Spectroscopy properties of a single praseodymium ion in a crystal

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Abstract

Addressing and coherent control of single atoms in solids, with both optical and nuclear spin degrees of freedom is of particular interest for applications ranging from nanoscale sensing to quantum computing. Here, we performed the spectroscopy study of single praseodymium ions in an yttrium aluminum garnet crystal at cryogenic temperature. The single nuclear spin of individual praseodymium ions is detected through a background-free optical upconversion readout technique. Single ions show stable photoluminescence with spectrally resolved hyperfine splitting of the praseodymium ground state. Based on this measurement, optical Rabi and optically detected nuclear magnetic resonance measurements are performed to study their spin coherence properties. We find short the spin coherence times of praseodymium nuclear spins which we attribute to spin phonon coupling.

Optical detection and coherent control of single quantum systems in solids is essential to various fields ranging from fundamental physics to quantum information technologies [1–3]. Among such systems, rare earth ions embedded in crystals are attracting increasing attention as they simultaneously show narrow optical transitions [4–7] long spin coherence times [8, 9] as well as on-chip photonics [10–14]. Most recently, the lifetime of the 4f states of rare earth ions were shortened under the photonic cavities and make the detection of single rare earth ions with 4f → 4f transitions possible [15–20]. A single rare earth ion having nuclear spin, which allows optical addressing and control, is particularly interesting as it potentially combines ultra-long coherence time with fast optical control. However, coherently addressing single rare earth ions with nuclear spins [21–23] is an ongoing challenge.

Up to now, in yttrium aluminum garnet (YAG) crystal, single electron spins of trivalent cerium ions have been optically detected, initialized, readout and coherently controlled [24–26]. Due to strong coupling to the surrounding spin baths, single Ce electron spin qubits lose their coherence on a sub-microsecond time scale. Although it is extended to millisecond by dynamical decoupling technique [25], the coherence time is still far below that of rare earth ion nuclear spins. Excellent examples are trivalent Pr nuclear spins with 1 min coherence time [27] and Eu:YSO nuclear spins with coherence times up to 6 h [28], when
Figure 1. Optical detection of single praseodymium ions in a YAG crystal. (a) Energy level of Pr:YAG. Upconversion process of Pr:YAG indicated by the blue and green arrows. The Pr$^{3+}$ ion is first excited from $^3H_4(1)$ to $^3P_0$ by a 487 nm wavelength laser. It is then promoted to the 4$f^5d$ band by absorbing a second photon of 532 nm wavelength. (b) Scanning electron microscopy (SEM) image of a SIL fabricated by focused ion beam milling. (c) Upconversion image of individual Pr ions underneath a SIL.

utilizing zero first order Zeeman shift and dynamical decoupling techniques [29]. Detection and coherent control of these two rare-earth ion single nuclear spins is hampered by their low fluorescence intensity.

In this work, we investigate the optical and spin properties of a single nuclear spin of praseodymium ion in YAG crystal at cryogenic temperature. In particular, we observe well resolved ground state hyperfine structure of praseodymium ions and demonstrate the initialization and readout of single nuclear spin through optical control. Moreover, we also perform optical Rabi and optically detected nuclear magnetic resonance (ODNMR) measurements to demonstrate optical control and radio frequency (RF) control capabilities of single praseodymium ions. Our experiments open the door to future implementation of more sophisticated techniques, such as all-optical and dynamical decoupling control [30].

The energy level structure of Pr:YAG is presented in figure 1. The ground state $^3H_4(1)$ is a 4$f$ shell state, and is composed of three double degenerate hyperfine sublevels with energy level splitting of 33.4 and 41.6 MHz [31]. In rare earth ions, the intra-4$f$-shell transitions are efficiently screened by closed outer lying 5$s$ and 5$p$ shells. This screening causes the narrow optical $4f^2 \leftrightarrow 4f^2$ transitions [32]. The $^3P_0$ state shows a lifetime of 8 μs [33]. The long lifetime of the excited states and their resulting weak fluorescence challenges the detection of single rare earth ions directly through the $4f^2 \leftrightarrow 4f^2$ transitions, which was successful only recently [22, 23, 34].

