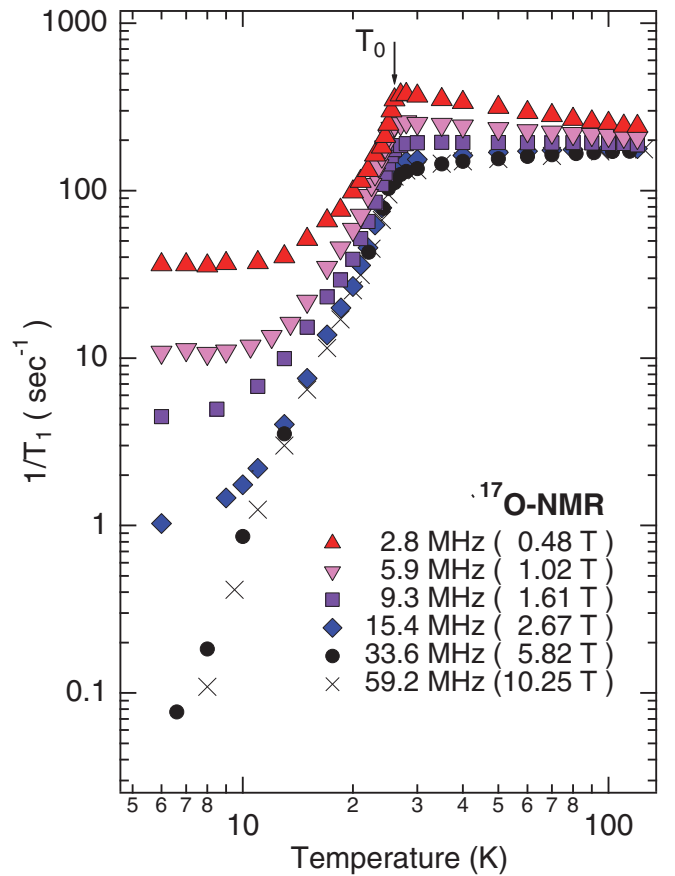

FIG. 1. Log-log plot of $1/T_1$ vs T for ^{17}O nuclear spins in NpO$_2$, emphasizing the low-temperature region of the available data. NMR frequencies $\omega_0/2\pi$ along with corresponding applied field values (ω_0/γ_S) are given in the key. While the low-T behavior of T_1 at the four lowest frequencies is evidently flat, the two highest frequency curves have clearly not yet reached their asymptotic limit. The CR effects seen above $T_0 \simeq 25$ K were analyzed in Ref. [9].

(see the Appendix)

$$\frac{1}{\tau_{CR}} = \int_0^\infty d\tau \, \cos(\omega_0\tau) \, Tr\left[\sum_i B_i^2 I_{zi} I_{zi}(\tau)\right], \quad (1)$$

where $B_i = 3\xi_{SP}\gamma_I\gamma_S\hbar \sin(\theta_i)\cos(\theta_i)/r_i^3$. Here, $\gamma_I/2\pi = 957.4$ Hz/Oe, and $\gamma_S/2\pi = 577.2$ Hz/Oe. Further, r_i is the distance from spin S to spin $\vec{I}_i$, and θ_i is the angle between the radius vector $\vec{r}_i$ and the applied field $\vec{H}_0$. The parameter ξ_{SP} represents the enhancement of the I-S coupling described above in the paramagnetic state. The quantity $a_I(\tau) = Tr[\sum_i I_{zi} I_{zi}(\tau)]/Tr[\sum_i I_{zi}^2]$ is the autocorrelation function of the fluctuating $\vec{I}_i$ spins. When such fluctuations are dominated by a T_1 process, we have $a_I(\tau) = \exp(-\tau/T_1)$, satisfying the condition $a_I(0) = 1$. With this relation, (1) becomes

$$\frac{1}{\tau_{CR}} = [I(I+1)/3]\left\langle\sum_i B_i^2\right\rangle T_{1I}/\left(1 + \omega_0^2 T_{1I}^2\right). \quad (2)$$

