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NMR studies of actinide dioxides

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Abstract

^{17}O NMR measurements have been performed on a series of the actinide dioxides, UO_2, NpO_2 and PuO_2. Although the ^{17}O NMR spectra in these materials are similar at higher temperatures, the low-temperature spectra present are significantly different. In UO_2 we have observed a wide spectrum, forming a rectangular shape below $T_N = 30$ K. In NpO_2, on the other hand, the spectra broaden rather gradually and exhibit a two-peak structure below $T_0 = 26$ K. In PuO_2, neither spectrum broadening nor splitting has been observed. We show that these NMR spectra clearly indicate the different nature of the low-temperature magnetic ground states in these actinide compounds.

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Keywords: Actinide dioxides; UO_2; NpO_2; PuO_2; NMR

1. Introduction

Actinide dioxides (AnO_2: An = U, Np and Pu) represent possibly the most intensely studied series of any actinide compounds. However, their surprisingly varied physical properties continue to be of interest for both theory and experiment. It is known that a low-temperature phase transition occurs in UO_2 and NpO_2, while not in PuO_2. UO_2 exhibits an antiferromagnetic (AFM) ordering with an ordered moment of 1.74 μ_B/U [1–5]. On the other hand, NpO_2exhibits a rather mysterious ordering [6,7], where neither long-range magnetic dipole order [8,9] nor structural distortions [10] appear. This phase transition has therefore been suggested to be a new class of order associated with multipolar degrees of freedom [11–15].

Although these actinide dioxides are all cubic insulators (the CaF_2 structure) with rather well-localized 5f electrons, their crystal electric field (CEF) ground states of the 5f electrons are different: these are suggested to be the Γ_5 triplet for UO_2 (U^{4+}: $5f^2$), the Γ_8 quartet for NpO_2 (Np^{4+}: 5 f^3) and the Γ_1 singlet for PuO_2 (Pu^{4+}: $5f^4$), respectively. These CEF ground states are believed to responsible for their varied magnetic properties at low temperatures.

In this paper, we report ^{17}O NMR studies performed on the series of the actinide dioxides, UO_2, NpO_2 and PuO_2. We show that the microscopic NMR clearly indicates the different nature of their magnetic ground states at low temperatures. In the next section, we shall offer a brief review of our previous ^{17}O and ^{235}U NMR studies on UO_2. Then, in Section 3 we will describe the details of our ^{17}O NMR study on NpO_2, and discuss the mechanism of a multipolar-induced hyperfine interactions observed in its ordered state. Finally, in Section 4 we shall provide our very recent ^{17}O NMR results on PuO_2.

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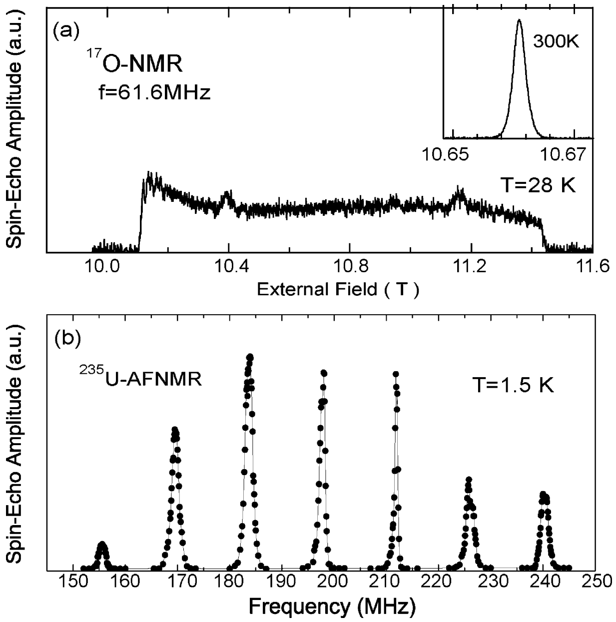

Fig. 1. UO$_2$: (a) The ^{17}O NMR spectra in the ordered state at $T = 28$ K and the paramagnetic state $T = 300$ K (inset). (b) The ^{235}U AFNMR spectrum at $T = 1.5$ K [5].

