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^{17}O NMR spin–lattice relaxation in NpO_2: Field-dependent cross-relaxation process driven by ^{237}Np spins

Y. Tokunaga[a,*], R.E. Walstedt[a], Y. Homma[b], D. Aoki[b], S. Kambe[a], H. Sakai[a], T. Fujimoto[a], S. Ikeda[a], E. Yamamoto[a], A. Nakamura[a], Y. Shiokawa[b], H. Yasuoka[a]

[a]*ASRC, Japan Atomic Energy Agency, Tokai, Ibaraki 319 1195, Japan*
[b]*IMR Tohoku University, Narita Oarai Higashiibaraki, Ibaraki 311 1313, Japan*

Abstract

We have performed ^{17}O NMR spin–lattice relaxation measurements with conventional NMR techniques on ^{17}O in NpO_2. The results have been found to exhibit a field-dependent cross-relaxation effect from ^{237}Np in addition to the field-independent exchange-fluctuation background rate which dominates at high fields. Analysis of the cross-relaxation process reveals a temperature-independent relaxation rate as well as a greatly enhanced unlike spin–spin coupling between the ^{237}Np spins and their ^{17}O nearest neighbors. We discuss the possibility of observing the cross-relaxation effects in other actinide dioxides.

Keywords: A. Oxides; D. Nuclear magnetic resonance (NMR); D. Magnetic properties

NpO_2 was thought for many years to be an antiferromagnet like UO_2, owing to the similarity of their susceptibility and specific heat behaviors [1–3]. However, Np dipolar moments in the ordered state were found to be less than $0.01\mu_B/\mathrm{Np}$ below $T_0 = 26\,\mathrm{K}$ [4]. Recently, Santini and Amoretti proposed a spontaneous ordering of magnetic octupoles of Γ_2 symmetry carried by the Γ_8 quartet crystalline electric field (CEF) ground state of Np^{4+} ($5f^3$) [5]. Soon after that, resonant X-ray scattering (RXS) measurements [6] were reported, announcing the appearance of longitudinal triple-**q** Γ_5 antiferroquadrupolar (AFQ) ordering below T_0. Since the AFQ order alone cannot successfully explain the breaking of time reversal symmetry suggested by susceptibility [3] and μSR [7] measurements, however, the RXS results only partially invalidated the Santini–Amoretti picture, leading to a proposal of Γ_5 antiferro-octupolar (AFO) ordering as the *primary* order parameter, with the Γ_5 quadrupole order as a *secondary* order parameter. This longitudinal triple-**q** Γ_5 AFO ordering ground state has also been suggested by recent microscopic calculations based on the *j–j* coupling scheme [8–10].

In this paper, we first review our recent ^{17}O NMR study of nuclear spin–lattice relaxation rate ($1/T_{1\mathrm{O}}$) in NpO_2, in which a strong, field-dependent $1/T_{1\mathrm{O}}$ has been observed at low fields [11]. Analysis based on the unlike-spin coupling model leads to quantitative estimates of the ^{237}Np relaxation rate $1/T_{1\mathrm{Np}}$ and of anomalously enhanced values of the ^{237}Np-^{17}O nuclear spin–spin coupling. We also compare the results with our recent $1/T_{1\mathrm{O}}$ data obtained in PuO_2 and UO_2, and discuss the possibility of observing the cross-relaxation effects in these compounds.

All the ^{17}O NMR $T_{1\mathrm{O}}$ measurements reported here were performed on powder samples containing ^{17}O. The method of sample preparation is described in detail elsewhere [12]. $T_{1\mathrm{O}}$ values were measured by the saturation-recovery method using standard spin–echo techniques. Recovery of the nuclear magnetization from a saturation pulse was found in all cases to follow a single-exponential functional form. This behavior reflects the fact that the ^{17}O NMR lines are relatively narrow and that quadrupole splittings are small if not absent altogether. Exponential fits to such data serve to determine a unique value of $T_{1\mathrm{O}}$ at each temperature and field.