One can circumvent the long lifetime of $^3P_0$ by further exciting the ion to the $4f^5d$ state. Compared to $^3P_0$, the $4f^5d$ state shows a much shorter lifetime of 18 ns [35, 36]. As a result, the emission rate of the single ion is largely enhanced. Previously, we used this upconversion method for optical detection of single Pr ions at room temperature [21]. In order to get access to the nuclear spin degrees of freedom, the same detection technique is applied in this work at cryogenic temperatures.

In the experiment, an ultrapure YAG crystal, previously used for single Pr ion detection, was studied [21]. We mounted a YAG crystal on a cold finger cryostat and cooled the crystal down to ~5 K. Single Pr$^{3+}$ ions are detected through an upconversion process $3H_4(1) \rightarrow ^3P_0 \rightarrow 4f^5d$, as shown in figure 1(a). A broadband diode laser with wavelength at 487 nm is applied to excite the $3H_4 \rightarrow ^3P_0$ transition. Another 532 nm laser is applied simultaneously to promote the Pr$^{3+}$ ion further to the $4f^5d$ band ($^3P_0 \rightarrow 4f^5d$). The emitted photons collected by a 0.85 NA objective lens are detected by a photomultiplier tube (PMT) in a spectral range between 300–400 nm. Figure 1(b) shows the SEM image of a solid immersion lens fabricated
Figure 2. Upconverted photoluminescence (PLE) of a single Pr ion in YAG. (a) Single sweep of upconverted PLE spectrum. The laser frequency sweeping rate is $12.6 \text{ MHz s}^{-1}$. (b) Plot of successive sweeping. Square spots represent center peak frequency. Error bar represents the width of the peak. (c) Sum of upconverted PLE spectra of a single Pr ion, indicating $\sim 2\pi \times 6 \text{ MHz}$ optical transition linewidth.

on the surface of the studied YAG crystal in order to enhance photon collection efficiency and spatial resolution [37]. Figure 1(c) displays the laser scanning fluorescence image of Pr ions in the focal area of a SIL.

The spectral properties of single Pr ions were investigated by PLE measurements. To this end, a narrow linewidth single mode laser (Toptica Photonics, DL Pro) working at 487 nm was used for narrow band optical excitation. The laser was kept at low power levels ($\sim 5\mu\text{W}$). While the 487 nm laser was swept through the resonant $3\text{H}_4 \rightarrow 3\text{P}_0$ transition, the 532 nm laser was constantly illuminating the sample completing the second upconversion step. By monitoring the fluorescence during frequency sweeping of the single mode laser ($12.6 \text{ MHz s}^{-1}$ sweeping rate), a single sweep PLE spectra is obtained as shown in figure 2(a). The spectrum shows a background-free upconversion signal. The spectrum consist of three well-resolved peaks with frequency differences of 32.7 and 42.3 MHz, respectively. These peaks correspond to the hyperfine splittings of the ground state $3\text{H}_4(1)$. The measured hyperfine splittings match bulk values within 0.7 MHz, but show linewidth of $2\pi \times 5 \text{ MHz}$ [31]. This linewidth is much larger than that in the bulk [31]. It is mainly due to laser induced dephasing and power broadening of the homogeneous linewidth $2\pi \times 1 \text{ MHz}$ (details are described in the supplemental material) (http://stacks.iop.org/NJP/22/073002/media). Due to this broadening, the hyperfine structure of the excited state $3\text{P}_0$ is not resolved. We monitor the peak frequency of the PLE signal in successive sweeps as shown in figure 2(b), and obtain a spectral diffusion of single Pr ions within a frequency range of $2\pi \times 3 \text{ MHz}$. We attribute this diffusion to interaction of the Pr ion with impurities like Ce, Eu, Cr, etc in the crystal. Figure 2(c) is an average of the spectra of successive sweeps in figure 2(c). The total linewidth is $\sim 2\pi \times 6\text{MHz}$.