The brackets $\langle \rangle$ around the sum on B_i^2 indicate an angular average, which is necessary, because the sample is a powder. These manipulations are carried out in the Appendix, giving

for the final result

$$\frac{1}{\tau_{CR}} = 4.65 \times 10^7 \xi_{SP}^2 T_{1I}/(1 + \omega_0^2 T_{1I}^2), \quad (3)$$

where the numerical prefactor is the value of $[I(I + 1)/3]\langle\sum_i B_i^2\rangle$ calculated using the classical dipolar expression given above with ξ_{SP} set to unity. Equation (3) has been fitted to data under a series of fields at temperatures ranging from 30 K up to 300 K, obtaining corresponding values for T_{1I} and for the prefactor, and thus for ξ_{SP}. The value $T_{1I} \simeq 40$ ns was found to be essentially constant across the paramagnetic temperature range. Values of ξ_{SP} range from 4.6 at 300 K up to 14.7 at $T = 30$ K. Thus, enhancement of $1/\tau_{CR}$ ranges from a factor ~20 up to ~200 over the temperature range measured. Similar results were reported in Ref. [9].

B. Analysis of the low-T CR effect in NpO$_2$

Prominently featured in Fig. 1 are the low-temperature (low-T) ^{17}O T_1 data, which were tentatively identified as a CR effect [9], though not analyzed in detail. Here, it is our purpose to analyze these presumably asymptotic low-T CR data in comparison with the behavior in the paramagnetic state. We suggest that the low-T behavior in Fig. 1 is evidently a CR effect, rather than just a T_1 process, for several reasons. First, the relaxation rates are asymptotically independent of temperature, making it very unlikely that the fluctuation spectrum involves electron-spin dynamics. Rather, these fluctuations are driven by enhanced nuclear spin-spin interactions, for which the high-temperature approximation would be very good. Second, the CR decay rate becomes progressively higher as the NMR frequency is lowered, as also seen in the paramagnetic state. This is because the fluctuations are relatively slow on the scale of typical NMR frequencies. As we shall see, however, they are remarkably fast on the scale of typical nuclear spin-spin coupling energies. Thus, the frequency dependence of τ_{CR} indicates a spectral width of the order of a few MHz. This is much larger than nuclear dipole-dipole interactions. We suggest that such a width reflects not only the enlarged moment mechanism identified in the paramagnetic state, but also the presence of a surprisingly large indirect spin-spin coupling among the ^{237}Np spins in the multipolar ground state of this compound.

To analyze the low-T spectrum of relaxation rates in Fig. 1, it is useful to plot them semilogarithmically as in Fig. 2. There we see that the spectrum, quite remarkably, has exponential form. This effect is reminiscent of a dipolar fluctuation spectrum observed in a rotating-frame double resonance experiment performed many years ago on CaF$_2$ [10]. There, the exponential form of the spectrum led to a quantitative analysis of the data in terms of classical dipolar couplings. Here we follow a similar path of reasoning, finding, however, a marked difference because of the compound enhancement process of ^{237}Np spin-spin couplings mentioned above.

The fluctuation spectrum in Fig. 2 is fitted with the simple form (solid line)

$$\frac{1}{\tau_{CR}} = \frac{1}{\tau_{CR}(0)} \exp(-\omega_0 \tau_c), \quad (4)$$

where ω_0 is the NMR frequency of the (^{17}O) S spins and τ_c is the correlation time of the fluctuating (^{237}Np) I spins. The
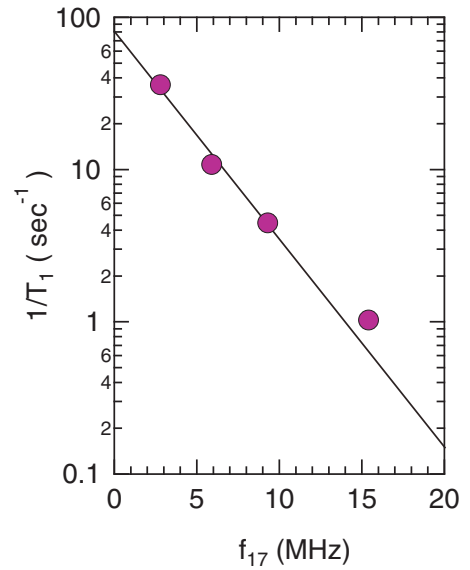

FIG. 2. Semilog plot of $1/T_1$ vs $f_{17} = \omega_0/2\pi$ for ^{17}O nuclear spins in NpO$_2$, The values of $1/T_1$ plotted are the apparently T-independent asymptotes taken from the four lowest-frequency data plots in Fig. 1. (Note that the point at 15 MHz has not quite reached its asymptotic low-T value.) The solid line passed is a fit showing the essentially exponential character of the fluctuation spectrum of the ^{237}Np nuclei. The slope and intercept of the solid line as a representation of Eq. (4) are given in the text. Note that T_1 data here are interpreted as a CR process in the text.

straight-line fit to the data shown in Fig. 2 yields the parameter values $\tau_{CR}(0)^{-1} \approx 80$ s^{-1} and $\tau_c \approx 4.98 \times 10^{-8}$ s. Again, we note that τ_c and the spectral width reflect much larger energies than are typically associated with nuclear spin-spin couplings. It is something of a challenge, then, to justify this line of interpretation.

