Probing dynamics of an electron-spin ensemble via a superconducting resonator

V. Ranjan*1, G. de Lange*,1, R. Schutjens,1 T. Debelhoir,2 J. P. Groen,1
D. Szombati,1 D. J. Thoen,1 T. M. Klapwijk,1 R. Hanson,1 and L. DiCarlo1

1Kavli Institute of Nanoscience, Delft University of Technology,
P.O. Box 5046, 2600 GA Delft, The Netherlands
2ICFP, Département de Physique de l'ENS, 24 rue Lhomond, 75005 Paris, France

Dated: August 28, 2012

We study spin relaxation and diffusion in an electron-spin ensemble of nitrogen impurities in diamond at low temperature (0.25-1.2 K) and polarizing magnetic field (80-300 mT). Measurements exploit mode- and temperature-dependent coupling of hyperfine-split sub-ensembles to the resonator. Temperature-independent spin linewidth and relaxation time suggest that spin diffusion limits spin relaxation. Depolarization of one sub-ensemble by resonant pumping of another indicates fast cross-relaxation compared to spin diffusion, with implications on use of sub-ensembles as independent quantum memories.

PACS numbers: 85.25.-j, 76.30.-v, 42.50.Pq, 03.67.Lx

The study of spin ensembles coupled to superconducting integrated circuits is of both technological and fundamental interest. An eventual quantum computer may involve a hybrid architecture [1–4] combining superconducting qubits for processing of information, solid-state spins for storage, and superconducting resonators for interconversion. Additionally, superconducting resonators allow the study of spin ensembles at low temperatures with ultra-low excitation powers and high spectral resolution [5, 6]. While one spin couples to one microwave photon with strength $g/2\pi \sim 10$ Hz, an ensemble of $N$ spins collectively couples with $g_{\text{ens}} = g\sqrt{N}$ [7, 8], reaching the strong-coupling regime $g_{\text{ens}} > \kappa, \gamma$ at $N \gtrsim 10^{12}$ [8–10], where $\kappa$ and $\gamma$ are the circuit damping and spin dephasing rates, respectively.

Among the solid-state spin ensembles under consideration, nitrogen defects in diamond (P1 centers) [11] are excellent candidates for quantum information processing. Diamond samples can be synthesized with P1 centers as only paramagnetic impurities. Additionally, samples with spin densities ranging from highly dense (> 200 ppm) to very dilute (< 5 ppb) are commercially available, allowing the tailoring of spin linewidth ($\gamma \propto N$ [12]) and collective strength ($g_{\text{ens}} \propto \sqrt{N}$). In contrast to nitrogen-vacancy centers in diamond [13] and rare-earth ions in Y$_2$SiO$_5$ [14, 15], P1 centers are optically inactive, making a coupled microwave resonator an ideal probe for their study. However, the magnetic fields $\gtrsim 100$ mT needed to polarize the ensemble at the few-GHz transition frequencies of circuits [16] must not compromise superconductivity. The freezing of all spin dynamics in a high-purity P1 ensemble by the field would allow quenching spin decoherence [17] through dynamical decoupling [18], realizing a useful quantum memory.

Here, we investigate the dynamics of a P1 electron-spin ensemble probed by controlled coupling to two modes of a coplanar waveguide (CPW) resonator. The resonator is patterned on a NbTiN film [19] withstandng applied magnetic fields beyond 300 mT. Three hyperfine-split spin sub-ensembles are clearly resolved over the temperature range 0.25-1.2 K. The collective coupling of each

$\kappa, \gamma$ indicates fast cross-relaxation compared to spin diffusion, with implications on use of sub-ensembles as independent quantum memories.

*These authors contributed equally to this work.

