First observation of ^{239}Pu NMR −A new frontier for the physics and chemistry of actinide compounds

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We present here a success story of the first observation of ^{239}Pu Nuclear Magnetic Resonance (NMR) signal [1]. This finding puts an end to a fifty-year long search for Pu NMR, and opens new frontiers for the study of plutonium in the fields of solid state physics, chemistry, and nuclear materials science.

There are two main reasons why ^{239}Pu NMR has remained elusive. First and foremost, in atoms with unpaired f electrons, like rare earths and actinides, an extremely strong hyperfine interaction between electron and nuclear spins gives rise to a large internal magnetic field at the nuclear site. As a consequence, the resonance frequency is shifted by several orders of magnitude and the nuclear spin-lattice relaxation time (T_1) becomes exceedingly short, rendering any NMR measurement on Pu-based compounds very challenging. Secondly, there is no accurate account of the ^{239}Pu nuclear moment, hence neither of the relevant value of nuclear gyromagnetic ratio (gamma value).

In order to overcome above difficulties we have selected a compound in which Pu ion is in tetravalent state, and coordinated in a cubic local symmetry. The best material we have selected is PuO_2 where Pu ions should be Pu^{4+} ($5f^4$, $^3H_4$) and the ground state in a cubic crystalline filed is Γ_1 singlet. Since the magnetic excited state Γ_4 is located 123 meV higher in energy, the Pu^{4+} ion in PuO_2 should be almost nonmagnetic below room temperature. As for the problem of undetermined gamma value, we have just made use of the way of scanning external filed from the minimum to the maximum expected values at a constant frequency.

A high purity PuO_2 powder sample which was prepared by nitric and anion exchange follows by oxalate precipitation was used [2]. The ^{239}Pu abundance is about 94%, and 48.7 mg of powder PuO_2 was mixed 24 mg stycast epoxy and casted the sample with a Teflon mold. The typical sample dimensions were 1.5 × 1.5 × 9 mm^3. All our NMR experiments were performed using a superconducting, highhomogeneity, variable 8 Tesla magnet. The low temperature environment was provided by a standard Variable Temperature Insert ^{4}He flow cryostat. A bottom-tuned NMR probe was used, with variable tuning and matching capacitors mounted near the NMR coil allowing for wide frequency coverage. The data were recorded with a commercial NMR spectrometer. All experiments have been executed at Los Alamos National Laboratory (U.S.A.).

The first field-swept scan was made at 16.51 MHz and 3.95K. The external field was scanned from 3 T to 8 T to cover wide range of the gamma values with 0.06 T step. In this scan we have used t_{90} = 3 μs and t_{180} = 6 μs pulse width for exciting and refocusing RF pulses, respectively. The time duration between the first and the second pulse (τ) was 60 μsec and the repetition time of 1 s was used. In the Fig. 1(a), one can observe a clear spin-echo signal at 5.8 T. *This is the first observation of ^{239}Pu NMR signal.*

In order to determine the gamma value in PuO_2 precisely, the NMR spectrum has been measured at several deferent frequencies and a frequency−field diagram has been constructed. From a least-square fit of the slope, the gamma value in PuO_2 has been determined to be $^{239}\gamma_n(PuO_2)$ = 2.856 ± 0.001 MHz/T.

We have tried to obtain the value of T_1 using the inversion recovery method. As is expected from the singlet ground state of Pu^{4+}, the T_1 value is expected to be extremely long at low temperatures. Actually, we could not obtain the correct value of T_1 by the inversion recovery method. Nevertheless, we could place the best estimate of 100 s at 4 K. This long T_1 assures that the observed NMR is really associated with Pu^{4+} in PuO_2.

The gamma value obtained here is exclusively for the case of ^{239}Pu in PuO_2 and it is not necessarily the "bare" gamma value of ^{239}Pu. In order to estimate bare gamma value, we have used the free ion value of the hyperfine coupling constant A_{hf} = 283.5 T/μ_B [3] to estimate the value of NMR shift (K) in PuO_2. Combined with the susceptibility data, χ_o=5.36×10^{-4} emu/mol, K is obtained to be +24.8% using a relation of K= ($\chi_o \cdot A_{hf}$) /($N_A \cdot \mu_B$). Since the bare gamma vale γ_n is expressed as $^{239}\gamma_n$= $^{239}\gamma(PuO_2)$/(1+K), we have the value of 2.29 MHz/T, corresponding to a nuclear moment of 0.15 μ_N for ^{239}Pu.

We also performed measurements on a sample known to be not fully oxidized, i.e., PuO_{2-x}. In Fig. 1(b) a ^{239}Pu NMR spectrum is shown, taken by sweeping the external magnetic field (Ho= 4.45 − 5.05 T) at f = 12.1 MHz and T = 4 K. The spectrum consists of two lines with NMR shifts K ≈ 11% and K ≈ 19%, respectively. Although we do not have a firm conclusion, we infer that those lines are associated with either Pu atoms nearby oxygen vacancies in PuO_{2-x} or Pu atoms in an α-Pu_2O_3 impurity phase. Controlled experiments are necessary for a definitive conclusion; nevertheless, this observation assures that the Pu NMR spectrum is sensitive to the oxygen coordination and can provide an atomic-scale fingerprint of the oxidation process. This is of particular importance for understanding the consequences of long-term storage of plutonium.

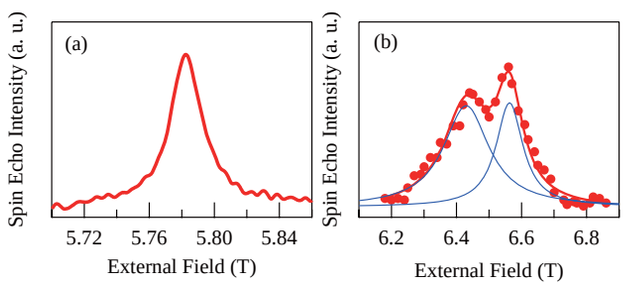

Fig. 1 ^{239}Pu NMR (Spin-echo) field swept spectra taken at 16.51 MHz and 3.95 K. (a): Pure PuO_2, (b) Nonstoichiometric PuO_{2-x}.

References

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