2. UO$_2$

UO$_2$ exhibits an AFM phase transition at $T_N = 30.8$ K. The magnetic structure is the *transverse* triple-q type, with an ordered moment of 1.74 μ_B/U atom [1–5]. The phase transition also introduces an internal distortion of the oxygen cube that surrounds the U cation [16,17]. Furthermore, very recent resonant X-ray scattering measurements have reported that a long-range antiferro-quadrupolar (AFQ) ordering coexists with the "primary" AFM ordering below T_N [18].

Fig. 1(a) shows the ^{17}O NMR spectra obtained using a powder sample of UO$_2$[5]. In the paramagnetic state (the inset), a narrow, symmetric spectrum has been observed. There is neither a quadrupole splitting nor an appreciable anisotropic NMR shift at the O sites, reflecting their cubic point symmetry above T_N [5]. In the AFM ordered state, on the other hand, the ^{17}O spectrum forms a rectangular shape with a full width of ∼1.3 T, which does not depend on the applied field. The rectangular shape is a typical powder pattern spectrum in the AFM ordered state for sites for which the internal field H_{int} is smaller than the applied external field H_{ext} [19]. From the linewidth in Fig. 1(a), we have obtained $H_{int} \sim 0.65$ T at the oxygen sites. This value is comparable to the dipolar field expected from the ordered moments of 1.74 μ_B at the U sites. We have observed that H_{int} appears discontinuously just below T_N, reflecting a 1st order-like phase transition.

In UO$_2$, we have also succeeded to detect the direct ^{235}U NMR signal in its AFM ordered state [5]. This was the first NMR observation for magnetic actinide ions. We have observed a quadrupole-split ^{235}U AFNMR spectrum over a range of ±40 MHz from a center frequency near 200 MHz, as shown in Fig. 1(b). The quadrupole-split spectrum indicates the presence of a quadrupole moment at the U sites due to the AFQ ordering and/or the distortion of the oxygen. At this frequency, with 93% enrichment of ^{235}U, there was ample signal strength for spin echoes to be observed up to 14 K or so, and for the spin-lattice relaxation time T_1 measurements to be performed as well. Above $T \simeq 14$ K, T_1 becomes unmanageably short.

3. NpO$_2$

The phase transition in NpO$_2$ was originally discovered more than half a century ago through specific heat and magnetic susceptibility measurements [6,7]. Similarities with UO$_2$suggested a phase transition of a magnetic nature in NpO$_2$. However, such a magnetic dipole ordering has been unambiguously ruled out by both neutron elastic scattering [8] and Mössbauer spectroscopy [9]. Instead, resonant X-ray scattering (RXS) measurements have been reported which suggest the occurrence of a longitudinal, triple-q, Γ_5 AFQ structure in the ordered state [12]. Moreover, the AFQ order has been proposed to be a *secondary* order parameter in a transition driven by *primary* Γ_5 antiferro-octupolar (AFO) order [12], since the AFQ order alone can not successfully explain the breaking of time reversal symmetry suggested by susceptibility [20] and μSR [21] measurements. The longitudinal triple-q Γ_5 AFO ordered ground state has also been corroborated by recent microscopic calculations based on the *j–j* coupling scheme [13,14]. Up to now, however, no direct evidence for spontaneous AFO order has been reported.

Recently, we have initiated the first NMR measurements on this system [15]. Fig. 2(a) shows the temperature dependence of