FIG. 1: (color online). (a) Schematic of the hybrid resonator-spin system. A single-crystal diamond piece (1.7 mm × 1.1 mm, type-Ib Sumicrystal, ~ 200 ppm N content) is placed on top of one of four CPW resonators capacitively coupled to a common feedline. The resonators are patterned on a NbTiN film (70 nm thick, critical temperature $T_c = 12.5$ K) on sapphire (C-plane, 430 µm thick). An external magnetic field $B_{||}$ is applied parallel to the film, along the diamond [100] direction. (b) Hyperfine interaction $A \approx 94$ MHz with the N host nuclear spin splits each electron-spin level into a triplet. Only electron-spin transitions that preserve nuclear spin (solid arrows) are allowed. (c) $B_{||}$ tunes the electron-spin energy levels through resonance with the $\lambda/4$ or $3\lambda/4$ modes of the resonator. The dashed line represents the thermal energy $k_B T/h \approx 5$ GHz at $T = 0.25$ K.
sub-ensemble to the resonator reaches \( g_{\text{ens}} = 17 \text{ MHz} \) at 250 mK, in accordance with field- and temperature-controlled spin polarization, and extrapolates to \( g_{\text{ens}} = 23 \text{ MHz} \) at full polarization. Using a pump-probe technique in the dispersive regime, we measure spin linewidth and relaxation time. The observed temperature independence indicates that internal spin equilibration is dominated by spin diffusion across the mode volume [20] rather than spin-lattice relaxation [21]. Finally, as an initial test of the possible use of sub-ensembles as independent memories, we measure the steady-state depolarization of a sub-ensemble by resonant pumping of another. The pump-power dependence observed indicates fast cross-relaxation compared to spin relaxation in the mode volume, calling for follow-up experiments probing the millisecond scale.

Our hybrid system, shown schematically in Fig. 1, consists of four resonators capacitively coupled to a common feedline and a type-Ib diamond sample placed above one of them. The electron-spin ensemble consists of unpaired electrons (spin-1/2) at substitutional nitrogen impurities [Fig. 1(a)]. Each electron spin exhibits strong anisotropic hyperfine interaction with the host nucleus (spin-1). The Hamiltonian for one defect is given by 

\[ H_N = -\hbar g_e B \cdot \vec{S} + \hbar g_s A \cdot \vec{I}, \]

with \( \vec{S} \) and \( \vec{I} \) the spin operators for the electron and nitrogen nucleus, respectively, \( \hbar g_e = 28.0 \text{ MHz/mT} \), \( h \) Planck’s constant, and \( A = \text{diag}(81.33, 81.33, 114.03) \text{ MHz} \) the hyperfine interaction tensor [22] (third (first, second) index parallel (normal) to the Jahn-Teller axis). Low-energy terms only involving \( \vec{I} \) have been left out. We tune the electron-spin transitions with a magnetic field (\( B_\parallel \)) applied along the diamond [100] direction. Because all N-C bonds have (111) orientation and make the same angle with \( B_\parallel \), the hyperfine interaction is the same for all impurities, creating three hyperfine-split electron-spin transitions [11].

Measurements [23] of the feedline transmission \( |S_{21}(f, B_\parallel)| \) near the fundamental (\( \lambda/4 \)) and the second-harmonic (\( 3\lambda/4 \)) modes at \( T = 0.25 \text{ K} \) and 1.2 K clearly show three avoided crossings [10], as expected for coherent coupling [24] (Fig. 2). The coupling strength of each hyperfine transition to the \( 3\lambda/4 \) mode is evidently stronger than to the \( \lambda/4 \) mode, and decreases for both modes with increasing temperature. The hybridized dips observed when spin sub-ensembles are resonant with the \( 3\lambda/4 \) mode [Fig. 3(a)] support strong coupling (\( 2g_{\text{ens}} > \gamma \)). The absence of double dips on resonance with the \( \lambda/4 \) mode indicate \( 2g_{\text{ens}} < \gamma \).

