Low field depolarization of NV⁻ centers through dipole-dipole coupling

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C'est trop bien

Blabla sur les NV, les ensembles etc.

In this letter/article, we characterize the depolarization of the spins observed for dense ensemble of NV centers in zero magnetic field and its potential application for DC magnetometry. While the main mechanism behind the depolarization, the lift in the degeneracy between the four classes of NV centers, is already well studied and can be exploited in a microwave-less vector magnetometry protocol, we found two other depolarization mechanisms specific to the zero-field region which could play an important role in a low-field magnetometry protocol.

The main signature of the spin depolarization in low field is the characteristic dip in photoluminescence (PL) observed only for high density ($\gtrsim 1$ ppm) of NV centers, as shown on fig 1. The decrease in the spins' lifetime in zero field makes the optical polarization scheme of the NV centers less effective and therefore reduce the population of the bright $|0\rangle$ spin state.

The T_1 depolarization dynamics of single or sparse NV centers at room temperature is dominated by a two-phonon Raman process, which depends on the crystal lattice temperature but does not (?) depend on the external magnetic field. However, it has been observed that dense NV centers ensemble have an additional spin decay channel which depends greatly on the magnetic field and not on the temperature. This effect has been attributed to cross-relaxation between the NV centers through dipole-dipole coupling. Some inhomogeneity between the NV centers is further needed in order to explain the depolarization of the spin ensemble. We will denote T_1^{ph} the characteristic time associated with the phonon relaxation process and T_1^{dd} the characteristic time associated with the dipole-dipole relaxation process.
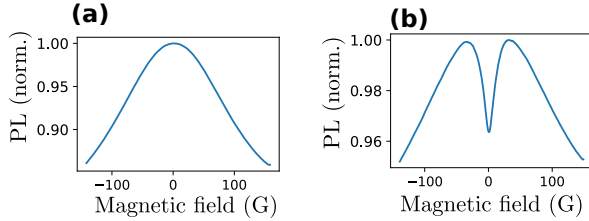

FIG. 1. Photoluminescence from NV centers as a function of an external magnetic field randomly oriented for two samples : (a) a CVD sample containing ≈ 4 ppb NV⁻ centers, (b) an HPHT sample containing ≈ 3 ppm NV⁻ centers
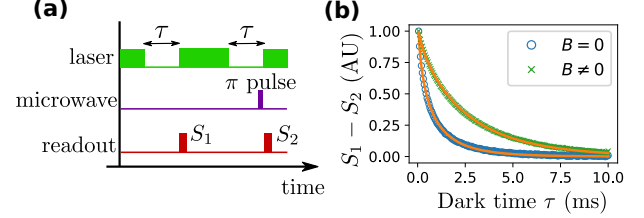

FIG. 2. Spin T_1 measurement protocol. (a) Sequence used to measure the spin lifetime : the laser is turned off for a time τ twice and the spin state is read at the end of the dark time by measuring the initial photoluminescence when the laser is turned back on. A microwave resonant with one of the spin transition is used in one of the sequence to project the $|0\rangle$ spin sate in either $|+1\rangle$ or $|-1\rangle$. The sequence result is the subtraction $S_1 - S_2$. (b) Measurement of a dense ensemble spin lifetime in zero field and non-zero field, fitted with an expression $A \exp\left(-\frac{\tau}{T_1^{\mathrm{ph}}} - \sqrt{\frac{\tau}{T_1^{\mathrm{dd}}}}\right)$

The spin lifetime protocol used here is described in Fig. 2 and is based on previous similar experiments. It consists in a pump-probe measurement where the spins are first polarized in the $|0\rangle$ state by a green laser, and read-out optically after a variable dark time τ. Using only this sequence can result in artifacts in the signal, mostly due to charge state transfer in the dark [4]. It is therefore convenient to repeat the sequence with an additional π pulse right before the spin read-out to project the remaining $|0\rangle$ polarization into a darker $|+1\rangle$ or $|-1\rangle$ state. By subtracting the result of the two sequences, we select only the spin-dependent part of the signal, with the added benefit of being able to select a specific class of NV centers.

The ensemble spin decay is non-exponential due to inhomogeneities between the NV⁻ centers. We will base our interpretations of the experimental results on the NV-fluctuator model developed in [1]. A conclusion of this model is that, for an homogeneous 3D distribution of fluctuator, the dipole-induced lifetime should be stretched-exponential with a stretch factor $\beta = 1/2$. Such an ensemble lifetime is indeed observed when $T_1^{\mathrm{dd}} \ll T_1^{\mathrm{ph}}$ (see SI).