The importance of the result in Eq. (4) is that, given the form and parameters of the I-I coupling Hamiltonian $\mathcal{H}_{II}$, it enables the evaluation of τ_c in terms of those quantities. We again use Eq. (1) as the basis for our analysis, and again, the coupling between the I_{zi} nuclei and $S_\pm$ is taken to be the dipolar interaction enhanced by a factor ξ_{SM}, where the subscript M denotes the multipolar ordered state. As noted above, the internuclear coupling among the I_{zi} is greatly enlarged on the scale of the classical dipolar interaction. Further, we don't know the detailed form of $\mathcal{H}_{II}$. It is of interest, however, to compare its magnitude in the multipolar state with that of the usual dipolar term. Thus, we represent it here as the $I_{zi}I_{zj}$ dipolar Hamiltonian term [13] multiplied by an enhancement factor $\eta_I \xi_{IM}^2$. In this factor, the factor ξ_{IM} occurs squared, because the interaction is the product of two enlarged moments. As noted earlier, the factor η_I represents the enhanced amplitude of spin-spin couplings via a putative indirect coupling process that is the analog of the Suhl-Nakamura effect [14] in ordinary magnets.

Using Eq. (1) for the low-T case, we arrive at the form

$$\frac{1}{\tau_{CR}} = \left\langle \sum_i B_i^2 \right\rangle \int_0^\infty d\tau \, \cos(\omega_0 \tau) \langle \text{Tr}_I[I_{zi} I_{zi}(\tau)]\rangle, \quad (5)$$

where $I_{zi}(\tau) = T I_{zi} T^\dagger$, with $T = \exp[i\mathcal{H}_{II}\tau]$ and $\mathcal{H}_{II} = (\eta_I \xi_{IM}^2/2) \sum_{i \neq j} A_{ij}[I_{zi}I_{zj} - I_{+i}I_{-j}/4 - I_{-i}I_{+j}/4]$. In Eq. (5) the prefactor $\sum_i B_i^2$ is independent of τ and is summed separately, since the quantity $\mathrm{Tr}_I[I_{zi}I_{zi}(\tau)]$ is independent of the index i. The brackets $\langle\rangle$ indicate averaging over the unit sphere, which is necessary here, because the sample is a powder. These averages for $\sum_i B_i^2$ and of the autocorrelation function are performed separately as a convenience. Furthermore, the autocorrelation function average is replaced by simply averaging $1/\tau_c^2$ over the unit sphere. These steps are admittedly approximate, but we note that the Hamiltonian $\mathcal{H}_{II}$ in the autocorrelation function $\sum_i \mathrm{Tr}_I[I_{zi}I_{zi}(\tau)]$ is dominated by nearest-neighbor (nn) shells of 12 sites in the fcc Np lattice. These 12 nn sites provide a rough spherical average that is built into the CaF$_2$ structure. This procedure, along with our adoption of the dipolar form for B_i offers, we suggest, a reasonable estimate of the enhanced fluctuation rate in the multipolar ground state of NpO$_2$.

To continue the development of Eq. (5), the quantity $\mathrm{Tr}_I[I_{zi}I_{zi}(\tau)]$ is expected to have the form $\mathrm{Tr}[I_{zi}^2] a_I(\tau)$, where $a_I(\tau) = (1 + \tau^2/\tau_c^2)^{-1}$, in order for $\int d\tau$ in Eq. (5) to yield the exponential form in Eq. (4). Expanding $a_I(\tau)$ to $\mathcal{O}(\tau^2)$ and equating the τ^2 term to the similar term in the expansion of $\mathrm{Tr}_I[I_{zi}I_{zi}(\tau)]$ then yields

$$\frac{1}{\tau_c^2} = \frac{1}{2} \frac{\mathrm{Tr}\{[I_{zi}, \mathcal{H}_{II}]^2\}}{\mathrm{Tr}[I_{zi}^2]}. \tag{6}$$

Thus, with an exponential spectrum, we are able to extract the width of the spectrum explicitly in terms of spin-spin interaction parameters. As noted above, $1/\tau_c^2$ is to be averaged over the unit sphere.