*Corresponding author. Tel.: +81 29 284 3525; fax: +81 29 282 5927.
E-mail address: tokunaga.yo@jaea.go.jp (Y. Tokunaga).

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Fig. 1 shows the temperature and field dependence of $1/T_{1O}$ of NpO_2 over temperatures ranging from 6 up to 250 K and fields from 0.5 up to 10 T. At higher field values above ~5 T, $1/T_{1O}$ show no field dependence and executes a flat temperature curve in the paramagnetic state, which drops just slightly as T approaches T_0. This field-independent rate $1/T_{1O}^{5f}$, which is shown by the dotted line in Fig. 1, is believed to be the usual relaxation process generated by fluctuating Np-5f moments in the paramagnetic state. On the other hand, at lower field values below ~5 T, $1/T_{1O}$ show a peculiar temperature and field dependence, where the relaxation rate intensifies at low temperatures and at low field. We designate this increase of $1/T_{1O}$ as $1/T_{1O}^{cr}$, namely, $1/T_{1O} = 1/T_{1O}^{5f}(T) + 1/T_{1O}^{cr}(T,H)$ at low fields. Although the $1/T_{1O}$ behavior changes drastically with applied field, the $1/T_{1O}$ anomaly associated with the ordering transition always occurs at 26 K in NpO_2. This reveals that the transition temperature T_0 is not affected by applied magnetic fields up to 10 T.

The $1/T_{1O}^{cr}$ follows the behavior expected for Lorentzian fluctuation spectra of ^{237}Np nuclear spins. Here we give an analysis based on the basic unlike-spin coupling model discussed by Abragam [13,14]. If the unlike-spin term in the nuclear spin Hamiltonian is treated as a perturbation, the result is the cross-relaxation rate [13],

$$\frac{1}{T_{1O}^{cr}} = \frac{\langle\Delta\omega^2\rangle_\alpha T_{1Np}}{(1+(\omega_O-\omega_{Np})^2T_{1Np}^2)} + \frac{\langle\Delta\omega^2\rangle_\beta T_{1Np}}{(1+\omega_O^2T_{1Np}^2)}, \quad (1)$$

where the $\langle\Delta\omega^2\rangle_{\alpha,\beta}$ are the respective contributions to the ^{17}O second moment. The first α and second β terms are seen to correspond to fluctuation peaks which are centered at frequencies ω_{Np} and zero, respectively, and which are "sensed" by the ^{17}O nuclear spins at their resonance frequency $\omega_O = (1 + K_O)\gamma_O$H. For the α term, the ^{17}O resonance frequency is located at a distance ω_O - ω_{Np} from peak of the fluctuation spectrum, while for the β term centered at zero, the frequency interval is simply ω_O.

In general, both of the terms in Eq. (1) can be important. However, for NpO_2, we can expect $\omega_O \ll \omega_{Np}$, since the ^{237}Np shift is suggested to be very large, i.e., $\omega_{Np} = \gamma_{Np}(1+K_{Np})$ with $K_{Np} \simeq 4$ near $T = 30$ K from ^{237}Np Mössbauer results [4]. For that reason, one would expect the α term to have an increasingly large denominator value, and thus to make a very small contribution to the cross-relaxation process in Eq. (1).

On the other hand, the β term is independent of K_{Np}, giving by itself the simple expression $1/T_{1O}^{cr} \simeq \langle\Delta\omega^2\rangle_\beta T_{1Np}/(1+\omega_O^2T_{1Np}^2)$. To test this equation, we have plotted T_{1O}^{cr} against ω_O^2 in Fig. 2 for two different temperatures, where values of $1/T_{1O}^{cr}$ are obtained by assuming that $1/T_{1O}^{cr} = 1/T_1^O(H) - 1/T_1^O(10T)$. As expected from the equation, a linear relation between T_{1O}^{cr} and ω_O^2 has been obtained. Although only the data for 30 and 70 K are shown here, the linear relation is found over the entire range of experimental temperatures, and thus by fitting to the data, we have obtained the slope $(S = T_{1Np}/\langle\Delta\omega^2\rangle_\beta)$ and intercept $(I = (T_{1Np}\langle\Delta\omega^2\rangle_\beta)^{-1})$ at $\omega_O^2 = 0$ at each temperature, as shown in the inset to Fig. 2.