For the samples used in this paper (detailed in SI), we observed that $T_1^{\mathrm{dd}} \sim T_1^{\mathrm{ph}}$, meaning that we had to include both in our analysis. The resulting fitting formula

is therefore :

$$S(\tau) = A \exp\left(-\frac{\tau}{T_1^{\mathrm{ph}}} - \sqrt{\frac{\tau}{T_1^{\mathrm{dd}}}}\right), \qquad (1)$$

Further details on the fitting procedure are available in SI. For the rest of the article we will be only interested on the stretched exponential lifetime T_1^{dd}.

One of the way we can isolate dipole-dipole related phenomena with NV centers is by tuning the number of NV centers resonant with each other. Indeed, Fig. 3 (bi) shows the characteristic 8 lines observed with ensemble NV optically detected magnetic resonance (ODMR) spectrum. These 8 lines correspond to the four "classes" of NV centers - that is physical orientation of the NV axis is the diamond crystal cell - multiplied by the two possible spin transitions $|0\rangle \to |-1\rangle$ and $|0\rangle \to |+1\rangle$. The transitions of the four different classes can be controlled somewhat independently by changing the amplitude and orientation of the external magnetic field, and in particular they can be brought to resonance for particular orientation of the magnetic field. Fig. 3 (ci) shows an example where all four classes are brought to resonance by placing the magnetic field along the [100] crystalline axis. Other example of class resonance are given in SI.

Fig. 3 (bii) and (biii) shows respectively the PL and the stretched exponential spin decay T_1^{dd} of an ensemble of NV centers with respect to the amplitude of the external magnetic field. The orientation of the magnetic field was chosen in order to lift the degeneracy between the four classes, as shown in Fig. 3 (bi). We observe that the drop in PL at low magnetic field is indeed correlated with an increase in the spin decay rate, as is expected due to the higher number of resonant spins in zero magnetic field, where all four classes are resonant, compared to the non-degenerate case for $\vec{\neq}0$. We can also see that the decrease in PL for $B > 40$ G due to state mixing by the transverse magnetic field is not correlated to a modification of the spin lifetime.

However, the splitting of the four classes is not sole reason to the decrease of the spin lifetime in low magnetic field. Indeed, we performed similar measurements in Fig. 3 (cii) and (ciii) but this time fixing the magnetic field orientation along the [100] axis. For this particular orientation, the four classes are always resonant, regardless of the field amplitude. We can see that, although considerably reduced, there still is an increase in the spin decay rate and a corresponding drop in PL for low magnetic field values. We attribute the slight drop in PL and the corresponding bump for $1/T_1^{\mathrm{dd}}$ at $B \sim 20$ G to dipolar interaction with NV having a first neighbor ^{13}C [6].

The aim of this paper is to understand the remaining contribution to the spin decay in this second case. We identified and isolated two additional effects : the domination by the local electric field for low magnetic field value which results in a change of the spin Hamiltonian eigenstates, and the presence of double-flip processes where both NV spins involved in the dipole-dipole coupling flip their spin in the same direction.

In order to distinguish these two contributions, we decided to exploit the transverse magnetic field.... (lis un peu ce que t'as déja écris avant de tout réécrire, je ter connais moi futur) The dipole-dipole interaction Hamiltonian between two spins $\vec{S}_1$ and $\vec{S}_2$ reads :

$$\mathcal{H}^{\mathrm{dd}} = -\frac{J_0}{r^3}\left(3\left(\vec{S}_1 \cdot \vec{u}\right)\left(\vec{S}_2 \cdot \vec{u}\right) - \vec{S}_1 \cdot \vec{S}_2\right), \quad (2)$$

Where $J_0 = (2\pi)52$ MHz$\cdot$nm^3, $\vec{r}$ is the relative positions of the two spins and $\vec{u} = \frac{\vec{r}}{\|\vec{r}\|}$. In situations such as the one described in Fig. ??, the only relevant terms of $\mathcal{H}^{\mathrm{dd}}$ in term of population transfer are the flip-flop terms such as $\langle 0, +1|\mathcal{H}^{\mathrm{dd}}|+1, 0\rangle$. In zero magnetic field however, we have to take into account other aspects of the dipolar Hamiltonian in consideration.