We extract \( g_{\text{ens}} \) using the model presented in Ref. 10, treating the spin sub-ensembles as separate harmonic oscillators coupled to the resonator, but not to each other:

\[
S_{21}(\omega) = 1 + \frac{\kappa_e}{i\Delta_c - (\kappa_i + \kappa_e)/2 + \sum_n \frac{92_{\Delta_n 0}^2}{(\Delta_n - \gamma/2)^2}}.
\]

Here, \( \Delta_c = \omega - \omega_c \) is the frequency detuning between the probe and bare resonator mode, \( \kappa_i \), and \( \kappa_e \) are the resonator intrinsic and extrinsic dissipation rates, \( \Delta_n = \omega - \omega_{m_n} \) is the probe detuning from the \( m_n = n \) hyperfine transition and \( \gamma \) is the transition linewidth (assumed independent of \( m_n \)). As shown in Figs. 3(a) and 3(b), fitting the double-dip spectrum for the \( 3\lambda/4 \) mode and the quality factors (Q) for \( \lambda/4 \) mode at 0.25 K using Eq. (1) yields collective coupling strengths \( g_{\text{ens}}/2\pi = 17.0 \pm 0.4 \text{ MHz} \) and \( 3.9 \pm 0.2 \text{ MHz} \), respectively [23].

To investigate the temperature dependence of the collective coupling strength to each mode, we measure transmission spectra at several temperatures in the range 0.25-1.2 K and perform the same analysis as above [14, 15, 25]. The results are shown in Fig. 3(c) together with the best fits to

\[
g_{\text{ens}}(T) = g_{\text{ens}}(0)\sqrt{P(B_\parallel T)},
\]

where \( g_{\text{ens}}(0) \) is the zero-temperature coupling strength, \( P(B_\parallel T) = \text{tanh}(m_\parallel B_\parallel /2k_B T) \) the spin polarization in thermal equilibrium, and \( k_B \) the Boltzmann constant. Two factors combine to make \( g_{\text{ens}}(T) \) higher for the \( 3\lambda/4 \) mode. First, \( P \) increases monotonically with the Zeeman energy \( m_\parallel B_\parallel \). Second, the bare spin-coupling strength \( g \) increases as \( \sqrt{\omega_c} \) owing to a larger vacuum magnetic field strength. The ratio 2.7 between the best-fit \( g_{\text{ens}}(0)/2\pi \) values for the \( 3\lambda/4 \) and \( \lambda/4 \) modes (22.7 ± 0.6 and

![FIG. 2: (color online). Transmission spectroscopy. Image plots of normalized feedline transmission as a function of \( B_\parallel \) and frequency near the \( \lambda/4 \) and \( 3\lambda/4 \) mode resonances at \( T = 0.25 \text{ K} \) (a,b) and 1.2 K (c,d). Each plot reveals three avoided crossings, corresponding to allowed hyperfine-split electron-spin transitions. Note that the frequency span in (b,d) is 10 times larger than in (a,c). The arrow in (a) points to a flux jump shifting the resonator frequency. All other image plots shown are corrected for these rare events.](image-url)
8.3 ± 0.2 MHz, respectively) differs from the expected \(\sqrt{3}\). This discrepancy may be due to inhomogeneous distribution of P1 centers in the mode volume [26] (see further below).

Having characterized coherent coupling in the hybrid system, we now turn to using the resonator as a probe of spin dynamics and equilibration. We first measure linewidth \(\gamma\) of the \(m_I = +1\) transition in the dispersive regime [8], with \(\sim 70\) MHz \(\gg g_{\text{ens}}\) detuning between the \(\lambda/4\) mode and \(m_I = +1\) transition. We extract \(\gamma\) by inferring [23] the frequency shift (\(\Delta f\)) of the \(\lambda/4\) mode immediately following a pump pulse whose frequency \(\omega_p\) is stepped through resonance with the \(m_I = +1\) transition [Fig. 4(b)]. The pump pulse slightly decreases the polarization of the ensemble, red-shifting the resonator. We fit a Lorentzian lineshape to \(|\Delta f|\), finding a full-width-at-half-maximum \(\gamma/2\pi = 9.0 \pm 0.3\) MHz. A similar dispersive measurement using the \(3\lambda/4\) mode at \(B_{||} = 263\) mT gives \(\gamma/2\pi = 12.0 \pm 0.7\) MHz. We find these values to be temperature independent in the range 0.25-1.2 K [Fig. 4(c)], indicating that \(\gamma\) is limited by dipolar interactions and field inhomogeneity. We attribute the \(\gamma\) increase with \(B_{||}\) to the latter.