The next steps are worked out in the Appendix, arriving at the expression

$$\frac{1}{\tau_{\mathrm{CR}}} = 7.30 \times 10^7 \xi_{SM}^2 \tau_c \exp(-\omega_0 \tau_c), \tag{7}$$

where $1/\tau_c = 3.803 \times 10^3 \eta_I \xi_{IM}^2$. Again, the numerical coefficient of the enhancement factor(s) is the classical dipolar value of $1/\tau_c$ for NpO$_2$.

To obtain estimates of the enhancement effects, we now employ the experimental parameter values given with Eq. (4). Equation (7) and the companion expression for τ_c then yield $\eta_I \xi_{IM}^2 = 5.280 \times 10^3$ from $\tau_c = 4.98 \times 10^{-8}$ s, and $\xi_S = 4.71$ from $1/\tau_{\mathrm{CR}}(0) = 80$ s$^{-1} = 7.30 \times 10^7 \xi_{IM}^2 \tau_c$. We have no independent estimate of ξ_{IM}, but we suggest that this parameter will not vary significantly among ligands. Thus, we adopt $\xi_{IM} \sim \xi_{SM} = 4.71$ for the present discussion. The foregoing values then lead to $\eta_I \sim 240$. Thus, the indirect spin coupling between the ^{237}Np nuclear spins in the multipolar ground state is enhanced by more than two orders of magnitude over the classical dipolar coupling. The significance of this finding is considered in Sec. III.

III. DISCUSSION

The low-T CR effect numbers are seen to form a stark contrast with those established earlier for the paramagnetic state [9] and revised modestly here. The analysis reveals a hugely enhanced indirect spin-spin coupling in the multipolar ground state. Such a noteworthy spin-spin coupling is no doubt a consequence of ground-state indirect interactions, presumably analogous to the Suhl-Nakamura mechanism in conventional magnets [14]. Moreover, the total spin-spin coupling is further enhanced by more than another order of magnitude by the simple "enlarged-moment" mechanism that was originally identified in earlier studies of the paramagnetic state [9]. Combined, the two account for a total that seems almost physically unrealistic for nuclear spins.

We are not aware of any existing analysis of this problem with which the latter estimate of indirect spin-spin coupling can be compared. There is ample evidence from μSR [2] and other experimental probes [7] that the multipolar ground state in NpO$_2$ is magnetic, i.e., time-reversal symmetry is broken. One might compare the indirect spin-spin coupling among ^{237}Np nuclei here with examples of the Suhl-Nakamura interaction made for magnetic systems containing d-band ions. The estimate made by Suhl for ^{55}Mn in an antiferromagnetic setting [14] gives roughly an order of magnitude linewidth enhancement over the classical dipolar case. Given the relatively much larger hyperfine couplings exhibited by f-electron orbitals, it is not surprising, then, that we would find more than another order of magnitude enhancement beyond d-electron Suhl-Nakamura for ^{237}Np in NpO$_2$. The latter is an apt comparison given that there is, up to now, no direct indication of magnetic excitations in multipolar states on which to base indirect nuclear spin-spin couplings. Here, we are inferring their existence indirectly from NMR cross-relaxation data.

But it is interesting to consider what physical basis there might be for enhanced indirect couplings in the putative magnetic triakontadipolar ground state [5,6]. Aspects of the latter picture have been confirmed in a powder sample INS study of NpO$_2$ [6]. There would definitely need to be some kind of spin-wave-like magnetic excitations to be virtually emitted and reabsorbed in a second-order perturbation process. A further parallel suggested by the Suhl-Nakamura model is that it would not significantly contribute to the $I_{zi}S_\pm$ term in the dipolar coupling Hamiltonian. Thus, the latter term is present in the data, but only at the minimal level seen in the paramagnetic state at the highest temperatures. The I-I terms in the indirect couplings are vastly greater.

Finally, it is interesting to note that the magnetic triakontadipolar (rank 5) ordering suggested to be present in NpO$_2$ can also occur in an electric form. Such an electric rank-5 order has recently been indicated to be the "hidden" order in the ground state of URu$_2$Si$_2$. This recommendation was made in part on the basis of an electronic state symmetry analysis derived from NMR T_2 studies [15]. Up to now the electrical, rank-5 order in URu$_2$Si$_2$ has no identifiable effect on the ^{29}Si NMR properties.