Figure 3 shows optical coherent control of a single Pr ion. A resonant laser with varying pulse length is applied to drive coherent oscillating between the $3\text{H}_4$ and $3\text{P}_0$ states. The readout typically is applied simultaneously with the driving laser, in difference with the standard optical Rabi measurement in which the readout is applied after the driving laser. Compared to the standard optical Rabi sequence, the experimental pulse scheme simplifies the experimental condition, however, introduces an additional decay
channel from the higher excited state which shortens the decay time. We discussed the mechanism of optical Rabi measurement in the supplemental material. As a result of its very weak oscillator strength of the $3H_4 \rightarrow 3P_0$ transitions, we observe an oscillation frequency of only $2\pi \times 53$ MHz at a laser power of 0.4 mW. This value is several orders of magnitude smaller than that of other atom-like systems, such as NV centers [38, 39] and quantum dots [40, 41]. The decay of the Rabi oscillation is consistent with optical linewidth measurement (see supplemental material).

In addition to optical control, the ground state hyperfine splitting resolved in the PLE spectrum enables resonant optical initialization and readout of single Pr nuclear spins. Thus, hyperfine resolved control and investigation of spin coherence properties by means of ODNMR measurements are feasible.

Figure 4(a) shows an ODNMR measurement by applying the single mode laser in resonance with middle peak of the PLE spectrum corresponding to the optical transition $3H_4(\pm 3/2) \rightarrow 3P_0$ and an RF source to simultaneously induce spin transitions. The laser power was set to 5 $\mu$W, corresponding to an excitation rate of $2\pi \times 6.8$ MHz according to the optical Rabi measurement in figure 3. By sweeping the RF frequency, upconverted ODNMR spectra were acquired, which are shown in figure 4(b). The figure shows transition peaks at frequency 33.4 and 43.7 MHz. The linewidth of the ODNMR spectrum is $\sim 2\pi \times 1.5$ MHz, indicating that the coherence time of single Pr nuclear spin is one order of magnitude longer than that of single Ce electron spins in the same crystal [25], but shorter than the values in the bulk YAG crystal performed at a lower temperature of 1.8 K [31]. We attribute the ODNMR linewidth broadening to the spin-lattice relaxation. The spin-lattice relaxation also causes single Pr ions to relax back to the $\pm 3/2$ state and induces the non-zero baseline observed in figure 4(b).

To understand the ODNMR kinetics more precisely, we describe the ODNMR measurement through three-level Bloch equations:

\[
\frac{d\rho_{aa}}{dt} = i\Omega(\rho_{ab} - \rho_{ba}) + \frac{\rho_{ab}}{2T_1} + \frac{\rho_{ba}}{2T_1} + \frac{\Gamma}{2}\rho_{bb}
\]

\[
\frac{d\rho_{bb}}{dt} = -i\Omega(\rho_{ab} - \rho_{ba}) - \frac{\rho_{ab}}{T_1} + \frac{\rho_{ba}}{2T_1} - \Gamma\rho_{bb}
\]

\[
\frac{d\rho_{cc}}{dt} = -\frac{\rho_{cc}}{2T_1} + \frac{\rho_{bb}}{2T_1} + \Gamma\rho_{bb}
\]

\[
\frac{d\rho_{ab}}{dt} = i\Delta\rho_{ab} + i\Omega(\rho_{aa} - \rho_{bb}) - \frac{\rho_{ab}}{T_2}
\]
Figure 4. Upconverted ODNMR of a single Pr ion in YAG. (a) Energy diagram of the ODNMR, the single mode narrow linewidth laser is on resonance with either of an optical transitions (3H4(±3/2) → 3P0). The 532 nm green laser is added to promote single Pr ions further to 4f5d band, while the RF frequency is swept. (b) Upconverted ODNMR of a single Pr ions in YAG crystal. The RF frequency sweeping rate is 12.5 MHz s⁻¹.

where the symbols a, b, c represent the sublevels ±1/2, ±3/2, and ±5/2 respectively. Δ is the detuning of the RF frequency, Ω is the RF induced Rabi frequency, T₁ and T₂ are the spin relaxation times. Γ is the population redistribution rate determined by the excitation–emission cycling rate under optical pumping. In this model, the population redistribution rates from the sublevels ±3/2 to ±1/2 and ±5/2 are considered to be identical as indicated by identical ODNMR peak intensity observed in figure 4(b). We omit spin relaxation between levels a and c since the transition between them is weak and assume the same relaxation between a, b and a, c. In addition we assume the spin relaxation times are the same for all spin transitions.