The spin relaxation time is measured by applying a pump pulse resonant with the \(m_I = +1\) transition and monitoring the frequency shift in time as the spin polarization returns to equilibrium. We observe a bi-exponential decay response with time constants \(\sim 20\) s and \(\sim 160\) s [Fig. 4(d)]. These constants are independent of temperature in the range 0.25-1 K [Fig. 4(e)], suggesting that spin polarization decay is not limited by spin-lattice relaxation [21] but spin diffusion instead. Through dipolar flip-flop processes, the depolarization diffuses out of the resonator mode volume, leading to repolarization of the ensemble. The rate for this process depends on the nominal dipolar coupling strength between spins in the ensemble, which itself depends on the spin density [12]. The two time constants may be explained by two diamond sectors inside the mode volume with electron-spin densities differing by a factor of \(\sim 8\) [23, 26, 27]. This is supported by the fact that relative amplitudes of the two exponentials do not change versus temperature.

To investigate spin dynamics across sub-ensembles, we measure how pumping one sub-ensemble can affect the coupling strength of other sub-ensembles to the resonator [23]. As shown in Fig. 5(a), pumping at \(f_{m_I=0}(B_{||})\) completely suppresses the avoided crossing between the \(m_I = 0\) transition and the resonator [28].
FIG. 5: (color online). (a) Transmission spectroscopy similar to Fig. 2(b), with an additional pump pulse resonant with the $m_I = 0$ transition (incident pump power $P_p = -50$ dBm, 100 ms duration) prior to $|S_{21}|$ measurement. A complete disappearance of the $m_I = 0$ avoided crossing and a reduction in the coupling strength of the undriven transitions are observed. Color scale is identical to Fig. 2(b). (b) Inset: vacuum-Rabi-split dips at $B_0 = 269.1$ mT as a function of $P_p$. The merging of dips with increasing $P_p$ indicates cross-relaxation between the sub-ensembles. Main panel: Extracted polarization $P$ (normalized to the value without pump) for the undriven $m_I = +1$ sub-ensemble. The curve corresponds to the steady-state solution of a rate equation modeling fast equilibration between the sub-ensembles compared to $T_1$ (see text and [23] for details).

Remarkably, partial depolarization is evident in the $m_I = \pm 1$ sub-ensembles. The coupling strengths of the undriven transitions ($m_I = \pm 1$) to the $3\lambda/4$ mode are reduced to $g_{\text{ens}}/2\pi = 12.5\pm 0.5$ and $12.0\pm 0.5$ MHz, respectively. To quantify this steady-state cross-relaxation, we measure the minimum-splitting between the hybridized dips at $B_0 = 269.1$ mT [arrow in Fig. 5(a)] as a function of pump power $P_p$. As shown in the inset of Fig. 5(b), the undriven $m_I = +1$ sub-ensemble depolarizes further with increasing $P_p$. We can reproduce [23] this power-dependent steady-state cross-depolarization using a rate equation including a spin diffusion rate $\Gamma_o$ across the mode volume and a cross-relaxation rate $\Gamma$ between sub-ensembles [20]. We assume $\Gamma \gg \Gamma_o$ consistent with previous measurements of cross-relaxation in high density P1-center samples by Sorokin et al. [27]. Under these assumptions, the steady-state normalized polarization of each sub-ensemble is $\tilde{P} = \Gamma_o/(\Gamma_o + \Omega_0/3)$, where $\Omega_0$ is the pumping rate for the $m_I = 0$ transition. Excellent agreement is found with the model, with only the lever arm between $\Omega_0$ and $P_p$ as free parameter. Using the best-fit lever arm in combination with Fermi’s golden rule $\Omega_0 = 2\pi g^2 N_{\text{phot}}/\gamma$ and the measured $\Gamma_o \approx 0.05$ s$^{-1}$ and $\gamma/2\pi \approx 12$ MHz, we estimate $g \sim 2.5$ Hz [29]. Comparing this $g$ to $g_{\text{ens}}(T = 0)$ suggests $N \sim 10^{14}$ spins in the resonator mode volume.