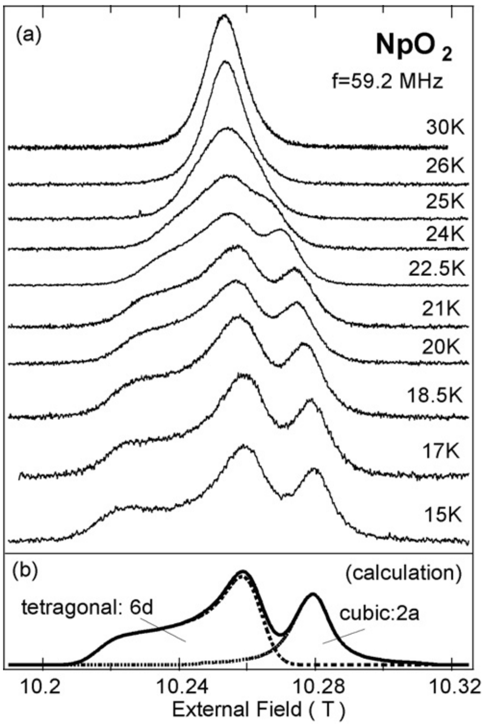

Fig. 2. (a) The temperature dependence of ^{17}O NMR spectra obtained at the resonant frequencies of 59.2 MHz for NpO$_2$. (b) An example of the spectrum analysis. The dotted lines show two theoretical powder-pattern for the 2a and the 6d oxygen sites, and the solid line shows their resulting envelopes.

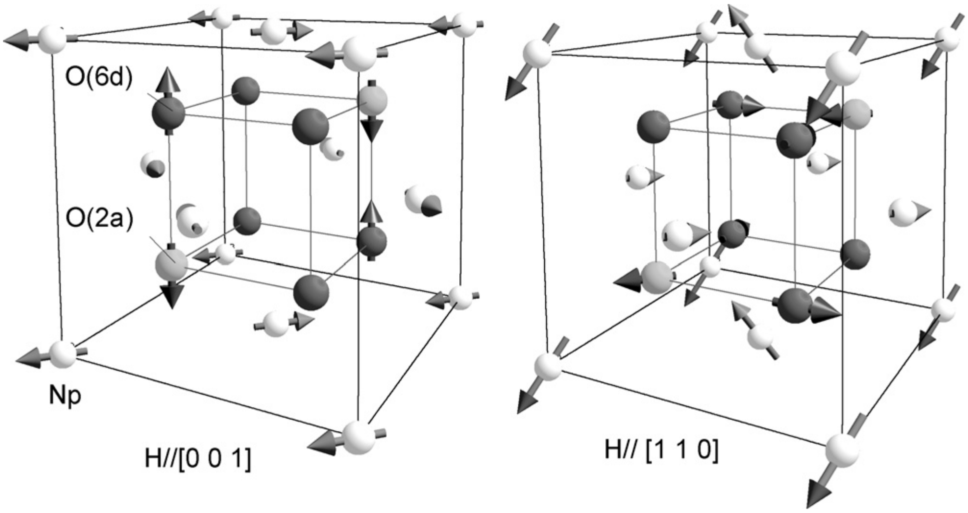

Fig. 3. The arrows on Np sites represent the field-induced AFM moments appearing in cooperation with the longitudinal triple- $\vec{q}$ AFQ order and the magnetic field applied parallel to the [0 0 1] and the [1 1 0] axes [22,23]. The arrows on O sites show the classical dipolar field produced by the field-induced AFM moments on the Np sites.

the ^{17}O NMR powder spectra. The spectra broaden in the ordered state, but do so rather gradually compared with those in UO_2. The linewidth was found to increase in proportion to the H_{ext}. However, the width is still less than 0.1 T even at $H_{\text{ext}} \sim 10$ T, as seen in Fig. 2(a). The spectral broadening rules out the appearance of large internal fields at O sites, which is apparently inadmissible within a simple AFM ordering picture. Furthermore, the spectra in the ordered state show a two-peak structure: one peak gradually broadens with decreasing temperature, while the other retains a narrow width while shifting to higher field. We found that the line shape is well reproduced by the sum of two powder patterns spectra characteristic of NMR in a powder sample, as shown in Fig. 2(b). The intensity ratio of 1:3 between these two powder pattern spectra indicates that 1/4 of the oxygen sites are in a different microscopic environment from the other 3/4 of the oxygen sites. In addition, the powder pattern spectra for these two inequivalent oxygen sites exhibit isotropic and anisotropic character, respectively, for their hyperfine (HF) interactions.