APPENDIX

Here we derive formulas for the cross relaxation rate $1/\tau_{CR}$ for the z-axis polarization of the S spins (^{17}O) in response to z-axis fluctuations of the I spins (^{237}Np). The perturbation operators for this process are the $I_{zi}S_{\pm}$ terms, where we focus on a single S spin and its I-spin neighbors. For the enhanced dipolar case discussed in the text, we have [13]

$$\mathcal{H}_{IS} = -(3/2)\xi_S\gamma_S\gamma_I\hbar\sum_i I_{zi}\cos\theta_i\sin\theta_i[S_-\exp(-i\phi_i)$$

$$+ S_+\exp(i\phi_i)]/r_i^3, \quad (A1)$$

where i is summed on the I-spin neighbors of S, $\vec{r}_i$ is the $\vec{S} \rightarrow \vec{I}_i$ radius vector, and θ_i, ϕ_i are the directional angles of $\vec{r}_i$ relative to the applied field $\vec{H}_0$. The enhancement factor ξ_S in Eq. (A1) will be ξ_{SP} or ξ_{SM} for the paramagnetic or multipolar state cases, respectively.

$\mathcal{H}_{IS}$ as given in Eq. (A1) is the perturbation term in the well-known density matrix-derived relaxation equation (Ref. [13], Chap. VIII), which here describes the CR process, namely [10]

$$\frac{1}{\tau_{CR}} = \frac{1}{\text{Tr}\{S_z^2\}}\int_0^\infty d\tau\,\text{Tr}\{S_z[\mathcal{H}_{IS}(0),[\mathcal{H}_{IS}(\tau),S_z]]\}, \quad (A2)$$

where in $\mathcal{H}_{IS}(\tau)$, $I_{zi}(\tau)$ reflects its time dependence owing either to the I-spin T_1 process or the I-spin spin-spin fluctuation process, whichever is dominant. $S_\pm(\tau)$ will reflect the precession of the S nuclear spins in the applied field H_0 ($\omega_0 = \gamma_S H_0$). For the paramagnetic state of NpO$_2$ we take [9] $\text{Tr}[I_{zi}I_{zi}(\tau)] = \text{Tr}[I_{zi}^2]\exp(-\tau/T_1)$, while for the low-temperature ordered state we employ a model introduced with Eq. (5), which is the classical dipolar form for $\mathcal{H}_{II}$ multiplied by the compound enhancement factor $\eta_I\xi_{IM}^2$. Again, we note that η_I is the enhancement of spin-spin couplings between I spins that represents the presence of an indirect interaction in the multipolar ground state driven by elementary magnetic excitations of unknown character. The experimental estimation of η_I is one of the main objectives of this study. With this model formalism we can then write for the low—T case

$$\text{Tr}_I[I_{zi}I_{zi}(\tau)] = \text{Tr}_I[I_{zi}\exp(-i\tau\mathcal{H}_{II})I_{zi}\exp(i\tau\mathcal{H}_{II})], \quad (A3)$$

where our model expression for $\mathcal{H}_{II}$ is written [13]

$$\mathcal{H}_{II} = \frac{1}{2}\sum_{i\neq j}A_{ij}\left(I_{zi}I_{zj} - \frac{1}{4}(I_{+i}I_{-j} + I_{-i}I_{+j})\right), \quad (A4)$$

with $A_{ij} = \eta_I\xi_{IM}^2\gamma_I^2\hbar(1 - 3\cos^2\theta_{ij})/r_{ij}^3$. Here A_{ij} is simply the classical dipolar expression times the enhancement factor $\eta_I\xi_{IM}^2$.

Considering first the paramagnetic state [9] and performing the double commutator in (A2), we arrive at

$$\frac{1}{\tau_{CR}} = \langle\omega_{IS}^2\rangle\int_0^\infty d\tau\,\cos(\omega_0\tau)\text{Tr}_I[I_{zi}(0)I_{zi}(\tau)]/\text{Tr}_I[I_{zi}^2], \quad (A5)$$

where $\langle\omega_{IS}^2\rangle = 3I(I+1)\xi_{SP}^2\gamma_I^2\gamma_S^2\hbar^2\sum_i\cos^2\theta_i\sin^2\theta_i/r_i^6$, and where the ratio of $\text{Tr}[\ ]$ quantities is the autocorrelation function of I_{zi}, $a_I(\tau) = \exp(-\tau/T_{1I})$, independent of i. The

formal result in this case is then

$$\frac{1}{\tau_{CR}} = \frac{\langle\omega_{IS}^2\rangle T_{1I}}{(1 + \omega_0^2 T_{1I}^2)}. \quad (A6)$$