In conclusion, we have used resonant and dispersive interactions with the two lowest-frequency modes of a NbTiN CPW resonator to probe the dynamics of a P1 electron-spin ensemble in diamond at low temperature and polarizing magnetic field. The observed temperature independence of spin linewidth and relaxation in the range 0.25-1 K supports spin out-diffusion as the dominant relaxation mechanism within the resonator mode volume. Resonant pumping of spin sub-ensembles indicates a balance of Zeeman and dipolar energies between sub-ensembles [20]. Follow-up experiments will pursue two directions: probing sub-ensemble response to one or more resonant pump pulses on millisecond timescales to shed light on the cross-relaxation mechanism, and cooling to 15 mK to fully polarize the ensemble [17] and extend spin coherence using sub-ensemble-selective dynamical decoupling [18]. Ultimately, cross-relaxation and achieved coherence will set the timescale over which sub-ensembles may serve as independent quantum memories.

We thank D. Ristè for experimental assistance and D. I. Schuster for helpful comments on the manuscript. We acknowledge funding from the Dutch Organization for Fundamental Research on Matter (FOM), the Netherlands Organization for Scientific Research (NWO, VIDI scheme), and a Marie Curie Career Integration Grant (L.D.C.).

[1] J. H. Wesenberg, A. Ardavan, G. A. D. Briggs, J. J. L. Morton, R. J. Schoelkopf, D. I. Schuster, and K. Mølmer, Phys. Rev. Lett., 103, 070502 (2009).
[2] D. Marcos, M. Wubs, J. M. Taylor, R. Aguado, M. D. Lukin, and A. S. Sørensen, Phys. Rev. Lett., 105, 210501 (2010).
[3] X. Zhu, et al., Nature, 478, 221 (2011).
[4] Y. Kubo, et al., Phys. Rev. Lett., 107, 220501 (2011).
[5] H. Malissa, D. I. Schuster, A. Tyryshkin, A. Houck, and S. Lyon, arXiv:1202.6305 (2012).
[6] Y. Kubo, et al., Phys. Rev. B, 86, 064514 (2012).
[7] A. Imamoglu, Phys. Rev. Lett., 102, 083602 (2009).
[8] R. Amsüss, et al., Phys. Rev. Lett., 107, 060502 (2011).
[9] Y. Kubo, et al., Phys. Rev. Lett., 105, 140502 (2010).
[10] D. I. Schuster, et al., Phys. Rev. Lett., 105, 140501 (2010).
[11] J. H. N. Louber and J. A. van Wyk, Rep. Prog. Phys., 41, 1201 (1978).
[12] J. A. van Wyk, W. E. Reinhart, G. L. High, and I. Kiwflwik, J. Phys. D: Appl. Phys., 30, 1790 (1997).
[13] M. V. G. Dutt, L. Childress, L. Jiang, E. Togan, J. Maze, F. Jelezko, A. S. Zibrov, P. R. Hemmer, and M. D. Lukin, Science, 316, 1312 (2007).
[14] P. Bushev, A. K. Feofanov, H. Rotzinger, I. Protopopov, J. H. Cole, C. M. Wilson, G. Fischer, A. Lukashenko, and A. V. Ustinov, Phys. Rev. B, 84, 060501 (2011).
[15] M. U. Staudt, et al., J. Phys. B: At. Mol. Opt. Phys., 45, 124019 (2012).
[16] J. Clarke and F. K. Wilhelm, Nature, 453, 1031 (2008).
[17] S. Takahashi, R. Hanson, J. van Tol, M. S. Sherwin, and D. D. Awschalom, Phys. Rev. Lett., 101, 047601 (2008).
[18] G. de Lange, T. van der Sar, M. Blok, Z.-H. Wang, V. Dobrovitski, and R. Hanson, Sci. Rep., 2, 382 (2012).
[19] R. Barends, et al., Appl. Phys. Lett., 97, 023508 (2010).
[20] N. Bloembergen, S. Shapiro, I. S. Pershan, and J. O. Artman, Phys. Rev., 114, 445 (1959).
[21] E. C. Reynhardt, G. L. High, and J. A. van Wyk, J. Chem. Phys., 109, 8471 (1998).
[22] R. J. Cook and D. H. Whiffen, Proc. R. Soc. Lond. A, 295, 99 (1966).
[23] See supplemental material.
[24] E. Abe, H. Wu, A. Ardavan, and J. J. L. Morton, Appl. Phys. Lett., 98, 251108 (2011).
[25] K. Sandner, H. Ritsch, R. Amsüss, C. Koller, T. Nöbauer, S. Putz, J. Schmiedmayer, and J. Majer, Phys. Rev. A, 85, 053806 (2012).
[26] R. C. Burns, V. Cvetkovic, C. N. Dodge, D. J. F. Evans, M. L. T. Rooney, P. M. Spear, and C. M. Welbourn, J. Crystal Growth, 104, 257 (1990).
[27] P. P. Sorokin, G. J. Lasher, and I. L. Gelles, Phys. Rev., 118, 939 (1960).
[28] This is surprising from a single-spin perspective, because the maximum Rabi driving strength ($f_{\text{Rabi}} = g\sqrt{N_{\text{phot}}}/2\pi \approx 100$ KHz for $N_{\text{phot}} = 10^8$ photons on mode resonance) is significantly smaller than the spin linewidth.
[29] Note that $N_{\text{phot}}$ is lower than on mode resonance by the filter factor $(\kappa_i + \kappa_e)^2/(\omega_c - \omega_p)^2$. 
Supplement to “Probing dynamics of an electron-spin ensemble via a superconducting resonator”