NpO_2 crystallizes in the fluorite structure with the cubic space group (SG) $Fm\bar{3}m$. Within this SG, all the oxygen ions occupy equivalent positions (the 8*c* position). Thus, the observation of two inequivalent O sites by NMR gives microscopic evidence for symmetry lowering in the ordered state. Since the phase transition is 2nd order, the SG of the ordered state must belong to the subgroups of $Fm\bar{3}m$. Among the subgroups of $Fm\bar{3}m$, only the $Pn\bar{3}m$ SG for the *longitudinal* triple-*q* order has two inequivalent O sites (one: cubic 2*a*, the other: tetragonal 6*d*) in a ratio of one to three, in agreement with our experimental findings. It should be noted further that all the O sites are equivalent in the $Pa\bar{3}$ SG for the *transverse* triple-*q* order of UO_2. This is also consistent with the spectra in Fig. 1(a), where the powder pattern spectrum for a single nuclear site has been observed.

The spectral broadening in the ordered state is well explained by invoking a characteristic HF interaction with field-induced multipolar moments arising from the longitudinal triple-*q* AFQ order of the Np ions [15]. This HF mechanism is illustrated in Fig. 3 [15,22], where the arrows on the Np sites represent the field-induced AFM moments expected to appear with an applied field along the [0 0 1] and the [1 1 0] directions, while the arrows on O sites represent the classical dipolar field appearing on the oxygen nuclei at the 2*a* and 6*d* positions, respectively [23]. As seen in the figure, the dipolar field is always along the applied field at the 2*a* positions and lies along the axis of symmetry, that is, along one of the cubic axes, at the 6*d* positions. Such dipolar fields lead to the isotropic and anisotropic character of the HF fields at the 2*a* and 6*d* positions, as is observed. Furthermore, the shifts are expected to have opposite signs for the 2*a* and 6*d* cases, as is observed.

Although the field-induced AFM moments in Fig. 3 are expected to give a major contribution to the HF mechanism, we can also expect HF interactions with other types of field-induced multipole moments. In a recent ^{17}O NMR work using a single crystal, we have succeeded to resolve the contributions from the field-induced AFO moments at the 6*d* oxygen sites [24]. The NMR results provide definitive support for the longitudinal triple-*q* type AFO ordering model proposed from the RXS study for NpO_2 [12].

In Fig. 4 we show the temperature dependence of $1/T_1$ in NpO_2. Since NpO_2 exhibits a field dependence of $1/T_1$, the data obtained at both $H = 0.5$ and 10.3 T are presented. In the paramagnetic state, $1/T_1$ increases monotonically as T decreases at low field values. With increasing field, $1/T_1$ is suppressed rapidly. In the ordered state below T_0, $1/T_1$ rapidly decreases; however, a field dependence of T_1 is still observed.

The field dependence of $1/T_1$ appears over a wide temperature range, but only in low fields. Above $H \simeq 5$ T, the field dependence disappears in both the paramagnetic and ordered states. We have found that cross-relaxation processes arising from the unlike-spin coupling of ^{237}Np and ^{17}O nuclear spins can naturally explain the H^2 dependence of $1/T_1$ observed in the measurements. Furthermore, the analysis of this cross-relaxation allows us to make the first quantitative estimations of the nuclear

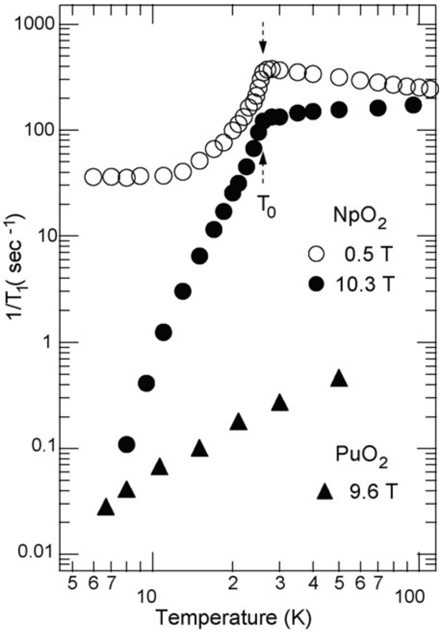

Fig. 4. The temperature dependence of $1/T_1$ measured at $H = 0.5$ and 10.3 T for NpO_2, and at $H = 9.6$ T for PuO_2.