From the S and I, the $1/T_{1Np}$ and $\langle\Delta\omega^2\rangle_\beta$ are evaluated directly using simple formulas $1/T_{1Np} = (I/S)^{1/2}$ and $\langle\Delta\omega^2\rangle_\beta = (SI)^{-1/2}$, respectively. Fig. 3 shows the resulting T dependence of $1/T_{1Np}$ and $\langle\Delta\omega^2\rangle_\beta$ above T_0. In the paramagnetic state, $1/T_{1Np}$ ~$2.5\times10^7\,s^{-1}$ is seen to be very nearly independent of temperature, similar to what was found earlier for the intrinsic relaxation of the ^{17}O. This type of T_1 behavior can be understood in terms of the exchange-driven fluctuations of the Np 5f moments. Using

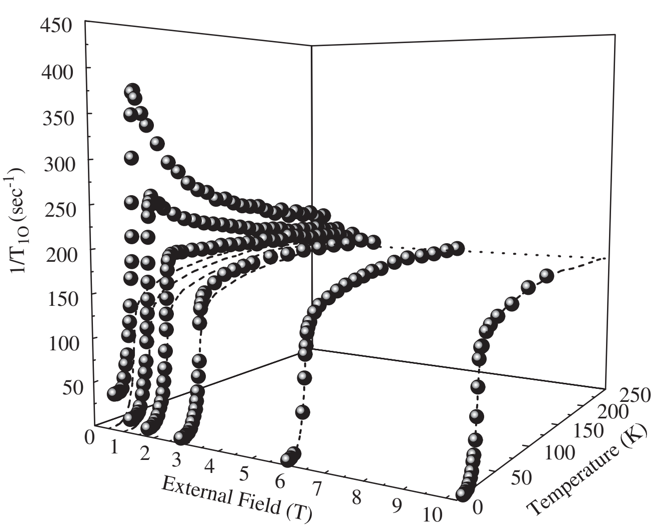

Fig. 1. The temperature and field dependence of $1/T_{1O}$ in NpO_2. The dotted lines indicates the $1/T_{1O}^{5f}$ (see text).

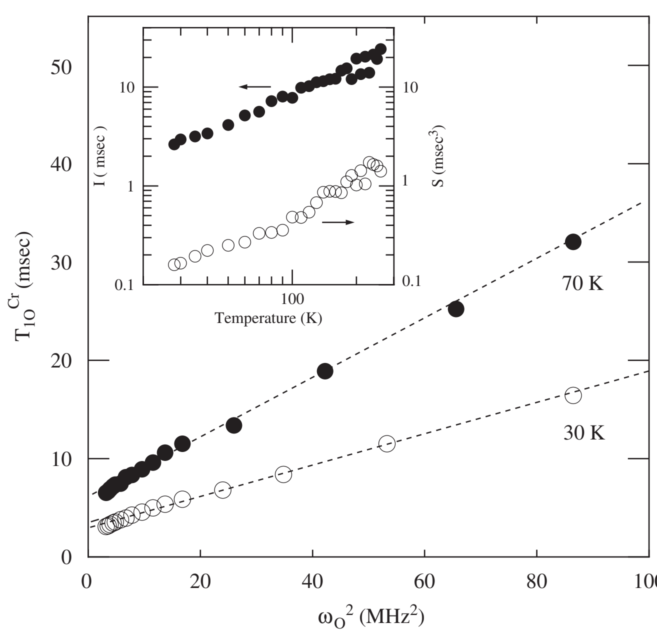

Fig. 2. A linear relation between T_{1O}^{cr} and ω_O^2 at 30 and 70 K, where ω_O is the ^{17}O NMR frequency. The inset shows the slope and intercept at $\omega_O^2 = 0$ obtained from the linear relation at each temperature (see text).