V. Ranjan*, 1 G. de Lange*, 1 R. Schutjens, 1 T. Debelhoir, 2 J. P. Groen, 1 D. Szombati, 1 D. J. Thoen, 1 T. M. Klappwijk, 1 R. Hanson, 1 and L. DiCarlo1

1Kavli Institute of Nanoscience, Delft University of Technology, P.O. Box 5046, 2600 GA Delft, The Netherlands
2ICFP, Département de Physique de l’ENS, 24 rue Lhomond, 75005 Paris, France

(Dated: August 28, 2012)

Supplement to “Probing dynamics of an electron-spin ensemble via a superconducting resonator”

MEASUREMENT SETUP

The device is operated in a 3He refrigerator with base temperature T = 0.25 K. All measurements involve continuous-wave heterodyne detection of feedline transmission S21 as a function of B∥ and T with 1 MHz intermediate frequency and 80 ms integration. Incident power on the feedline ranges from −115 to −95 dBm (−110 to −90 dBm) for the λ/4 (3λ/4) mode, corresponding to ~ 10^3 to 10^5 intra-cavity photons on resonance (incident power for one photon on resonance ≈ hω_c/(κ_i + κ_e)/2κ_e [1]). All other microwave pulses are also applied through the feedline. At B∥ = 0 the diamond-coupled resonator has λ/4 and 3λ/4 modes at 2.59 and 7.67 GHz, respectively (~ 11% lower than the values without the diamond). The reduction in frequency of the resonator after mounting diamond is due to the higher effective dielectric constant of the diamond (~ 5.7). The corresponding loaded quality factors are Q = ω_c/(κ_i + κ_e) = 1.8 × 10^4 and 6 × 10^3 (~ 3 times lower than the values without the diamond). Increase in intrinsic losses could come from the surface of the diamond and from the vacuum grease used to glue the diamond to the resonator. Increasing B∥ to 300 mT further decreases Q by ~ 15%. To reduce microwave losses in the superconducting film resulting from trapped flux, the system is frequently reset by warming above the film Tc and cooling back down with B∥ = 0.

AVOİDED CROSSINGS

Transmission spectroscopy measurements in Fig. 2 reveal two regimes of spin-resonator coupling. Rabi-split dips are clearly resolved [Fig. 3(a)] when the m_I = 0 transition is resonant with the 3λ/4 mode, evidencing strong coupling (2g_{ens} > γ, κ). To extract g_{ens} in this case, we fit Eq. (1) to |S21| (f) [2]. For this fit, we fix κ_i, κ_e and γ to independently-measured values: κ_i/2π = 1.4 ± 0.1 MHz and κ_e/2π = 120 ± 10 KHz are extracted on both sides of the avoided crossings, and γ/2π = 12.0 ± 0.7 MHz is obtained from dispersive pump-probe linewidth measurements (Fig. 4).