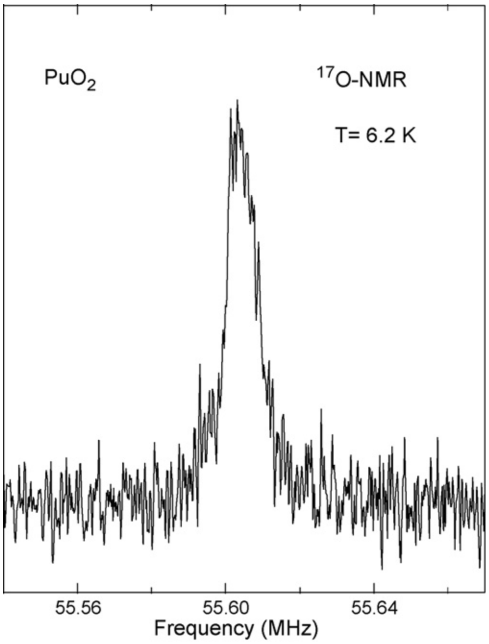

Fig. 5. The fast Fourier-transform ^{17}O NMR spectrum obtained at $T = 6.2$ K and $H = 9.63$ T for PuO_2.

spin-lattice relaxation rate of ^{237}Np in NpO_2. This analysis will be presented in detail in separate papers [25].

4. PuO_2

Due to the restrictions in handling plutonium, far fewer experiments have been done on PuO_2. The magnetic susceptibility of PuO_2 has been found to take a small and constant value of 5.4×10^{-4} emu/mol for all temperature up to 1000 K, so that the CEF ground state has been suggested to be a Γ_1 singlet [26]. On the other hand, recent neutron inelastic experiments have suggested a separation of 123 meV between the Γ_1 ground state and the first excited Γ_4 triplet state [27]. This value is, however, in complete disagreement with that derived from the susceptibility measurements. In a simple model, a separation of 123 meV corresponds to a susceptibility of $\sim 10 \times 10^{-4}$ emu/mol, and requires a deviation from T-constant behavior above $T \sim 400$ K [27,28].

In order to investigate the magnetic ground state of PuO_2, we have performed ^{17}O NMR measurements, for the first time, on this system. The powder sample used in our ^{17}O NMR was prepared by oxidizing Pu metal powder in O_2 gas containing ^{17}O. X-ray diffraction patterns confirmed a cubic fluorite PuO_2 structure for our sample. The ^{17}O NMR spectra were measured using a superconducting magnet and a phase coherent, pulsed spectrometer at several temperatures between 6 and 70 K.

Fig. 5 shows the ^{17}O NMR spectrum at $T = 6.2$ K. We have obtained a narrow spectrum with half-width of ~ 8 KHz. The narrow spectrum is very similar to those in the paramagnetic state of NpO_2 and UO_2, suggesting that there is no quadrupole splitting and no appreciable anisotropic NMR shift at the O sites. In PuO_2, however, we have observed neither spectrum broadening nor splitting through the temperature region studied. This confirms the absence of magnetic ordering or structural distortions, at least, down to 6 K. The Knight shift values are estimated to be $K < 0.01\%$, and are nearly temperature independent. This agrees with the temperature independent magnetic susceptibility in PuO_2 [26].

In Fig. 4, we also plot the temperature dependence of $1/T_1$ in PuO_2. The $1/T_1$ values were measured by the saturation-recovery method using standard spin-echo techniques. Recovery of the nuclear magnetization from a saturation pulse was found to follow in all cases a single-exponential functional form. As seen in Fig. 4, the $1/T_1$ values in PuO_2 are 2–3 orders of magnitude smaller than those in the paramagnetic state of NpO_2. Obviously, this small $1/T_1$ is attributed to the non-magnetic CEF ground state of PuO_2. The $1/T_1$ gradually decreases with decreasing temperature below 50 K. For the relaxation process in PuO_2, we may expect contributions from Pu- 5f spins in the first-excited Γ_4 triplet state. These contributions, however, should be more important at high temperatures, since the Γ_1 to Γ_4 splitting is suggested to be more than 100 meV in PuO_2 [25,26]. At low temperatures, we can also expect relaxation processes caused by phonons and/or by a small quantity of magnetic impurities, to the extent that they exist. To completely derive the $1/T_1$ mechanisms in PuO_2, further experimental effort in a wider temperature range is certainly required.