First is the change of basis of the single spin Hamiltonian $\mathcal{H}_s$: in zero external magnetic field, the eigenstates of $\mathcal{H}_s$ in the $\{|+1\rangle, |-1\rangle\}$ manifold are determined by local electric and magnetic field coming from nearby impurities [5]. For the samples used in this study, $\mathcal{H}_s$ was dominated by local electric field (see SI), meaning that the proper eigenstates of $\mathcal{H}_s$ in zero magnetic field are $\{|0\rangle, |+\rangle = \frac{|+1\rangle + |-1\rangle}{\sqrt{2}}, |-\rangle = \frac{|+1\rangle - |-1\rangle}{\sqrt{2}}\}$

Because the splitting between $|+\rangle$ and $|-\rangle$ (≈ 9 MHz) is much greater than the dipole-dipole interaction ($J_0/r^3 \approx 30$ kHz), the flip-flop terms of $\mathcal{H}^{\mathrm{dd}}$ now reads $\langle 0, +|\mathcal{H}^{\mathrm{dd}}|+, 0\rangle$. Averaging over all relative positions of two aligned NV centers, we found that on average $\left|\langle 0, +|\mathcal{H}^{\mathrm{dd}}|+, 0\rangle\right|$ was greater than $\left|\langle 0, +1|\mathcal{H}^{\mathrm{dd}}|+1, 0\rangle\right|$ by a factor $1.8 \sim 2$ depending on the correlation lengths of the local electric field. When all four classes are resonant, the theoretical decrease in the spin lifetime due to the change of basis is $\sim 20\%$ (See SI de ouf).

Second is the near-resonance condition of the double-flip processes such as $\langle 0, +1|\mathcal{H}^{\mathrm{dd}}|-1, 0\rangle$ or $\langle 0, +|\mathcal{H}^{\mathrm{dd}}|-, 0\rangle$. These terms usually couple non resonant states due to the energy mismatch between $|+1\rangle$ and $|-1\rangle$. However in zero field, the energy splitting between $|+\rangle$ and $|-\rangle$ is comparable with the fluctuator's spectral width measured in Fig. ?? to be ≈ 8 MHz, making the double-flip population transfer possible.

In order to evaluate the relative contribution of these two factors, we investigate the spin relaxation in the case of pure transverse magnetic field. Calling $\{|g\rangle, |d\rangle, |e\rangle\}$ the three eigenstates of the spin Hamiltonian in the presence of purely transverse magnetic field, Fig. 4 shows that for small enough magnetic field, the $\{|g\rangle, |d\rangle, |e\rangle\}$ basis is almost equal to the $\{|0\rangle, |+\rangle, |-\rangle\}$ basis : for $B = 120$ G, $\langle 0|g\rangle \approx 0.99$, $\langle -|d\rangle = 1$ and $\langle +|e\rangle \approx 0.99$. However the energy difference between $|d\rangle$ and $|e\rangle$ reaches ≈ 45 G which is high enough to cancel out the double-flip processes and allows us to isolate the change of basis hypothesis from the double-flip one.

Fig. 5 shows the dipole-dipole spin relaxation T_1^{dd} for a class of NV whose axis is orthogonal to the applied magnetic field. By monitoring the frequencies of the transitions $|g\rangle \leftrightarrow |d\rangle$ and $|g\rangle \leftrightarrow |e\rangle$, we can deduce the detuning
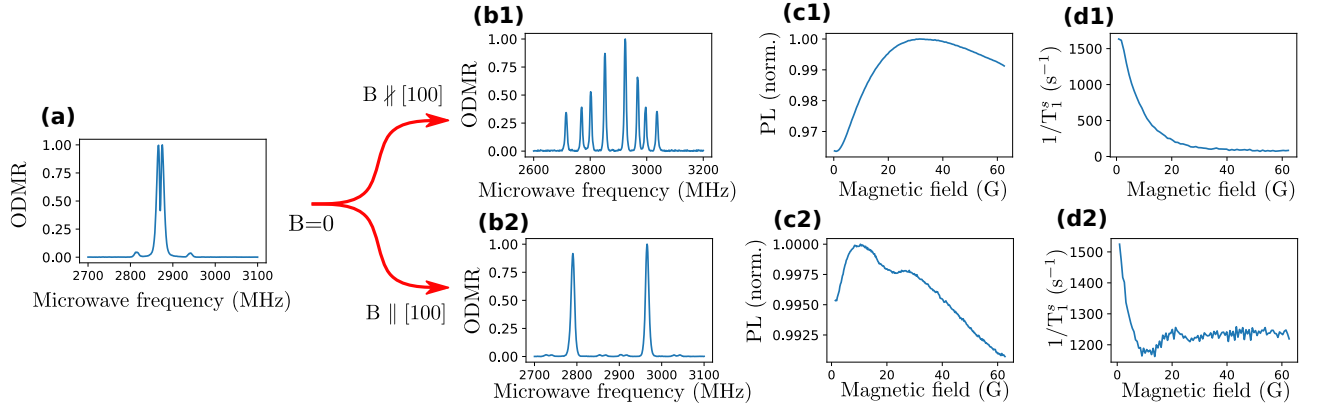
FIG. 3. Dependency of the magnetic field angle for the zero field depolarization. (a) ODMR spectrum in zero field. (b) ODMR spectrum for a magnetic field ≈ 60 G. The field is aligned (b2) or misaligned (b1, $\approx 24°$ of misalignment) with the crystalline [100] direction. (c) Normalized photoluminescence of the NV$^-$ ensemble as a function of the magnetic field amplitude for the same field orientations as fig (b). (d) Stretch part of the lifetime decay as a function of the magnetic field amplitude for the same field orientations as fig (b).
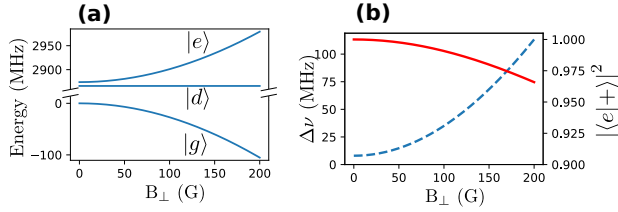