The λ/4 mode is weakly coupled to the resonator (2g_{ens} < γ) and Rabi-split dips are not resolved on resonance. The extraction of a coupling strength to this mode involves several steps. First, we extract the field-dependent loaded quality factor Q by fitting a lineshape [1]

S_{21}(ω) = \frac{S_{21}^{\text{min}} + i2Q(ω - ω_r)/\omega_r}{1 + i2Q(ω - ω_r)/\omega_r}

to the measured |S_{21}| (ω) at each magnetic field. Figure 3(b) shows Q(B∥) near the avoided crossings for the λ/4 mode at T = 0.25 K. The decrease in Q when the spin transitions are tuned into resonance with the resonator is caused by absorption of microwave energy by the spin ensemble. An analytic approximation of Q = ω_r/Δω_r, valid away from the avoided crossings can be obtained from Eq. (1) and noting that on resonance, where |S_{21}| is minimum, Im(S_{21}) ≈ 0. Here,

\Delta ω_r = (κ_i + κ_e) + \sum_{n} g_{ens,n}^2 (γ/2)(\Delta_n^2 + γ^2/4)

and Δ_n = ω_r - ω_{m,I=0}. The fixed values, γ/2π = 9.0 ± 0.3 MHz, κ_i/2π = 140 ± 10 KHz and κ_e/2π = 32 ± 1 KHz, are obtained by the same methods as described for the 3λ/4 mode.

The extraction of g_{ens} requires accounting for all ensembles in the last term of Δω_r. We also observe two small dips ~ 4.1 mT away from the avoided crossings with the m_I = ±1 transitions [indicated by arrows in Fig. 3(b)]. These dips are consistent with coupling to the nuclear spin (I = 1/2) of a 13C (1.1% natural abundance) at the nearest-neighbor carbon site present on the Jahn-Teller axis (A_{13C,a} = diag(141.8, 141.8, 340.8) MHz [3]). These give rise to six sub-ensembles with coupling strengths g_{ens,13C}^a ≈ g_{ens} /0.011/2. The factor 1/2 comes from the fact that 13C has nuclear spin of I = 1/2 in contrast to 14N (I = 1). Additionally, there are six more 13C transitions with A_{13C,b} = diag(32.1, 32.1, 41.0) MHz [3], which arise from 13C located at the three remaining nearest-neighbor sites. These are three times more abundant with g_{ens,13C}^b ≈ √3g_{ens,13C}. Although they are

*These authors contributed equally to this work.
not visible as separate dips in the data, they do modify $Q(B_\parallel)$. We therefore include all of these sub-ensembles in our modeling.

One can in principle also find an analytical expression for the dispersive shift of the resonance with respect to $\omega_c$ and use it to extract $g_{\text{ens}}$ for the $\lambda/4$ mode. In our experiments, however, this is problematic due to sudden changes in $\omega_c$ [indicated by the arrow in Fig. 2(a)] caused by flux jumps in the NbTiN film. The absorption, however, only depends on $\omega_c$, which is extracted with high precision from the transmission lineshape.

**DISPERSE MEASUREMENTS**

When performing the dispersive measurements shown in Fig. 4, we measure the change in $|S_{21}|$ at fixed frequency $f = (\omega_c - \Delta \omega_c/2)/2\pi$. Immediately before the pumping step, we measure the resonator lineshape and calibrate the slope of $|S_{21}|$ at $f$. We use this calibration to infer the resonator shift $\Delta f$. To ensure linearity within 10%, the pump pulse power and duration are chosen as to keep the maximum $|\Delta f| \lesssim \Delta \omega_c/8\pi$.