5. Summary

^{17}O NMR measurements have been carried out on UO_2, NpO_2 and PuO_2. Although the ^{17}O NMR spectra in these compounds are similar at higher temperatures, they exhibit entirely different aspects at low temperatures. The ^{17}O NMR spectra in UO_2 broaden discontinuously below T_N. The wide spectrum (forming a rectangular shape) is consistent with the appearance of an internal field $H_{\mathrm{int}} \sim 6.5$ kOe at the O sites. In NpO_2, on the other hand, the spectra broaden continuously below T_0. The two-peak structure of the spectra reveals the appearance of two inequivalent O sites associated with the symmetry lowering in the ordered state. The spectrum broadening is well understood in terms of the characteristic HF interactions with the field-induced AFM and AFO moments arising from the longitudinal, triple-q AFQ order. In PuO_2, we have observed neither spectrum broadening nor splitting down to 6 K.

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References

[1] B.T. Willis, R.I. Taylor, Phys. Lett. 17 (1965) 188.
[2] B.C. Frazer, et al., Phys. Rev. A 140 (1965) 1448.
[3] P. Burlet, et al., J. Less-Common Met. 121 (1986) 121.
[4] G. Amoretti, et al., Phys. Rev. B 40 (1989) 1856.
[5] K. Ikushima, et al., Phys. Rev. B 63 (2001) 104404.
[6] D.W. Osborne, et al., J. Chem. Phys. 21 (1953) 1884.
[7] J.W. Ross, D.J. Lam, J. Appl. Phys. 38 (1967) 1451.
[8] R. Caciuffo, et al., Solid State Commun. 64 (1987) 149.
[9] J.M. Friedt, et al., Phys. Rev. B 32 (1985) 257.
[10] D. Mannix, et al., Phys. Rev. B 60 (1999) 15187.
[11] P. Santini, G. Amoretti, Phys. Rev. Lett. 85 (2000) 2188.
[12] J.A. Paix ao, et al., Phys. Rev. Lett. 89 (2002) 187202.
[13] K. Kubo, T. Hotta, Phys. Rev. B 71 (2005) 140404R.
[14] K. Kubo, T. Hotta, Phys. Rev. B 72 (2005) 132411.
[15] Y. Tokunaga, et al., Phys. Rev. Lett. 94 (2005) 137209.
[16] J. Faber, et al., Phys. Rev. Lett. 35 (1975) 1770.
[17] J. Faber, G.H. Lander, Phys. Rev. B 14 (1976) 1151.
[18] S.B. Wilkins, et al., Phys. Rev. B 73 (2006) 060406.
[19] A.C. Gossard, et al., Phys. Rev. 9 (1974) 1230.
[20] P. Erdös, et al., Physica B 102 (1980) 164.
[21] W. Kopmann, et al., J. Alloys Compd. 271 (1998) 463.
[22] O. Sakai, et al., J. Phys. Soc. Jpn. 74 (2005) 457.
[23] O. Sakai, et al., J. Phys. Soc. Jpn. 72 (2003) 1534.
[24] Y. Tokunaga, et al., Phys. Rev. Lett. 97 (2006) 257601.
[25] Y. Tokunaga, et al., Phys. Rev. B 74 (2006) 064421.
[26] G. Raphael, R. Lallement, Solid State Commun. 6 (1968) 383.
[27] S. Kern, et al., Phys. Rev. B 59 (1999) 104.
[28] M. Colarieti-Tosti, et al., Phys. Rev. B 65 (2002) 195102.