The optical excitation is a two-step transition with the combination of 3H4 → 3P0 transition and upconverted readout 3P0 → 4f5d transition. Both the oscillation strength and the applied laser power (5 mW) for the transition 3P0 → 4f5d is much stronger than for the transition 3H4 → 3P0. The excitation rate is thus dominated by the optical pumping rate of 2π × 6.8 MHz between 3H4 → 3P0. This rate is much slower than the spontaneous emission rate of state 4f5d and thus determines the decay rate of Γ = 2π × 6.8 MHz.

The steady solution for ρbb under resonant (Δ = 0, ρbb(on)) and off-resonant condition (Δ ≫ 0, ρbb(off)) give the relative intensity of the ODNMR peak and baseline. The contrast of the ODNMR peak is defined by:

\[
\text{Contrast} = \frac{\rho_{\text{bb(on)}} - \rho_{\text{bb(off)}}}{\rho_{\text{bb(off)}}},
\]

and can be calculated to be:

\[
\text{Contrast} = \frac{4T_1^3\Gamma^2}{3 + 2T_1\Gamma + 12T_1^2\Omega^2 + 4T_1^3\Omega^4},
\]

where \(T_2 = 2T_1\). The RF induced Rabi frequency Ω is estimated to be \(2\pi \times 15 ± 5\) kHz \[43\]. We deduced the contrast to be 14 ± 5\%. According to these parameters we estimated the \(T_1\) time of single Pr ion nuclear spin at 4 K to be 3.6 ± 1.8\(\mu s\). This fast relaxation time is consistent with the measured ODNMR linewidth.

Under our experimental condition, Orbach relaxation is usually the dominated mechanism for spin-lattice relaxation \[42\].

\[
T_1 = \frac{1}{c - \Delta} \exp\left(\frac{\Delta}{kT}\right),
\]

\(T_1\) follows equation (3), which is exponentially dependent on the energy difference between the lowest and the second lowest ground states \(\Delta\) and it is exponentially dependent on the reciprocal of the temperature \(T\). Lower experimental temperature will prolong the spin lifetime. From figure 1 we see that for single Pr ions in YAG, \(\Delta\) is 19 cm⁻¹, which is much smaller than other hosts like YSO with 57 cm⁻¹. According to literature, at 4 K the nuclear spin lifetime of Pr:YSO is 100 s \[44\]. If we assume Pr:YAG and Pr:YSO have the
same pre-factor $c$ here, Pr:YAG is calculated to have 10 µs spin lifetime at 6 K, close to our experimental finding. It indicates, that the local temperature of the measured Pr ion is probably 2 K higher than the estimated temperature of the crystal. This might be caused by laser induced local heating, as more than 10 mW power is focused onto the Pr ion.

In conclusion, spectroscopic investigations of single Pr ions in YAG have been performed at cryogenic temperature by using the upconversion readout technique. The upconversion process largely enhances the cycling transition and provides an efficient readout of single Pr nuclear spin compared to conventional readout method through $4f \rightarrow 4f$ transitions. Single Pr ions in YAG show narrow optical transition linewidths and good photostability even at high excitation laser power. In order to unleash the full potential of single Pr ions, with respect to their spin coherence properties, experiments should be performed at lower temperatures. Under such improved experimental conditions, single Pr ions in YAG will show long lived nuclear spin. Our upconversion technique make these states particularly accessible paving the way for their use in quantum technology. With 91% yield for Pr ion implantation obtained in our previous study [45] and the capability to position a single ion with nanometer resolution [46], constructing arrays of coupled Pr nuclear spins in a YAG crystal might become feasible with potential application in quantum simulation research.

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