Measuring the relaxation of pumped spins over time reveals bi-exponential decay curves. A possible reason for this observation would be the presence of two sectors with different spin densities within the mode volume. This is suggested by several tests. First, we repeat the experiment with the pump far detuned from any spin transition and observe no shift in the resonance frequency. This excludes the possibility that one of the time constants results from the pump influencing the resonator shift (for example, through heating). Second, we perform the experiment varying the pump pulse frequency around $f_{m_I=\pm 1}$ and observe that the amplitudes of both exponentials are modulated by the spin linewidth (see Fig. S1). This excludes the possibility of a broad background spin ensemble such as paramagnetic impurities on the surface of NbTiN or diamond itself. In addition, the ratio of $g_{\text{ens}}(T=0)$ values for the two modes differs from the expected $\sqrt{3}$ by a factor $\sim 1.6$. This further hints at a strong inhomogeneity of P1 concentration across the diamond.

**PUMPING AND DEPOLARIZATION OF ENSEMBLES**

To study the dynamics of spins within and between the sub-ensembles, we resonantly pump the $m_I = 0$ transition and measure the effect on the sub-ensembles. The pulse sequence used for transmission spectroscopy $|S_{21}|(f, B_\parallel)$ in Fig. 5(a) is shown in Fig. S2.

We model the depolarization of spin ensembles due to pumping with a simple rate equation. In addition to the pumping rate $\Omega_0$ for the driven transition ($m_I = 0$), we include a spin-equilibration rate $\Gamma_o$ (spin diffusion rate across the resonator mode volume) within each sub-ensemble and a nominal rate $\Gamma$ that characterizes cross-relaxation between the sub-ensembles. The rate of change of polarization (equal for $m_I = \pm 1$ due to symmetry), is modeled by

$$\frac{d}{dt} \bar{P} = -M \bar{P} + \Gamma,$$  \hspace{1cm} (S1)

with

$$\bar{P} = \begin{bmatrix} \bar{P}(\pm 1) \\ \bar{P}(0) \end{bmatrix},$$

$$\Gamma = \Gamma_o \begin{bmatrix} 1 \\ 1 \end{bmatrix},$$

and

$$M = \begin{bmatrix} \Gamma_o + \Gamma & -\Gamma \\ -2\Gamma & \Gamma_o + \Omega_0 + 2\Gamma \end{bmatrix}.$$  \hspace{1cm} (S2)

The steady-state polarization ($d\bar{P}/dt = 0$ condition) is

$$\bar{P}(\pm 1) = \frac{\Gamma_o(\Gamma_o + 3\Gamma + \Omega_0)}{\Gamma_o(\Gamma_o + 3\Gamma + \Omega_0) + \Gamma \Omega_0}.$$

For $\Gamma \gg \Gamma_o$ [4], this expression simplifies to

$$\bar{P}(\pm 1) = \bar{P}(0) = \Gamma_o/(\Gamma_o + \Omega_0/3).$$

In this limit, the fast equilibration between sub-ensembles causes pumping of each transition with an effective rate $\Omega/3$, even though only one transition is directly driven by the pump.

[1] R. Barends, *Photon detecting superconducting resonator*, Ph.D. thesis, TU Delft (2009).
FIG. S2: Schematic of pump- and probe-tone timings used in Fig. 5. At each $B_{\parallel}$ setting, following a 5 s waiting time, pump pulses resonant on driven transitions are applied for 20 s. This is followed by a periodic series of pumping and probing steps (period $2\tau$), with the probe frequency $f$ stepped at the start of every cycle. The probe is always on, but $|S_{21}|(f)$ only measured for a time $\tau - \tau'$. Here $\tau'$ is a settling time of 20 ms. We use $\tau = 100$ ms for 2-D transmission spectroscopy [Fig. 5(a)], and $\tau = 270$ ms for measurements of Rabi-split dip separation as a function of pump power at fixed $B_{\parallel}$ [Fig. 5(b)].

[2] D. I. Schuster, et al., Phys. Rev. Lett., 105, 140501 (2010).
[3] A. Cox, M. E. Newton, and J. M. Baker, J. Phys.: Condens. Matter, 6, 551 (1994).
[4] P. P. Sorokin, G. J. Lasher, and I. L. Gelles, Phys. Rev., 118, 939 (1960).