FIG. 4. Simulated eigenstates of the spin Hamiltonian in the presence of purely transverse magnetic field. (a) Energies of the three eigenstates $|g\rangle$, $|d\rangle$ and $|e\rangle$ as a function of the magnetic field amplitude. (b) Blue dashed curve : frequency detuning between the two transitions $|g\rangle \leftrightarrow |d\rangle$ and $|g\rangle \leftrightarrow |e\rangle$. Plain red curve : projection of $|e\rangle$ on $|+\rangle = (|+1\rangle + |-1\rangle)/\sqrt{2}$ as a function the magnetic field. Is equal to the projection of $|g\rangle$ on $|0\rangle$.

$\Delta\nu$ between the two-spin states $|0,+\rangle$ and $|-,0\rangle$. Plotting then $1/T_1^{dd}$ as a function of $\Delta\nu$, we can notice two things.

First the decrease of $1/T_1^{dd}$ as $\Delta\nu$ increases which corresponds to the loss in effectiveness of the double flip processes. The shape of the curve matches decently well with the tail of a Lorentzian centered in $\Delta\nu = 0$ with a width of 8 MHz, confirming that the double-flip process interaction range is likely determined by the fluctuators noise spectrum just like the flip-flop processes.

Second is the plateau reached for $\Delta\nu \gtrsim 30$ MHz. The final $1/T_1^{dd}$ value is about twice as high as that for a spin well aligned with the magnetic field, showing the increased depolarization due to the change of basis.

This experiment shows that, for the sample studied here, the depolarization due to the double-flip processes dominates the one due to the change of basis in zero magnetic field.
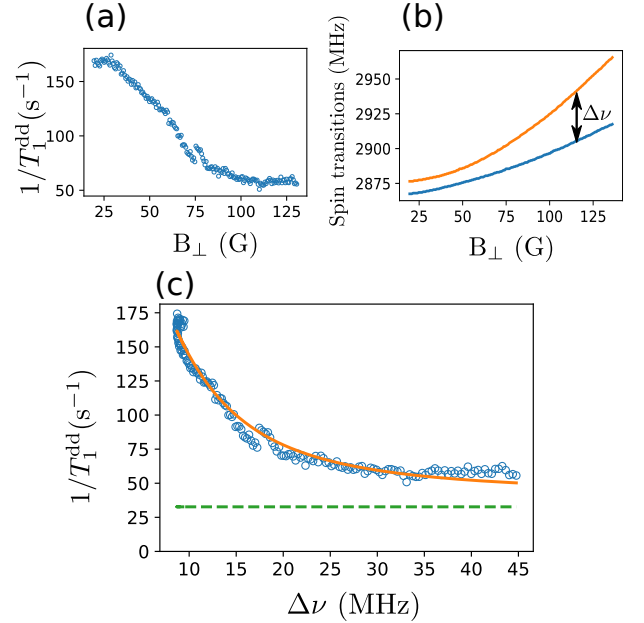

FIG. 5. Modification of the stretch lifetime in the presence of purely transverse magnetic field. (a) Stretch component of the ensemble lifetime as a function of the field amplitude. (b) Transition frequencies for the $|g\rangle \leftrightarrow |d\rangle$ and $|g\rangle \leftrightarrow |e\rangle$ transitions, measured through ODMR. (c) Stretch component of the lifetime as a function of the frequency detuning between the two transistions (blue circles), fitted by a Lorentzian centered in $\Delta\nu = 0$ with half width at half maximum 8MHz. The green dashed line correspond to the lifetime of a single class aligned with the magnetic field.