To evaluate $1/\tau_{CR}$ for the paramagnetic phase of NpO$_2$ we perform a powder average of $\langle\omega_{IS}^2\rangle$ using $\gamma_S = 2\pi\times 577.2$ Hz/Oe, $\gamma_I = 2\pi\times 957.4$ Hz/Oe, powder average of $\sin^2\theta_i\cos^2\theta_i = 2/15$, and $\sum_i r_i^{-6} = 644a^{-6}$, with $a = 5.43\times 10^{-8}$ cm. With these numbers we find

$$\frac{1}{\tau_{CR}} = 4.65\times 10^7\xi_{SP}^2 T_{1I}/(1 + \omega_0^2 T_{1I}^2)\,s^{-1}. \quad (A7)$$

The latter result is quoted in the text as Eq. (3), and we note that if we set $\xi_{SP} = 1$, it would represent a powder average for the case of classical dipolar I-S coupling.

For the low-T case, it seems clear that the very short T_{1I} process from the paramagnetic state is quenched out in the multipolar ground state, and the I-spin fluctuations are now dominated by spin-spin couplings, which we model with enhanced dipolar interactions. The enhancement factor $\eta_I\xi_{IM}^2$ for the multipolar state spin-spin coupling term $\mathcal{H}_{II}$ was introduced in the main text with Eq. (5) and is stated again with Eq. (A4) above. The I-S enhancement parameter ξ_{SM}^2 was introduced above following Eq. (A1).

Thus, evaluating the double commutator in Eq. (A2), the $\text{Tr}[S_z^2]$ cancels out and we find

$$\frac{1}{\tau_{CR}} = \langle\omega_{IS}^2\rangle\int_0^\infty d\tau\,\cos(\omega_0\tau)\text{Tr}_I[I_{zi}I_{zi}(\tau)]/\text{Tr}[I_{zi}^2], \quad (A8)$$

where $\langle\omega_{IS}^2\rangle$ is given with Eq. (A5). Here, with $\xi_{SP}\rightarrow\xi_{SM}$, the correlation function $\text{Tr}_I[I_{zi}I_{zi}(\tau)]$ is given by Eq. (A3). For the low-T case, the form of the autocorrelation function $a_I(\tau)$ has to be a Lorentzian in order for $1/\tau_{CR}$ to vary exponentially with ω_0. Thus, we require $a_I(\tau) = 1/(1 + \tau^2/\tau_c^2)$. Performing the integral in Eq. (A8) yields the same angle-averaged prefactor as in Eq. (3), but here multiplied by $\pi/2$. The result for the low-T case is then written

$$\frac{1}{\tau_{CR}} = \langle\omega_{IS}^2\rangle(\pi/2)\tau_c\exp(-\omega_0\tau_c). \quad (A9)$$

Replacing the prefactor with its powder average as in Eq. (A7) then leads to Eq. (7), with τ_c to be determined.

It remains to obtain an expression for τ_c. As explained in the main text, $1/\tau_c^2$ may evaluated with Eq. (6). Using the latter equation with $\mathcal{H}_{II}$ as given in Eq. (A4), we find

$$1/\tau_c^2 = (1/3)I(I+1)\eta_I^2\xi_{IM}^4\gamma_I^4\hbar^2\sum_i(1 - 3\cos^2\theta_i)^2/r_i^6, \quad (A10)$$

where the sum is over the fcc lattice of Np^{4+} neighbor sites surrounding any Np^{4+} site. For the CR data in Fig. 2 the experimental sample is a powder, so we take a powder average of the angular factor $\langle(1 - 3\cos^2\theta_i)^2\rangle = 4/5$ and evaluate the Np-Np lattice sum in (A10) as $\sum_i r_i^{-6} = 109.1/a^6$. Using the numbers given with Eq. (A6), we find $1/\tau_c = 3.803\times 10^3\eta_I\xi_{IM}^2$. The numerical coefficient of the enhancement factor(s) is the classical dipolar value of $1/\tau_c$ for ^{237}Np in NpO$_2$. This result is included along with the discussion of Eq. (7).

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