MAGNETOMETRY

DC microwave-less magnetometry has already been performed with NV ensembles, using either cross-relaxations [les russes] or level anti-crossing [bubu]. Here
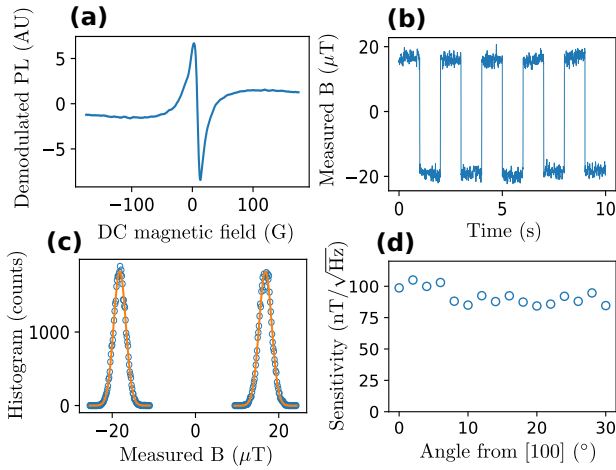
FIG. 6. Low field magnetometry protocol. (a) Demodulated photoluminescence as a function of an externally applied magnetic field with an additional oscillatory magnetic field. (b) Measured magnetic field when alternating a small external magnetic field offset. (c) Histogram of the measurement in Fig. (b) fitted with gaussians of standard deviation $\sigma = 1.5\ \mu$T
. (d) Measured sensitivity as function of the angle between the external magnetic field and the [100] crystalline axis.

we propose to perform a similar protocol, but using the spin depolarization in zero-field. The main difference with the previously mentioned protocols is the fact that this one doesn't rely on crystalline orientation, making this protocol usable with diamond powders or polycrystalline samples. The idea of performing optical magnetometry on the zero-field photoluminescence feature of NV ensembles has been suggested before [2, 3] but had not been implemented so far.

Fig. 6 (a) shows the demodulated PL when a DC magnetic field is scanned in a random direction and an additional alternating magnetic field of a few Gauss at $\sim$ kHz is added through the same electromagnet (see experimental details in SI). We can see a sharp and relatively linear slope in low field $|B| < 5$ G. Once calibrated, in this case with ODMR, the slope can provide a 1D magnetic field measurement, which could be extended to 3D with a set of 3 coils or 3 electromagnets, as seen in [7].

In order to measure the sensitivity of the measurement, we alternate a small DC field of ≈ 40G every few seconds and take an histogram of the measured fields, as shown in Fig. 6 (b) and (c). The histogram is well fitted with

gaussians of standard deviation $\sigma = 1.5\ \mu$T. The measurement was performed here with an output low-pass filter of time constant $\tau = 3$ ms, which allows us to measure the sensitivity $\eta = \sigma\sqrt{\tau} = 82$ nT$/\sqrt{\text{Hz}}$.

We can then try to measure the relative importance of the three causes of spin depolarization on the field sensitivity. In order to do so, we measure the sensitivity while changing the angle of the field. When $\vec{B}$ is aligned with the [100] crystalline axis, only the double flips and the change of basis are present, whereas in every other orientation the three effects are at play.

The results are shown in Fig. 6 (d). We can see a slight increase of $\sim 10\%$ in the sensitivity as we leave the [100] region, but overall the sensitivity remains relatively flat, which means that the double-flips and change of basis effects are the dominant factors in the sensitivity of this protocol. It should be noted though that this observation is sample dependent, and that other samples, including from the same batch, have shown a higher orientation dependence, corresponding to a lower contribution from the double flips and change of basis.

CONCLUSION

In this work we have identified three mechanisms causing the extra spin depolarization observed in zero field for dense ensemble of NV$^-$ centers, all related to an increase in the dipole-dipole cross-relaxations between the spins : the lift of degeneracy between the four classes caused by the magnetic field, the change of basis in the spin Hamiltonian when the transverse electric field becomes dominant, and the double-flip process allowed by the proximity in energy of the spin $|\pm\rangle$ states. We identified the lift in degeneracy as the main cause in the zero-field depolarization, followed by the double-flip process and then the change of basis. With have demonstrated a potential use of this depolarization as a DC microwave-less and orientation-free magnetometer with senstivity below 100 nm$/\sqrt{\text{Hz}}$ for a single 10 μm crystal.We have observed that in some cases the double-flips and change of basis depolarization play a more important role than the lift of degeneracy in the low field sensitivity.

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